DUPONT RECORDS CONTROL SCHEDULE

RECORDS CATEGORY OR TITLE:

Handbook

COPY "O" (OFFICIAL) ☑ "X" (EXTRA) ☐

TOTAL RETENTION:

Until superseded

GS-11050 Rev. 9/78

S814½R
SUPPORTED
VIRGIN VINYL

McMillan Book Co., Inc.
Syracuse, N. Y. 13201

LPH 0072319

N50179

INDUSTRIAL COATINGS

LEAD CHROMATE SUBSTITUTES

	AUTOMOTIVE AUTO REFINISH		FARM IMPLEMENT CONSTRUCTION EQUIPMENT		ALL OTHER
MASSTONES	SUBSTITUTES	CHROME YELLOW	SUBSTITUTES	CHROME YELLOW	SUBSTITUTES
PRIMROSE (not used currently)	-	(NIL)	-	(NIL)	-
LIGHT		(1.0)		(0.6)	
	ANTHRAPYRIMIDINE/ YELLOW 10/TiO_2	5-7X	YT-808-D	3.5X	YT-808-D
			FGL	7.0X	HANSA YELLOW G
MEDIUM		(1.4)		(5.7)	
	3RLT/YELL 10/TiO_2	5-7X	YT 808-D/ YT-820-D	6.0X	YT-808-D/YT-820-D
	FLAVANTHRONE/YELL 10/ TiO_2	5-7X			DIARYLIDE YELLOW
MOLY ORANGE		(4.5)		(3.0)	
RED SHADE					
	PERYLENE RED/ ORANGE RK	10.0X	YT-820-D/ RT-427-D	4.0X	YT-820-D/RT-427-D
			DNA	2.5X	DNA
					BENZIDINE ORANGE
INT HARV RED					
	PERYLENE RED/MON RED Y	5.0X	RT-695-D/ RT-565-D	0.9X	RT-695-D/RT-565-D
	MON RED Y/TiO_2	5.0X	TOLUIDINE RED	3.0X	NAPTHANIL RED/RED
			F5RK	6.0X	RED 2B
					TOLUIDINE RED
					DYBAZOLONE RED/

PLASTICS

LEAD CHROMATE SUBSTITUTES

Parts/hundred (phr) resin MEDIUM TINTS 0.5/1.0 PHR	UP TO 400° F. FLEX PVC LDPE SUBSTITUTES	CHROME YELLOW	ABOVE 400° F. RIGID PVC, HDVE, PP, PS, ABS SUBSTITUTES	KR
PRIMROSE		(0.6)		(0
	DAIRYLIDE H 10 G	2.0X	CONDENSATION AZO	1
	ISOINDOLINONE 2GLT	5.0X	NICKEL AZO	1
LIGHT		(2.7)		(1
	ANTHRAPYRIMIDINE	8.0X	CONDENSATION AZO 3G	1
MEDIUM		(2.7)		(1
	DAIRYLIDE HR	3.0X	ISOINDOLINONE 3RLT	2
	FLAVANTHRONE	10.0X	FLAVANTHRONE	3
MOLY ORANGE		(4.0)		(1
RED SHADE	RT-618-D/HR	1.2X	RT-618-D/COND AZO 3G	0
1.0 PHR	PERYLENE/HR	4.5X	PERYLENE/HR	1
	RT-787-D/ISOINDOLINONE 3RLT	7.3X	RT-787-D/ISOINDOLINONE3RLT	2
INT HARV RED	RT-428-D/RT-618-D	2.3X	RT-428-D/RT-618-D	1
90/10 BLEND	PYRAZOLONE RED	5.9X	PYRAZOLONE RED	3

*( )MM LBS

RT PVC - Polyvinylchloride PS -
LDPE + HDPE Low + High density Polyethylene ABS -
PP Polypropylene

INKS

LEAD CHROMATE SUBSTITUTES

	PUBLICATION BOOKS, NEWSPAPERS, MAGAZINES		PACKAGING FLEX PKG, BAGS, LABELS,
MASSTONES	SUBSTITUTES	CHROME YELLOW	SUBSTITUTES
PRIMROSE		(2.0)	
	HANSA 10G/YT-717-D/TiO_2	2.6X	HANSA 10G/YT-717-D/TiO_2
	HANSA 10G YT-717-D/YT-714-DTiO_2	2.2X 1.6X	HANSA 10G/YT-808-D/TiO_2
LIGHT	-	(NIL)	-
MEDIUM		(6.0)	
			YT-717-D/YT-729-D/TiO_2 YT-808-D/YT-820-D/TiO_2 DAIRYLIDE YELL OT OR AAA/YT-729-D/TiO_2
MOLY ORANGE		(NIL)	DNA/ORG RED*/TiO_2 YT-729-D/ORG RED* YT-808-D/RT-695-D

*INCLUDES: RT-427-D, RT-618-D, RT-531-D, LAKE RED C, CITATION RED

( )XXX LBS

CONFIDENTIAL

PIGMENTS COLORS RESEARCH ORIENTATION MANUAL

This is Book No. 39

Assigned to:

H. Valdsaar

Please keep your Manual up-to-date by inserting new sheets and destroying old sheets as directed.

If the assignment of this Manual is changed, please notify R and D Division, Pigments, Newark, New Jersey

LPH 0072323

Progress in Pigments Comes from DuPont

SECOND IN A SERIES

CONFIDENTIAL

Some great ideas were born in this house

Oliver Evans, one of our country's most brilliant and prolific inventors, lived here in the late 18th century. He was first in America with the high-pressure steam-engine and the steam road vehicle (forerunner of the automobile). He even built a steam-powered dredge that ran on both land *and* water. Always the scholar, he named it "Orukter Amphibolos" (Greek for "Amphibious Digger").

A Danish immigrant named Henrik Johannes Krebs built a large chemical plant around this house, which he used for offices, in the late 1800's. Krebs was a single-minded genius who believed that brain power, generously applied, could do most anything. Appropriately, a nearby school bears his name.

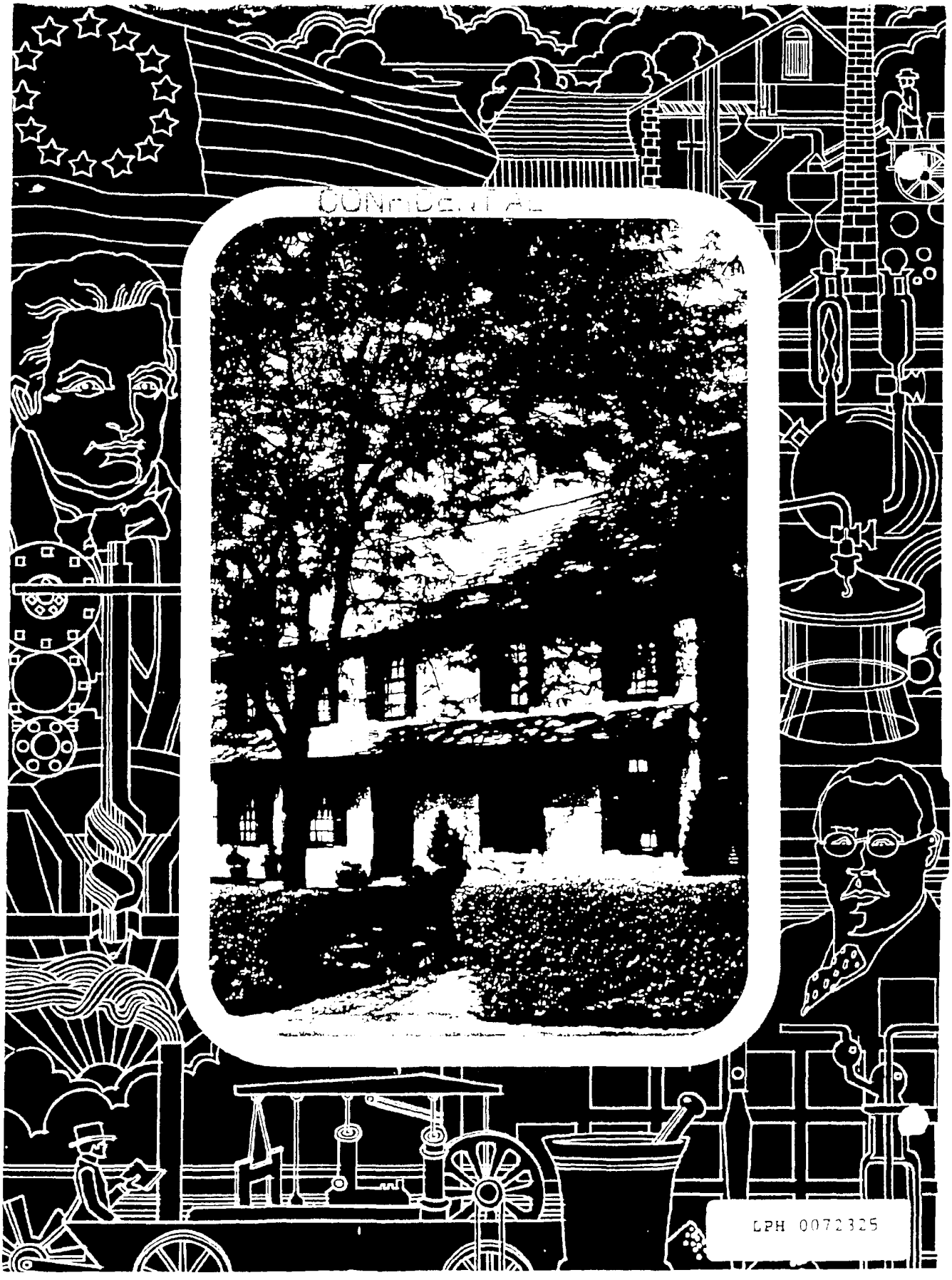
In 1929, this site became part of the Du Pont Pigments Department, and pigment colors have been produced here ever since. Our phthalocyanine capacity is now over 5½ million pounds a year and our quinacridone capacity is over 2 million pounds. We have ambitious expansion plans for both of these much-needed products.

The house is now used by some of the research people charged with filling Du Pont's traditional and highly successful role in developing new pigments. That's challenging work, but the old place is used to challenging work.

Oh yes, you'll find this house in Newport, Delaware. Come see it when you're in the neighborhood. *Some great ideas are still being born here.*

DU PONT PIGMENTS

LPH 0072324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PIGMENT COLORS RESEARCH AND DEVELOPMENT ORIENTATION MANUAL - 2ND EDITION

The Pigment Colors Research and Development Orientation Manual is designed to assist in the technical and administrative orientation of newly employed or transferred technical personnel. The manual is primarily an introduction to pigment technology and is not intended to be comprehensive.

This second edition represents the first complete revision since the manual was originally issued in 1968. New material will be added from time to time as the need arises. Suggestions for additions or changes are solicited. New or revised pages as issued should be inserted in the proper places and the replaced sheets destroyed.

The material contained in this manual includes some proprietary information and circulation, therefore, is restricted "FOR DUPONT USE ONLY". It should be circulated outside of the Pigments Department only with the permission of the Manager, Colors Research and Development. The person to whom one of the numbered copies is distributed will be responsible for its maintenance and safekeeping.

The Pigment Colors Research and Development Orientation Manual represents the combined efforts of Colors Research and Development personnel at Newark, Newport, and the Experimental Station, with assistance from Manufacturing and Marketing personnel. Materials have been drawn from the Sales Training Manual and other Marketing publications.

Newark, New Jersey
July 1975

Revised by B. H. Perkins - 1975

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[redacted]

PIGMENTS - DEFINITION

A pigment can be defined as a particulate solid which is insoluble, or substantially so, in the vehicle or medium in which it is incorporated, principally for the purpose of imparting color and/or opacity. Other functional purposes, however, may be served. It imparts color by the selective absorption of visible light, and affects the opacity of the medium in which it is dispersed by its contribution to light scattering and by absorption. At the same time, it usually alters the rheological or flow properties of the pigmented system as well as its durability.

A pigment is distinguished from a dye principally on the basis of the method of application rather than on its chemical constitution or composition. A dye is applied to a fabric generally in a soluble form and then fixed by being rendered insoluble. Coloration with a dye can also be effected directly by solution, as for example, in a plastic or ink system. Pigmentation, on the other hand, is accomplished by dispersing the finely divided, insoluble solid directly into the vehicle without prior solubilization. An example where the same chemical composition serves either as a dye or as a pigment is the yellow coloring matter, flavanthrone. When used as a dye, it is first reduced (leuco) form in which form it is applied in solution to the fabric. It is then fixed to the fabric by an oxidation process whereby the insoluble flavanthrone is regenerated. As a pigment, flavanthrone, as a particulate, insoluble solid, is dispersed directly into a vehicle such as a paint or plastic.

Revised by B. H. Perkins - 1975

PIGMENTS HISTORY

Prior to the discovery of mauve by Perkin in 1856, color was obtained from such natural sources as madder, indigo, cochineal, and logwood. The development of synthetic coloring matters followed rapidly thereafter with the discovery of fuchsine in 1858, and subsequently, the discovery of other triphenylmethane dyes such as alkali blue (1862), methyl violet (1865), and malachite green (1872). This group gave, for the first time, a variety of brilliant colors of synthetic origin, and lakes of these dyes were used as the first synthetic organic pigments.

The initial synthetic developments were concerned principally with dyestuffs for the textile industry, and the period up to the early 1900's saw the discovery and development of many dyes derived from coal tar intermediates. Rapid advances in color chemistry were initiated by the discovery of diazo compounds in 1858 and of azo derivatives in 1870. The obvious color potential of this class of compounds and the ease of preparation led to development of the azo colors which today represent the largest volume of organic pigments. Azo dyes for pigment use first came into prominence with the discovery of the lithol reds in 1899.

Many of the dyes synthesized during this period possessed pigment properties or could be laked in a variety of ways to give pigment colors. Many of the early pigment manufacturers in the United States produced lakes from dyestuffs and production consisted mostly of peacock blue, Persian orange, yellow lakes, and scarlets. Such synthetic products gradually replaced the natural products because of their superior characteristics including uniformity, brilliance of shade, and resistance to light and other chemical and physical agents.

The years up to 1915 saw the appearance of many patents relating to organic pigments although there was a considerable lag in the commercial development of these products. This has been attributed to a variety of factors including the unavailability of suitable intermediates and the lack of process ''know-how'' and of product demand. While the development and use of textile dyestuffs showed considerable progress, pigment colors received relatively little attention and early pigment manufacture was regarded more as an art than a science.

The increased interest and demand for color after World War I provided a stimulus for pigment development and application, and many old pigments came into volume usage and remain so to this day. Among the first pigments produced in the United States subsequent to World War I were phloxine red and peacock blue. The first synthetic azos included toluidine red, lake red C, para red, Hansa yellow, and lithol red. The blockade imposed by World War I provided the impetus for domestic manufacture inasmuch as the naphthol and amine intermediates required for pigment manufacture were imported mostly from Germany.

The discovery in 1913 of the brilliant lakes of complex heteropoly acids of phosphorus, molybdenum, and tungsten with basic dyes such as rhodamine, victoria blue, and methyl violet gave products with fastness superior to the tannin-tartar emetic precipitations of these dyes. These products, however, were still deficient in their resistance to solvents and alkali and were not sufficiently durable for outdoor use.

The subsequent period up to the discovery of the phthalocyanines was characterized by the commercial development and improvement of the pigment types already known but no notable discovery of novel chromophores or pigment types. This period up to 1933 saw the commercial development of permanent red 2B lakes, the rosinated lithol reds, chlorinated para toner, pigment green B, and toluidine maroon.

The biggest single advance in pigment technology up to this point was the discovery of the phthalocyanines in Great Britain in 1927. Its commercial introduction in 1935 set new standards of excellence in the pigment consuming industries. These blue and green pigments are characterized by excellent lightfastness, color intensity, bleed, and chemical resistance.

Major pigment advance in the last two decades include the commercial development in 1958 of the quinacridone pigments which offer superior pigmentary properties, approximating those of the phthalocyanines, in the gold, orange, scarlet, maroon, red, magenta, and violet color regions, the Afflair® nacreous pigments and the silica-coated lead chromate pigments.

Revised by E. E. Jaffe - 1975

2. In the early years of the current plant, day men worked 10 hour and night men, 14 hours per day. Rates of pay were:

15 cents per hour for color makers, 20 cents per hour for leaders, and $13 per week for foremen.

If a man worked 31 days without an absence, he received one extra day's pay.

3. During slow periods, the plant manufactured perfumed soap.

4. Color mixes were made in the open on steel plates with shovels.

5. Two chemists, a working director and a bench chemist were acquired in 1923, and the group was then known as the Chemical Division.

6. The Passaic Street plant was discontinued in 1924.

7. Lithopone manufacture was discontinued at Newark in 1938.

8. During World War II, from 1943 to 1945, a silica gel plant was built and operated at the Newark site.

9. During the period 1946 - 1949, a continuous unit for the manufacture of chrome and zinc yellows was constructed and a modern unit for azo colors installed.

10. The current Newark Research Laboratory was built in 1954.

Some amusing highlights of the early days.

1. Since there was no shower facilities, a large vat was used for taking a bath.

2. The press room floor was made of large planks. This section of Newark is slightly below sea level and only several miles from the waterfront; thus, when unusually high tides occurred, some of the loose planking would float away.

3. In 1923, offices were on the first floor and laboratories on the second of an old brick building (No. 23 Building) which was formerly used as a stable and wagon house.

The assignment in 1923 of two chemists to colors was primarily for the purpose of putting the color operations on a more scientific basis. Although the basic chemistry appeared to be quite simple, duplication of tinctorial and other pigment properties was poor. In the early days, the manufacture of pigment colors was more of an art than a science. Although the early studies contributed appreciably to product and process improvement, the task was a formidable one owing to the many products and processes, both organic and inorganic, which required attention. At one time in this period, the standard color line comprised more than 400 items.

HISTORY OF THE NEWARK PLANT

The Newark Plant of the DuPont Company is the outgrowth of a pigments business started in 1878 in a plant on the banks of the Passaic River in Newark, New Jersey and known as Hoare Barnett and Company. The plant was built for the manufacture of Griffith Patent White (Lithopone), a new white pigment discovered in Europe. The product was put on the market in 1880 as a non-poisonous substitute for white lead. Owing to the well-entrenched position of white lead and the discovery that the new pigment was subject to changes in color under certain conditions, it met with only limited success. After three or four years, manufacture was discontinued and the plant converted to color manufacture, undergoing successive changes in name to ''Estate of James P. Barnett'' in 1886 and ''Cawley Clark and Co., shortly afterwards. At this time, relatively few organic coloring matters of any kind were manufactured anywhere and these were confined to a few triphenylmethane dyes, a few azos, and to lakes of natural coloring matters such as cochineal, logwood, quercitron, and hypernic. It is of interest that as recently as the late 1920's, DuPont manufactured lakes of some of these natural dyes.

Cawley, Clark and Company's rapidly expanding business soon necessitated enlargement of the plant. At the same time (about 1892) arrangements were made for manufacture of an improved lithopone. Continued growth of the colors business prompted further expansion in 1898. Since there was insufficient space at the Passaic River site, the new plant was built on the present site, in 1898. Colors, sodium chromate, and sodium dichromate were manufactured initially. Prussiate of Potash was also manufactured later but this operation was discontinued after a short period. Facilities for manufacture of an improved lithopone replaced the Prussiate of Potash unit. The entire plant, including the lithopone unit which had just started operations was destroyed by fire. A colors manufacturing unit was hurriedly installed in a building at Clay Street adjoining the old Passaic Street plant and rebuilding of the Vanderpool Street plant was also started immediately. On completion of the rebuilding, yellows, reds, lithopone, and bichromate were made at the Vanderpool Street plant and blues, greens, and also lithopone were made at the Passaic Street unit. Operation continued under Cawley, Clark and Company and the Harrison Brothers and Company, paint and chemical manufacturers of Philadelphia, who had an interest in Cawley, Clark and Company.

In 1916, Harrison Brothers was acquired outright by DuPont, including the interest in Cawley, Clark and Company. In subsequent years, the plant was known as the Grasselli Plant (1928), Krebs Pigment and Color Corporation (1931), Krebs Pigment Department (1935), and finally the Pigments Department of E. I. Du Pont DeNemours and Co., the present name.

The following are interesting historical highlights:

1. Sulfuric acid manufacture was added to the Vanderpool Street plant in 1914 and continued until 1931.

With the development of Duco lacquer by DuPont, and the demand by General Motors for a durable maroon for use in this system, DuPont, in 1924, embarked on its first pioneering work in pigments.

The successful accomplishment, in 1926, was probably the first pioneering research done in this country on organic pigments and provided the impetus which has made DuPont a leader in the pigments manufacturing industry. Furthermore, the increasing interest in color after World War I provided further stimulus to pigment research. One can say, therefore, that DuPont entered this business on the ground floor. Such pigments as para reds, toluidine red, Lake Red C, Persian Orange, Peacock Blue, lithol reds, phloxines, and eosines, Lithol Rubine, basic dye pigments and toluidine yellows, all relatively old, came into volume usage. The volume of the old inorganic standbys, chrome yellows, chrome greens, and iron blues, likewise, increased greatly. Although most of these are still important volume items in the pigments industry, many lack the high quality properties such as lightfastness, bleed, heat resistance, dispersibility, etc., to meet the stringent demands of modern applications. For example, pigment dyes such as para and toluidine reds lack fastness to solvents and show migration in some compositions; lake colors such as lithols and Lithol Rubine, are sensitive to alkalis and soap; many azo pigments fail to perform satisfactorily at the elevated temperatures employed in modern finishing, printing, and extrusion operations; and only few organic pigments are sufficiently lightfast to withstand the conditions of outdoor exposure. Many other properties such as color intensity, working properties, etc., are important factors in utility and no one pigment meets all of these requirements.

Pigments research during recent years has resulted in substantial advances not only in the development of new pigments but in the improvement of existing ones. Although the phthalocyanines and quinacridones provide a high quality line in a large portion of the visible spectrum including blues, greens, reds, and violets, an important gap remains, principally in the yellow region.

Revised by B. H. Perkins - 1975

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HISTORY OF THE NEWPORT PLANT

The history of the Krebs Company, by which name the Newport Pigments Plant was known before it became a DuPont plant, is actually the story of the founder.

When Henry J. Krebs came to Newport in 1901 in search of a plant site, he found a suitable location adjacent to the Christina River. The site was ideal in that it had excellent water and rail facilities, good natural underground water supplies, and the village of Newport was known to have a good and reliable source of labor supply.

Henry J. Krebs was born in Denmark in 1847. He came to this country at the age of 32 and worked with and for various companies and was credited with various inventions including a milk-cream separator. He was also in the sugar beet industry and the anhydrous ammonia business, neither of which was particularly successful. He then became interested in paint pigment manufacturing and in 1900 decided to enter the lithopone chemical business. When he first set sight at Newport, there was a small lithopone plant in operation at the site now occupied by Building A-47. There were also two other homes at this plant site, one which was torn down in 1938 and the other (Building A-60) which still stands today, and which dates back to early colonial days. It was in Building A-60 that Oliver Evans, an early American inventor born in 1755, discovered the possibilities of steam as a motive power for land vehicles in 1773, and where he developed the idea of the Orukter Amphiboles, the original motor car which he built in 1804. This building is located on the left side of the Gatehouse as you enter the plant. This home, with some slight office modifications, still standa as originally constructed and houses the main Newport plant research offices. (See the following article by Pigments Advertising).

In the late summer of 1901, after the summer wheat crop had been harvested, Mr. Krebs, at the age of 54 and with $37,000 cash on hand, broke ground for a new lithopone industry here at Newport. The funds for this plant were his own plus that of a close friend. The plant production was scaled at 10,000 pounds of lithopone per day. Of necessity, some of the equipment purchased was second-hand. Some of the foundations for the boilers and engines were uncovered in a recent sewer project excavation. The original factory site covered some seven acres and, in 1902, the first production effort was made. Considerable difficulty was encountered and, after one year's operation, the balance sheet showed a net loss of $1,000. The major start-up operating difficulties were overcome in time, and at the end of the next year a dividend was declared. Plant records show that, in 1904, there were approximately 27 wage roll men employed in the operation.

During the ensuing years, the plant struggled with problems in a competitive market and the sale of lithopone in a lead and oil market created considerable sales resistance. The founder was well aware of the need for uniformity in quality, strength, hiding power, and other necessary pigment qualifications and set about developing a research organization. Chemists were not easily attracted to this area and Newport, being a little known village and Krebs an unknown Company, this became a problem. By 1906, however, there were eight chemists employed.

The product continued to improve and sales grew. In 1916, the Krebs Company developed its first major plant expansion amounting to some one-half million dollars. At this time, Buildings A-17, 19, 20, 21, 23, 24, and 30 were built, which consisted of the filtering, drying, storage, and power-house operations. One hundred and sixty two wage roll personnel were now employed.

In 1926, the lithopone production rate was 75 tons per day. At this time, Mr. Krebs, the principal stockholder, and a close friend split their holdings, giving parcels of stock to their families and a few close business associates. There were now 23 stockholders. Plant expansions were financed with monies on hand without the need to borrow funds.

It was in 1929 when the DuPont Company decided to expand into other peace-time chemical industries that the Krebs Company was purchased. The records show that there were then approximately 200 wage roll and 50 salary personnel employed at Newport.

Shortly after DuPont purchased the Krebs plant, a research building (A-47) was established in 1932. Demands for a better pigment were being made and it was during the early 1930's that titanium pigments were developed. In 1935, the Edge Moor plant began production of ''Ti-Cal'' pigments. During the next 15 years, a product transition occurred in which the titanium pigments were favored and lithopone, because of its inferior characteristics, became less popular with the trade, and its manufacture was finally discontinued in 1953.

Meanwhile, Pigments management, being aware of the limited future of the lithopone business, set about searching for other products. Research had been making considerable progress in the color pigment business, so that with the limited capacity of the Newark, New Jersey plant, the Newport plant was chosen as the site for the manufacture of the blue and green phthalocyanine pigments. A phthalocyanine plant was constructed in 1948, and expanded with a highly automated process in 1972.

Subsequent to 1948, DuPont developed the quinacridone pigments, a range of red colors which have high quality properties as do the phthalocyanines, and a quinacridone plant was started up in 1958, and expanded in kind in 1968.

Over the years, several other products were processed at Newport at some stage of their development including titanium metal sponge, titanium organics, high purity silicon, and fibrous potassium titanate. The plant for awhile carried on a finishing operation for certain grades of white pigments made in slurry form at Edge Moor, discontinuing this in 1971. The Newport plant began the manufacture of Afflair® flake pigments in 1962.

The Photo Products Department is a tenant at the Newport plant, manufacturing chromium dioxide and magnetic tape at this location.

A substantial part of the R and D Semi-Works area is presently in use by the R and D $TiCl_4$ Process Task Force for selective chlorination of ilmenite ore and chloride process by-product treatment studies.

April 1975

Revised by O. E. Ringwald - 1975

THE U. S. COLORED PIGMENTS BUSINESS

DU PONT SALES

	1973	1974	1974 as % of 1973
Inorganics	$25.5MM	$34.5	135%
Monastral® Blue and Green	13.5	19.7	146
Monastral® Red	16.8	18.5	110
Other Organics	9.0	12.7	141
Total	$64.8MM	$85.4MM	132%

YEAR	DOMESTIC CONSUMPTION*	DU PONT DOMESTIC SALES AND TRANSFERS	DU PONT SHARE OF MARKET
1973	$351.1MM	$54.2MM	15.4%
1974	441.5	74.4	16.9

*Estimates of consumption exclude iron oxides and black pigments.

Estimated domestic consumption is broken down by pigment type as shown below:

	1973	1974
TiO_2 Mica Flake	$ 4.4MM	$ 5.6MM
Molybdate Orange	16.6	23.5
Chrome Yellow and Orange	35.2	50.6
Chrome Green and Chrome Oxides	7.5	8.6
Zinc Yellow	5.9	11.6
Iron Blue	8.4	9.5
Cadmiums	31.2	35.6
QA	13.5	18.5
CPC	53.4	70.0
Other Organics	175.0	208.0
Total Domestic Consumption	$351.1MM	$441.5MM

Du Pont's domestic market share for each of the pigment types in which we compete is estimated below. The Other Organics group does include certain chemical types (such as lithols and diarylides) that we do not make.

		Du Pont Domestic Market Share (Based on Dollars)	
		1973	1974
Inorganics:	Krolor®	99%	97%
	Afflair®	29	34
	Molybdate Orange	37	37
	Chrome Yellow	20	20
	Zinc Yellow	20	26
QA		76	79
CPC Green		29	34
CPC Blue		22	23
Other Organics		5	6
Total Du Pont		15%	17%

INORGANICS

CHROME YELLOW

	(M Lbs)		
	1972 Actual	1973 Actual	Percent 73/72
Domestic Production	67,500	80,100	118.7
Imports	15,000	9,000	60.0
Du Pont Export	500	1,100	220.0
Net Domestic Consumption	82,000	88,000	107.3
Du Pont Domestic Sales	13,900	14,200	102.1
Du Pont Share Market %	17.0	16.1	

MOLYBDATE ORANGE

	(M Lbs)		
	1972 Actual	1973 Actual	Percent 73/72
Domestic Production	24,800	27,500	108.8
Imports	1,300	1,100	84.6
Du Pont Export	950	1,000	105.3
Net Domestic Consumption	25,150	27,600	109.7
Du Pont Domestic Sales	9,600	9,700	101.0
Du Pont Share Market %	38.2	35.1	

CPC BLUE AND GREEN

1974 DOMESTIC CPC FINISHING CAPACITIES

	CAPACITY - LBS MM				PRIMARY CRUDE PURCHASER
	BETA BLUE	ALPHA BLUE	GREEN	TOTAL	
Du Pont (Forecast)	1.2	1.5	1.5	4.2*	
Sun	1.9	.6	.5	3.0	x
American Cyanamid	.9	.4	.5	1.9	
Chemetron	1.0	.4	.2	1.6	
Hilton-Davis	.4	.2	.0	.6	x
Levey	.6	.1	.0	.7	x
Harmon	.1	.3	.1	.5	
Ridgeway(S and V)	.4	.0	.0	.4	x
Imperial	.1	.2	.0	.3	
Blackman-Uhler	.25	.0	.0	.25	x
Pope Chemical	.25	.0	.0	.25	x
Kohnstamm	.1	.1	.0	.2	x
BASF	.1	.0	.1	.2	
Cal Ink	.0	.0	.15	.15	x
Crown-Metro	.15	.0	.0	.15	x
Apollo	.1	.0	.0	.1	x
Inmont	.1	.0	.0	.1	x
Total	7.7	3.8	3.1	14.6	

*Installed capacity is 5.6MM lbs.

The beta blue market is growing at 10% annually, resulting from the increasing use of process printing where beta CPC is one of the three primary colors. Alpha blue and green are each growing at 4% annually. Our market shares are strongest in alpha blue (30%) and in green (48%), and the industries where these CPC types are mainly used (finishes and plastics) are those in which Du Pont has particular strengths. We have only a 20% share of the beta market, which primarily goes to the ink industry, but we cannot consider expansions in this area until the economics of our process are improved. Below is the industry breakdown for each of the CPC types.

1974 CPC MARKET (LBS MM)

	GREEN	ALPHA BLUE	BETA BLUE	TOTAL	DU PONT MARKET SHARE
Finishes	1.9	2.6	1.1	5.5	36%
Ink	1.3	1.7	4.7	7.7	21%
Plastics	.4	.6	.4	1.4	39%
Other	.3	.3	.2	.8	40%
Total	3.9	5.2	6.4	15.4	30%

American Cyanamid and Du Pont are, by far, in the best position to expand. The other major competitors, Sun and Chemetron, rely heavily on purchased crude and face either financial, labor or antiquated investment problems.

There is a large portion of the beta market that is met via CPC in the flushed form, which we do not make. We are working on a very easy dispersing dry product which could be used as an alternative to flushes by the ink maker with attractive economics to both Du Pont and the ink industry.

QUINACRIDONE

CURRENT MARKET POSITION

AREA	1974 DEMAND (M LBS CONTENT	MARKET SHARE (1974) DU PONT	LARGEST COMPETITOR	ESTIMATED 1979 DEMAND (M LBS CONTENT)
North America	1,500	75%	10%(Harmon)	1650
Far East	425	65%	20%(Tekkosha)	925
Europe/South America	500	25%	65%(Hoechst)	1125

The key element in our growth projections is the rate and extent of quinacridone used in foreign automotive stylings. Extensive domestic marketing and technical programs in support of our automotive business have paid major dividends. Similar programs will be used to expand our foreign automotive styling penetration.

OTHER ORGANICS

Our other organics business, which includes Dalamar® yellows, "Watchung" reds, Rhodamines, Green-Gold, etc., was slightly over $9MM in 1973.

Assuming no intermediate or manufacturing equipment limitations, we project other organic pigment sales to grow four-to-five times the 1973 sales level of $9MM/year by 1983.

LPH 0072344

OUTLOOK

We view our major long-term competition to be foreign-based pigment manufacturers such as American Hoechst, BASF, and Ciba-Geigy. This is based on their integrated operations which include the manufacture of pigment intermediates, pigments and pigment consuming products such as ink,paints and plastics. To varying extents,they have made a major commitment in pigment research and follow a world market growth concept.

From Marketing
Edited by B. H. Perkins - 1975

PIGMENT PROPERTIES - GENERAL

The physical and chemical characteristics that control and define the performance of a commercial pigment in a vehicle system include its chemical composition, chemical and physical stability, solubility, particle size and shape, degree of dispersion or aggregation, crystal geometry including polymorphic crystalline form, refractive index, specific gravity, absorption in the visible, ultraviolet and infrared regions of the spectrum, extinction coefficients, surface area, surface character, and the presence of impurities, extenders or surface modifying agents. These properties or circumstances are ultimately reflected in the pigmentary qualities which are used to a greater or lesser degree as the basis for pigment product selection by the trade.

Although a pigment type has inherent chemical and physical characteristics, the pigment is almost invariably used in a vehicle system so that its ultimate performance in use derives from a pigment-vehicle interaction, physical or chemical, in a specific vehicle system.

The following are the most important pigment properties which, in conjunction with hue, are considered by the pigment using trade as the basis for pigment selection:

1. Strength

The strength or tinting value of a colored pigment is a major factor in determining its utility. The inherent strength of a pigment is controlled by its light absorbing properties which are related to its molecular and crystalline structure. The inherent strength of a pigment is seldom obtained in practical application but is compromised by considerations of particle size and exposed surface area as they are controlled by the degree of dispersion, aggregation, flocculation, etc. Pigment strength in a vehicle system is also determined by the optical character of the other constituents in the pigmented system insofar as they absorb or scatter light. To achieve the maximum practical strength, and to develop its full tinctorial properties, a dry pigment usually requires dispersion in a vehicle by applying work, usually by attrition, to break up the dry pigment aggregates and to obtain maximum wetting by the vehicle.

As a point of interest, the phthalocyanine pigments manufactured today have considerably greater strength than those first marketed, owing to more sophisticated methods for particle size control and techniques for obtaining maximum dispersion. Further, some chromophores have greater inherent strength than others. For example, the disazo pigment, benzidine yellow, is about twice as strong as the monoazo toluidine yellow.

2. Color Intensity or Saturation

The color intensity (or saturation or Munsell Chroma) of a colored pigment is a measure of its departure from a gray of the same hue and may be thought of as color concentration. (c.f. Section 3).

Generally, a pigment whose molecular structure reveals two or more chromophores is more likely to be less intense in color than one containing a single chromophore. A pigment color which reflects visible light over a relatively wide band of wavelengths or in several wavelength bands will probably be less intense than a similarly hued color which reflects over a narrow wavelength band or in a single band. The intensity of a blend of pigments is significantly altered by the selective absorption of the different pigments in the blends, and this significantly controls the intensity of the color seen by the eye.

3. Fastness

The fastness of a colored pigment refers to its inherent ability to withstand the chemical and physical factors to which it is or will be exposed both during and subsequent to its incorporation into the pigmented system and in its end-use application. Fastness refers to the behavior of a pigment in terms of retaining its initial color value, either alone or in combination in a pigmented system, on exposure to light, weather, heat, solvents, or chemicals. Ideally, a pigment should be chemically inert but few synthetic organic pigments show such perfection, although it may be approached by one such as carbon black.

The fastness requirements for pigments have become increasingly stringent due to the proliferation of pigment vehicles fostered by the introduction and use of a wide variety of synthetic media including resins, plastics, fibers, lacquers, enamels, printing ink vehicles, elastomers, molding resins, etc. The use of plasticizers, curing agents, more potent solvents, higher operating and curing temperatures has made many pigments previously acceptable in the older oleoresinous systems unusable in the newer systems.

Inasmuch as one of the major pigment uses is for the manufacture of paints both for decorative and protective purposes, pigment durability is of prime importance. The term durability implies the ability to withstand the combined chemical and physical agencies inherent in "weather", including light, temperature, water, gases, industrial effluents, etc. Ultimately, the total pigmented system must meet the requirements of durability inasmuch as each component plays a role and may interact with the others. The pigment, for example, may be responsible for the deterioration of the film, or the vehicle can contribute to the deterioration of the pigment. A given pigment may perform as a lightfast pigment in one system and fail considerably in another, so that a pigment generally described as excellent in lightfastness may not come up to expectations in some systems.

The quantitative expression of the lightfastness of a pigment is difficult due to the variable lightfastness performance under different conditions including the chemical nature of the vehicle, the presence of other pigments and extenders, variable conditions of exposure, and the concentration at which the pigment is exposed. There are no commonly accepted numerical standards for lightfastness, nor standard conditions for carrying out such tests, so that each manufacturer reports fastness in his own way. Representations of lightfastness from manufacturer for this reason may at times be only qualitatively consistent.

Another increasingly important aspect of fastness is that of heat stability which may be affected either by the chemical or physical factors incident to the use of temperatures such as may be applied during the process of incorporating the pigment into the vehicle as in the manufacture of vinyl sheet, in the high temperature extrusion of plastics, or in the high temperature baking of automotive and industrial finishes. High temperature conditions, on the other hand, can also be encountered under use conditions of the pigmented article. A pigment color may be inherently unstable to heat due to its chemical decomposition, or unstable as a consequence of chemical interaction with the vehicle or other components of the pigmented system under the influence of heat.

Heat or color instability also result from melting, sublimation, change in crystal form, or from the variable solubility of the pigment in a vehicle as a function of temperature insofar as the dissolved color shade differs tinctorially from that of the particulate, dispersed solid color. The hue of a colored plastic would then vary with the plastics extrusion temperature, under these circumstances.

Fastness also includes pigment resistance to bleed which is dependent on the inherent solubility of the pigment in the vehicles, plasticizers and solvents to which it is exposed. Bleed may occur in the course of pigment incorporation, or in the application of the pigmented system as when applying a coating, or in the end-use of the pigmented system. Pigment solubility may be apparent in the case of pigment transfer or migration from one pigmented surface to another as when colored vinyl sheets are pressed together, or when a paint film is applied over another of a different color.

The solvent, plasticizer, and vehicle types to which pigments may be exposed include alcohols, aromatic and aliphatic hydrocarbons including paraffin wax, ketones, ether alcohols, acids such as oleic, soap formulations, nitrocellulose and acrylic lacquers, linseed oil and a host of synthetic resins.

Chemical fastness refers to the resistance of the pigment in the pigmented vehicle principally to such agents as acid or alkali or to air contaminants such as hydrogen sulfide. The cleansing of a pigmented coating with soap, detergent, or bleaching agents would require such resistance. Specialized uses as, for example, paint for swimming pools would require resistance to alkaline hypochlorite.

4. Dispersibility

The dispersibility of a pigment is measured by the effort required to develop its full tinctorial potential in a vehicle system. The practical, commercial utility of a pigment color, including the economics of its use, is profoundly affected by its particle size, crystallinity, wettability, agglomeration, aggregation, potential to flocculate, surface properties and general compatibility, all of which materially affect dispersibility. The dispersibility of a given pigment, however, will vary from vehicle to vehicle insofar as wetting, flocculation, etc. are dependent on the interaction of pigment and vehicle. Other attributes of the pigment such as aggregation, etc. may, if sufficiently severe, make a pigment impractical to use in any system unless sufficient physical work is done to break up the aggregates. Aggregates arise from the very strong forces of attraction between the discrete pigment particles, most often greater as the particle size decreases. Aggregation can also possibly arise from a physical bridging between particles due to solvent action and crystallization which may occur during the drying of a pigment color during its manufacture.

Dispersibility is ultimately important to the pigment user in attaining maximum surface area, and homogeneity of the pigmented system. These assure his getting maximum economic value per unit weight of pigment and improved properties in some applications such as gloss and transparency in certain systems.

The term ''texture'' is often used to designate ease of dispersion, a pigment of hard texture requiring greater and costlier effort on the part of the user to achieve an acceptable level of dispersion. Many techniques are currently employed by pigment manufacturers to provide pigments of good texture, as well as compatibility in most vehicle systems. These methods include the use of special extenders and surface active agents, among others. Unfortunately, the attainment of one useful property in a pigment may compromise another. the achievement of transparency in an automotive paint, for example, is accomplished primarily by the removal or reduction in size of larger particles which scatter light appreciably. Very small particles, however, give rise to greater aggregation with resulting texture and dispersion problems, so that a compromise in properties may be necessary.

5. Working Properties

Working properties refer broadly and generally to those characteristics of a pigment which facilitate its incorporation, handling, or use in a given system. These characteristics include compatibility, oil absorption, contribution to rheology, ease of grinding, wettability, gloss, bronzing, hiding power, flocculation, etc. These considerations account in many instances for the proliferation of different pigment standards, developed from a single chemical type. The working properties or aggregate size, crystallinity, flocculation,

surface modification and characteristics, as they affect wetting and dispersion in the vehicle, etc.), and by suitable formulation by the pigment user.

From a practical point of view, a pigment need be no more durable than that of the vehicle or film in which it will be used so that careful pigment selection with due consideration to economics must be exercised. Likewise, a pigment need be no more durable or possess other properties than are demanded by the use for which it is intended. Durability is a minor consideration in the printing of a comic book in contrast with the needs of an automotive finish. The demands made of a pigment, therefore, depend on the varied needs of the system to be pigmented and the requirements of the end-use application. A potential pigment user must rely on his own pre-use testing, or obtain technical advice and assistance from the pigment manufacturer.

Revised by B. H. Perkins - 1975


7

INTERACTIONS OF COLORED PIGMENTS WITH LIGHT

I. INTRODUCTION

The pigments manufactured at the Newark and Newport plants are used principally to impart color to dispersion media. The color they contribute is a consequence of the interaction of pigment with light. The interactions which may lead to color, and which will be discussed briefly here, are absorption, scattering, reflection, interference and emission.

II. LIGHT ABSORPTION

All molecules absorb electromagnetic radiation. Those which absorb in the visible region of the spectrum (4000-7000Å) appear colored.

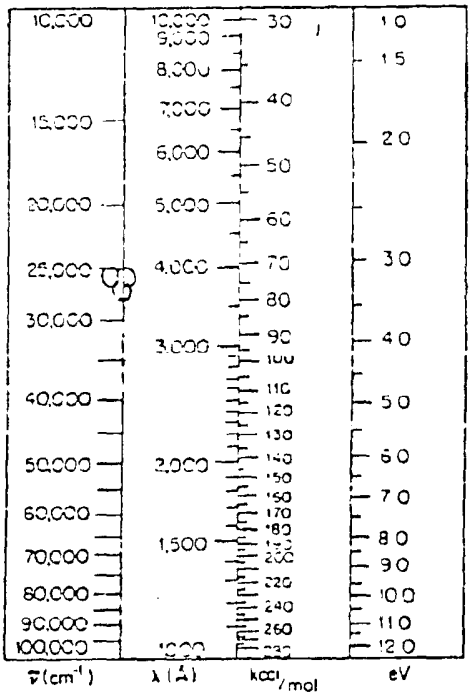
Absorption of light by a molecule is associated with a shift of an electron from a ground state level to a higher one. Subject to specific selection rules (Ref. 1) which are based on symmetry and spin multiplicity requirements, only those frequencies can be absorbed that coincide in energy content with the energy difference between electron levels of the molecule.

The energy increase on absorption of light is given by

$$\Delta E(\text{kcal/mole}) = h\nu = \frac{2.860 \times 10^{5}}{\lambda(\text{Å})}$$

where h is Planck's constant (6.62×10^{-27} erg sec), ν is frequency (sec^{-1}) and λ is wavelength (Å). The dependence of ΔE upon wavelength and upon frequency is summarized in Table I. It should be noted that, in general, the use of wavenumber $\bar{\nu}$ (cm^{-1}) = $1/\lambda(\text{cm})$, rather than wavelength, is often preferable since the relationship between energy and wavenumber is linear, whereas a non-linear relationship holds between energy and wavelength.

TABLE I



If all the visible light falling on a substance such as a pigment is absorbed, it appears black or grey if light is absorbed uniformly but incompletely. If, on the other hand, only specific frequencies are absorbed, color is imparted. The color of the absorbed light, its wavelength and the resulting complementary visible color of the absorbing substance are summarized in Table II (Ref. 2). Thus, for example, light which is composed of wavelengths between 5950-6050A appears orange. If a pigment absorbs all the wavelengths in the visible spectrum except those in the 5950-6050A range which it reflects, it will appear as orange. If, on the other hand, it absorbs only the orange wavelengths (i.e. 5950-6050A), then the pigment will be green-blue, the complementary color of orange. Conversely, the complement of blue is orange. When a pigment absorbs over a wide range of wavelengths or in many parts of the visible spectrum, it will appear as a mixture of colors complementary to those absorbed, and consequently dull.

LPH 0072352

TABLE II

Color of Absorbed Light	λ(Å)	Visible Color of Substance
Violet	4000-4350	Yellow-Green
Blue	4350-4800	Yellow
Green-Blue	4800-4900	Orange
Blue-Green	4900-5000	Red
Green	5000-5600	Purple
Yellow-Green	5600-5800	Violet
Yellow	5800-5950	Blue
Orange	5950-6050	Green-Blue
Red	6050-7000	Blue-Green

The color of a pigment crystal may also vary markedly with crystal direction. Pigments are generally anisotropic and color differences corresponding to as much as 20 NBS (where 1 NBS unit may be considered significant) have been reported for different directions. The slow ray (greater refractive index) has a more intense absorption at a longer wavelength than the fast ray. Thus, markedly different colors may occur with change in angle of view with oriented pigments, as may be the case with pigments in a stretched or brushed film or an extruded fiber or film. Crystal habit color effects, which have been noted with some of our pigments, are related to this dichroism.

In the case of para red, such anisotropy has been explained on the basis of dichroism of individual molecules and their orientation in the crystal (Ref. 3). The molecule is planar and the π orbitals are in the plane of the molecule. A markedly greater absorption can be expected when the molecular plane and the plane of light polarization are parallel, as compared to absorption when these planes are perpendicular (Ref. 2). Light in a pigmented system tends to become polarized since every refraction or reflection is accompanied by a polarization effect.

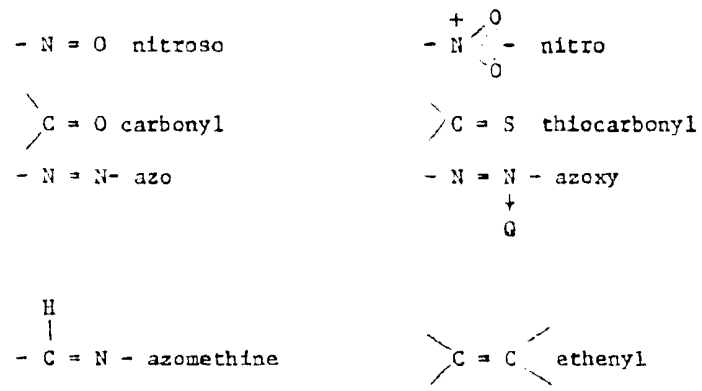
Pronounced differences in color of pigment crystals have also been noted with change in crystal thickness (same crystallographic direction). This is primarily an absorption effect.

III. QUALITATIVE AND SEMIQUANTITATIVE INTERPRETATIONS OF LIGHT ABSORPTION

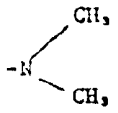
A. Organic Compounds

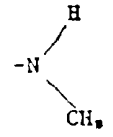
Near the end of the nineteenth century, it was recognized that color is associated with the presence of multiple bonds in organic compounds. The specific groups responsible for the color were subsequently termed ''chromophores'', from the Greek ''chromo'' meaning color and ''phoros'' meaning bearer. The unsaturated, conjugated double bonds present in the chromophore contribute to the selective absorption of light in the visible portion of the spectrum, thereby giving rise to

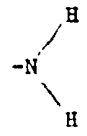
color. Some of the more common chromophores found in colored organic materials are as follows:



Chemical groups which play an auxiliary function in intensifying or modifying the color are termed ''auxochromes'' from the Greek ''auxo'' meaning increase. The greater the extent or degree of conjugation in the molecule, the deeper the color, whereby the dominant absorption band in the visible portion of the spectrum is shifted to longer wavelengths. This latter shift is referred to as bathochromic in contrast with a hypsochromic effect where the dominant absorption band is shifted to shorter wavelengths. The incorporation of chemical groups which effectively participate in the resonating system play a significant and enhancing role in color development. Some typical auxochrome groups are as follows:


dialkylamino

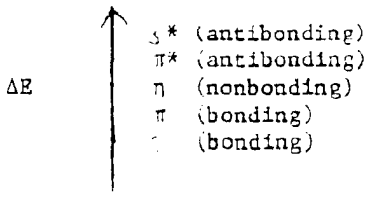

alkylamino


amino

-OH hydroxy

$-OCH_3$ methoxy

Qualitative molecular orbital theory provides a simple interpretation of the above generalizations (Ref. 1,4,5). From this point of view, the electronic energy levels of a molecule may be represented as follows, where * refers to excited states. The



absorption of light by a conjugated system involves an excitation of an electron from the highest occupied (π) molecular orbital to the lowest unoccupied (π^*) molecular orbital of the molecule. As conjugation increases, both the highest occupied (π) molecular orbital and the lowest unoccupied (π^*) molecular orbital approach the nonbonded (n) level. The π-π^* energy separation decreases. Longer wavelength radiation may be absorbed.

Electronegative substituents on a conjugated system, as well as more electronegative atoms (e.g. N vs. C) in the conjugated chain itself have the effect of lowering all energy levels in a molecule. The effect of such substitutions on the absorption spectrum of the molecule is small, however, since the net π-π^* energy separation is essentially unaffected.

The π-π^* separation of a conjugated system may be substantially reduced, however, by the introduction of electropositive donor substituents (auxochromes). In effect, such substituents introduce a new occupied molecular orbital, which, according to simple Hückel theory, would be near the nonbonding (n) energy level.

Thus, a new, smaller π-π^* energy separation has been generated. The absorption spectrum is shifted to longer wavelengths. Obviously, the magnitude of this shift will be greater when electronegative substituents are also present since they lower the π^* level of the system as mentioned above, further decreasing the effective π-π^* energy separation.

While the above discussion is certainly an oversimplification, we have described the fundamental concepts of light absorption and, basically, how organic pigments produce color. Other discussions of this subject in terms of resonance (valence bond) and free-electron theory may be found in references 1, 2, 6-8.

It should be noted that within the company (Orchem), a computer program is available for the calculation of the electronic spectra of conjugated molecules using the semi-empirical Pariser-Parr-Pople (PPP) self-consistent field molecular orbital (SCF-MO) method. The user should keep in mind the fact that in addition to chemical composition, the frequencies of the radiation which may be absorbed by a pigment may also be influenced by external forces such as crystal structure (polymorphism, crystal strain), temperature, and dispersion medium.

B. Inorganic Compounds

As in the case of organic compounds, an absorption band in the UV, visible or near IR for an inorganic compound is due to a transition of an electron from a lower to a higher energy state. The approach used with the inorganic compounds ordinarily differs, however, from that used with the organic ones. Two types of spectra are of predominant interest with inorganic pigments; charge transfer spectra and d - d spectra. Color due to electron transfer between two different valence states of the same metal is important in particular cases. An interesting review of the causes of colors of inorganic pigments is given by Feitknecht (Ref. 9).

1. Charge Transfer Spectra

In the ideal case of an ionic inorganic compound, the absorption spectrum is simply that of the ions. For metal ions with a filled s-, p-, or d-shell, the first excited level is very high so light absorption occurs only in the ultraviolet. The energy to excite or split off an electron is much less for the negatively charged non-metallic ions. Thus, the absorption spectrum of alkali halides in the ultraviolet is attributed to the halide ions, and the adsorbed energy is used to transfer an electron from the halide ion to the metal ion. Such a spectrum is called a ''charge transfer spectrum''.

In the case of halides and chalcogenides of Group B and transition metal ions, the charge transfer spectrum may be shifted into the visible and the overall spectrum may consist of the spectrum of the metal ion and the charge transfer spectrum of the anion. The colors of permanganate and chromate ions are due to charge transfer from a ligand to a metal ion. The absorption color of the pigment red lead is also due to charge transfer. The shift of the charge transfer spectrum produced by metal ions has been correlated with polarizability of the negative ion and the polarizing effect of the positive ions, in the case of a series of halides. The sequence of absorption bands of transition metal complexes containing halide ions agree with the redox potentials and the bands shift to longer wavelength as the oxidizing power of the metal ion increases. The relationship does not hold for the oxides. In these cases (oxides), the crystal structure is believed to influence the charge transfer to upset the aforementioned relationship. The pronounced effect of structure is evident in the marked color differences between polymorphs (e.g., red and yellow PbO).

2. d-d Transition Spectrum

The five d orbitals have preferred directions in space, the dxy, dxz, and dyz orbitals being directed along the bisectors of the angles between the axes, the $dx^2 - y^2$ orbital being directed along the x and y axes and the dz^2 orbital having its maximum charge density along the z axis. The three classes of orbitals behave differently when they are in the field of ligands which leads to a splitting of the energy levels which might exist in the absence of a ligand. The kind of splitting depends on the number of d electrons and the symmetry of the field, and is treated by crystal field theory. As a result of light absorption, a d electron is shifted from the lowest level to a higher one of these split d levels. These lead to the

bands on the long wavelength end of the spectrum. More energy is required for a transition to an excited state and the corresponding absorption bands lie at shorter wavelengths.

3. Compounds with Metal Ion in Two Valence States

Some compounds which contain a metal in two valency states are strongly colored (e.g., iron blue). The absorption band in the visible in the case of iron blue $KFeFe(CN)_6$ is believed due to a charge transfer between $(Fe^{II}(CN)_6)^{4-}$ and Fe^{III+} ions. This type of transfer of an electron from the ion of lower valency to an ion of the same metal in a higher valence state is believed to be responsible for the color of such compounds which have a metal ion in two oxidation states.

4. Color Due to Trapped Groups

Colored molecules or radicals trapped in a solid may also confer strong color. The color of ultramarine blue is believed to be due to sulfur trapped in cavities in the alumino silicate lattice. This source of color is of interest only in such special cases.

IV. SCATTERING

Scattering, as the term is used here, is the result of reflection, refraction, and diffraction. The contribution of each to scattering and the influence of scattering will be reviewed here.

A. Reflection and Refraction

Pigment particle size, down to a diameter approximately equal to the wavelength of light, has little effect on light reflection. However, the number of particles for a given weight of pigment increases with decreasing size, and hence the total scatter by reflection increases with decreasing size in the range of Fresnel reflection (particles large vs. λ). In this region, intensity of reflected light varies with the difference in refractive index between pigment and medium, the angle of incidence, and polarization of incident light.

For colored materials, refractive index may vary markedly with wavelength (maximum index on long wavelength side of absorption maximum) so there may be a marked variation of reflection and refraction with wavelength. Maximum scattering, for a given size in this (Fresnel) region, is thus usually obtained at the wavelength of maximum refractive index. It is worthy of note that the refractive index, and hence reflection-refraction scattering, is different for different crystal faces for the usual anisotropic pigment crystals.

B. Diffraction

We now turn to the effect of diffraction on light scattering. An optimum particle size for scattering occurs at a particle size in the range of about 1/2 to 1 wavelength. In this size range, scattering is considerably more important than in the ''Fresnel'' region discussed previously, or in the ''Rayleigh'' region, to be covered later. Diffraction is the major contributor to scattering in this size region. Light waves tend to bend as they pass the edge of an object in their path; this results in the phenomenon called diffraction. Small particles can bend considerably more light than actually falls on them, because of the diffraction effect at the edges. The diffraction effect reaches a maximum for particle sizes in the range 1/2 to 1 wavelength. It should be noted that no one size of colored pigment gives maximum scattering for all wavelengths, since refractive index varies with wavelength and scattering increases with the refractive index difference between a pigment and the surrounding medium. Also, the particle size for maximum scattering is influenced by pigment concentration.

C. ''Rayleigh'' Scattering

Scattering falls off markedly as the particle size becomes very small relative to wavelength. In this region of very small particle size, Rayleigh's law applies and scattering is inversely proportional to the 4th power of the wavelength and, for a given weight or volume concentration of pigment, directly proportional to the third power of particle diameter, and also varies with the refractive index of the dispersion medium and the pigment/dispersion medium refractive index ratio. (The apparent sixth power relationship between scattering and particle diameter, indicated by a common form of the Rayleigh equation, applies only if the number of particles is constant as the size is changed (i.e. weight and volume concentrations change).)Hence, very small particles do not hide well by scattering but may hide by absorption.

D. Scattering, Hiding, and Transparency

The foregoing considerations indicate that scattering can be minimized by using particles very much smaller or much larger than the wavelength of light. Control of particle size is thus the key to transparency, with very small particles yielding the greatest transparency.

It is worthy of note that a relatively small proportion of particles in the size range for optimum diffraction scattering can have a marked effect in decreasing transparency. Also, since different wavelengths are usually scattered differently, the color of the scattered light varies with particle size distribution. This can affect tinctorial properties very significantly.

E. Color Calculations Based on Scattering and Absorption

The Kubelka and Munk treatment of color (Ref. 10) in terms of scattering and absorption forms the basis for many systems (e.g., Pigments - Chestnut Run) for color calculations and matching. Kubelka and Munk characterized the optical properties of a particle dispersed in a medium by two constants, K, an absorption coefficient, and S, a scattering coefficient. For colored materials, one needs to know these constants as a function of wavelength. The now well known Kubelka-Munk equation is:

$$\frac{K}{S} = \frac{(1 - R\infty)^2}{2R\infty}$$

where $R\infty$ is reflectance of a film of sufficient thickness to give maximum reflectance, and K and S are as just indicated. Application of this equation to calculation of the color of pigment mixtures is based on Duncan's finding (Ref. 11) that in pigment mixtures the scattering and absorption coefficients of the mixture are additive functions of the scattering and absorption coefficients of the components. Thus, for a mixture of a parts of pigment A and b parts of pigment B,

$$\frac{K}{S} = \frac{aK_A + bK_B}{aS_A + bS_B} = \frac{(1-R\infty)^2}{2\ R\infty}$$

In principle, the reflectivity, and hence the color, of a pigmented film can be calculated by this method. For colored materials, the calculations must be carried out for wavelengths covering the visible spectrum. This method works out reasonably well in many cases and forms the basis for widely used methods of instrumental color matching.

V. LIGHT INTERFERENCE

Color may result from interference phenomena, as in the case of our Afflair® pigments wherein interference occurs as one of the optical effects consequent on a TiO_2 coating on mica. The color is controlled by varying the thickness of the coating to shift the interference band.

VI. OTHER PIGMENT/LIGHT INTERACTIONS

Fluorescence and phosphorescence are two other possible results of interaction of light with colored pigments. Fluorescence occurs when the excited molecule returns rapidly ($< 10^{-8}$ sec.) to the ground state with emission of light. The fluorescent light is of lower energy than the exciting light since some of the energy is dissipated in other ways (cf., however, anti-Stokes fluorescence). Fluorescence is much influenced by the medium surrounding the pigment molecules and few stable pigments exhibit appreciable fluorescence when not in solution. (The so-called fluorescent pigments are mostly dyes in an organic polymer.)

Delayed emission of light following excitation is called phosphorescence. Few commercial colored pigments exhibit phosphorescence. The Pigments Department does not, at present, manufacture any colored pigments which owe their utility to phosphorescence or fluorescence.

Interaction of light with pigments to produce photochemical reactions will not be covered here.

VII. FLAKE PIGMENTS

A. Nacreous Pigments

A pearlescent effect is produced by pigments of particle size much larger than the wavelength of light, so oriented that the reflected light is not diffuse. Simultaneous perception of parallel reflections from particles at various depths in the medium results in a nacreous lustar (Ref. 12). A large difference in refractive index between the medium and the pigment is required for optimum effect. Composite platelets of several layers, one layer having an index of refraction higher than the medium, and the other lower, produce greatest degree of reflection (Ref. 12).

B. Metallic Pigments

Metals contain electrons which have much greater mobility than is the case with the electrons of the usual pigments which are non-metals (dielectrics). (Some dielectrics with a high degree of electron delocalization can also produce metallic reflection (bronzing). The greater electron mobility in metals results in much greater light reflectance relative to non-metals. Metallic colors result from selective reflection at the surface, the reflection being highest at wavelengths where absorption is also highest, in contrast to nonmetallic colors where the observed colors represent wavelengths which are not strongly absorbed. Metallic pigments are usually flaky with the larger dimensions much greater than the wavelength of light.

VII. MULTIPLE PIGMENT/LIGHT INTERACTIONS

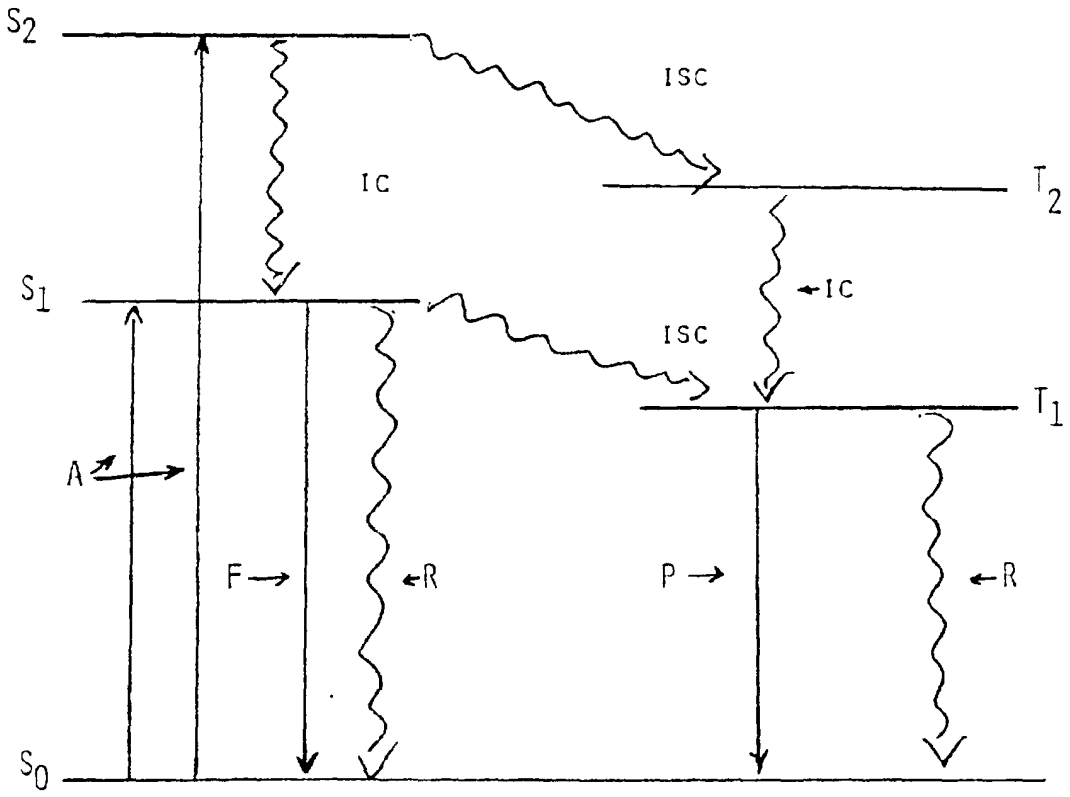
An interesting discussion of effects of scattering and absorption on color and the effects of particle size is given in Reference 12.

References

1. H. H. Jaffe and M. Orchin, ''Theory and Applications of Ultraviolet Spectroscopy'', Wiley, New York 1962.
2. F. Jones in ''Pigments'', D. Patterson, Ed., Elsevier, New York, 1967, p. 26.
3. D. Patterson, ibid., p. 50.
4. G. Hallas, J. Soc. Dyers and Colourists, 84, 510 (1968).
5. A. Streitwieser, Jr., ''Molecular Orbital Theory for Organic Chemists'', Wiley, New York, 1961.
6. E. Coates, J. Soc. Dyers and Colourists, 83, 95 (1967).
7. D. Graham in ''The Chemistry of Synthetic Dyes and Pigments'', H. Lubs, Ed., Reinhold, New York, 1955, p. 662.
8. N. J. Juster, J. Chem. Ed., 39, 596 (1962).
9. W. Feitknecht, in ''Pigments'', D. Patterson, Ed., Elsevier, New York, 1967, p. 1.
10. P. Kubelka and F. Munk, Z. Tech. Physik, 12, 593 (1931).
11. D. R. Duncan, J. Oil Col. Chem. Assn., 32, 296 (1949).
12. P. J. Papillo, Modern Plastics, pp. 131-134, 139-140, 142, 144, 146, 178, 184-185 (December 1967).

Revised by R. C. Bingham - 1975

PHOTO PHYSICAL PROCESSES



A - Absorption

F - Fluorescence

P - Phosphorescence

R - Radiationless deactivation

IC - Internal conversion

ISC - Intersystem crossing

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EXCITED STATES

N, π^* - LOCALIZED ON GROUP HAVING HETEROATOM POSSESSING NON BONDING ELECTRONS. REACTIONS DOMINATED BY HETEROATOM GROUP AND BY UNFILLED N-ORBITAL

EXAMPLE: 

π, π^* - USUALLY DELOCALIZED OVER CONJUGATED SYSTEM. MOST COMPOUNDS HAVING EXTENDED CONJUGATION, WITH OR WITHOUT HETEROATOM WILL HAVE LOWEST π,π^* STATE.

SPIN MULTIPLICITY

SINGLET - USUALLY SHORT LIFETIME, ESPECIALLY π,π^* SYSTEMS - NEED FAST REACTION TO COMPETE WITH DEACTIVATION.

TRIPLET - LONG LIFETIME - MOST REACTIONS OCCUR FROM THIS STATE.

PHOTO REACTIONS

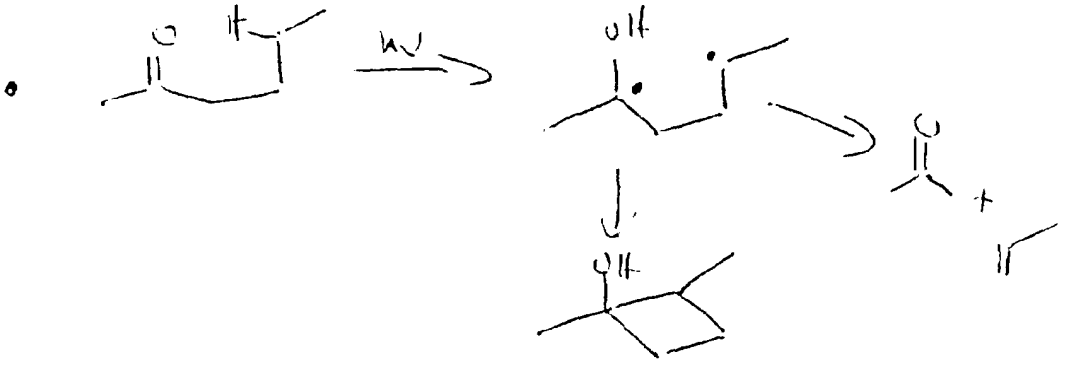
UNIMOLECULAR - COMPETE DIRECTLY WITH PHOTOPHYSICAL PROCESSES. TYPE OF REACTION AND PROBABILITY OF OCCURRENCE DEPENDENT ON STRUCTURE OF MOLECULE

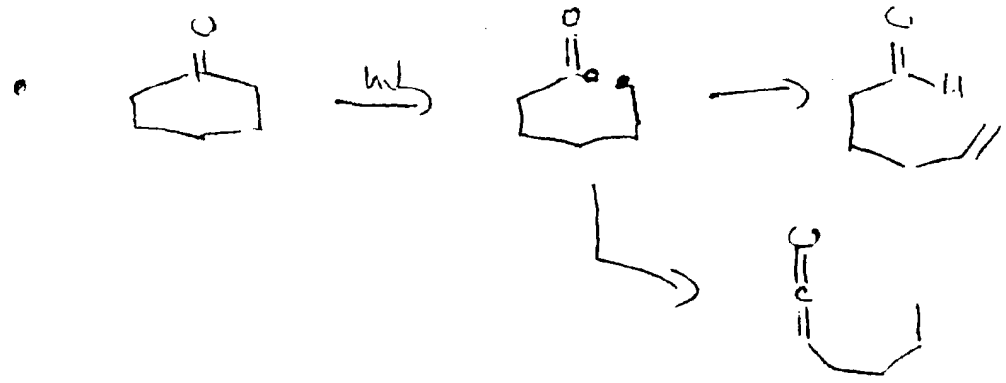
EXAMPLES: INTRAMOLECULAR HYDROGEN ABSTRACTION, BOND CLEAVAGE, ISOMERIZATION, PHOTO EXTRUSION, PHOTO ADDITION

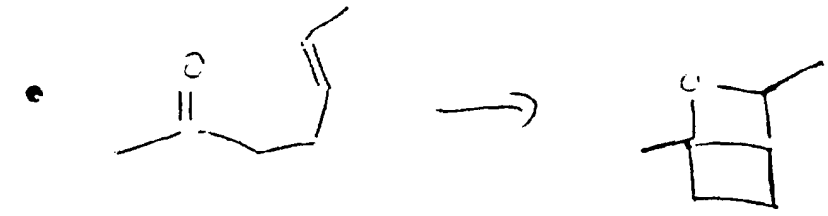
BIMOLECULAR - DEPENDING ON EFFICIENCY OF REACTION - THESE CAN BE VERY FAST, LIMITED ONLY BY DIFFUSION, TO VERY SLOW PROCESSES.

EXAMPLES: PHOTOREDUCTION, PHOTO OXIDATION, PHOTO ADDITION, DIMERIZATION.

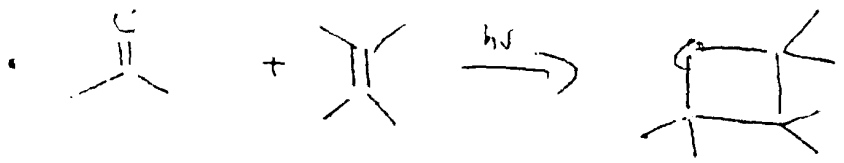
UNIMOLECULAR

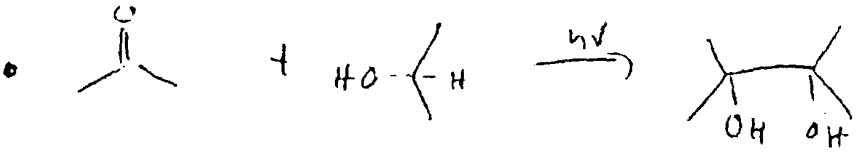


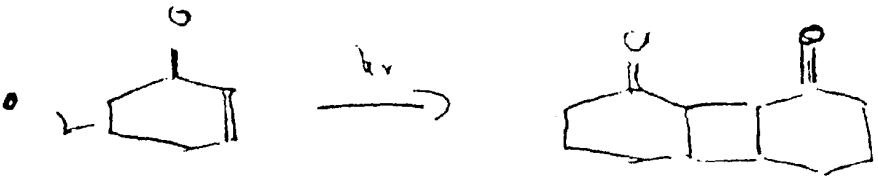




BIMOLECULAR

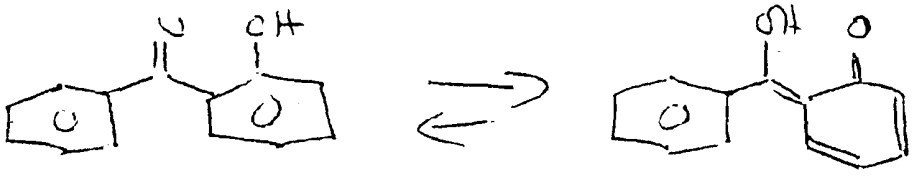






DEACTIVATION OF EXCITED STATES

- REVERSIBLE INTRAMOLECULAR REACTION



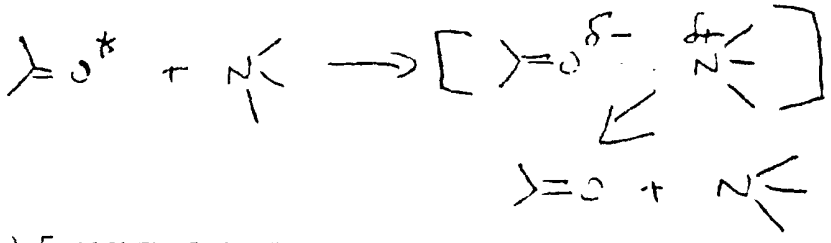
- INTRAMOLECULAR H-BONDING

- ENERGY TRANSFER

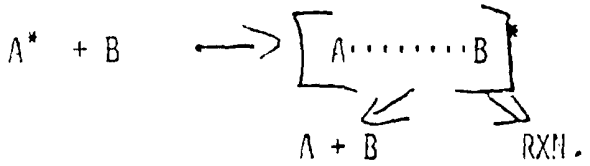
$$D^* + A \longrightarrow D + A^*$$

- BIMOLECULAR COMPLEXATION

  (A) ELECTRON ABSTRACTION



  (B) EXCIPLEX FORMATION



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SOLID STATE LIGHTFASTNESS

- AUTOMOTIVE GRADE PIGMENTS NEED HIGH STABILITY - QUANTUM YIELDS $\sim 10^{-7}$. TO ACHIEVE THIS STABILITY:
  - PIGMENTS CANNOT POSSESS OBVIOUS PHOTOREACTIVE CENTERS
  - CRYSTAL STRUCTURE MUST INCLUDE STRONG INTERACTION TO ALLOW FAST DEACTIVATION
- PHOTOREACTION OCCURS BETWEEN PIGMENT AND VEHICLE COMPONENTS - USUALLY AT DEFECT SITES ON SURFACE

STABILIZATION OF PIGMENTS

- DEACTIVATION OF EXCITED STATES
  - ENERGY TRAPS
  - VIBRATIONAL DEACTIVATION
  - ELECTRON TRANSFER
- SURFACE QUENCHERS

PROBLEMS

- LIGHT STABILITY OFTEN VEHICLE RELATED - MINOR ADDITIVES MAY INTRODUCE NEW PHOTOCHEMICAL REACTIONS

- EFFECTS OF OUTDOOR ENVIRONMENT - MANY PIGMENTS PERFORM WELL IN ACCELERATED TESTS, BUT FAIL RAPIDLY OUTDOORS.

COLOR TERMINOLOGY AND MEASUREMENT

I. COLOR TERMINOLOGY

Color requires three and only three parameters for its complete description. These are:

Hue - Color (red,yellow,green, etc.)

Lightness - Degree of lightness or darkness, also referred to as depth, value, or luminous reflectance.

Color Intensity - Departure from a gray of the same hue, also referred to as chroma, saturation, or purity.

Hue relates to particular wavelengths present in the radiation, lightness to the amount of radiation, and intensity to the purity of the radiation. Such additional factors as gloss, which relates to the amount of specular reflectance, ''flip-flop'', which relates to the change in color with viewing angle, and sparkle, which relates to the metallic effect, are not, strictly speaking, color parameters.

A number of terms have come into common usage for specifying the three color attributes. Some, such as the Munsell system, are based on a subjective visual analysis and some such as the CIE (Commission International d'Eclairage), are based on spectrophotometric data. The following table illustrates some of this terminology.

Pigments Department	Munsell	C.I.E.
Hue	Hue	Dominant Wavelength
Lightness	Value	Luminous reflectance
Color Intensity	Chroma	Excitation purity

Scattering affects all three

II. SUBJECTIVE COLOR COMPARISONS

The color business relies heavily on subjective visual color comparisons. In our work, hue is usually limited to red, yellow, green, and blue. This sequence is considered as following around in a circle with red following blue to complete the circle. Hue differences are designated by indicating a deviation of hue in the direction of the adjacent color. For example, a green of slightly different hue from that of a reference green would be designated as either yellower or bluer than the reference green. A red would be designated as either yellower or bluer than the reference red. The lightness parameter is designated as either lighter or darker than a reference color and the color intensity parameter is designated as either more intense or duller than the reference color.

The quantitative aspect of subjectively expressing color difference began at Newark as simply a rather poorly defined verbal description. The terms in common usage were vvs (very, very slight), vs (very slight), and s (slight). Later, a more precise numerical system was introduced and both systems are in current use. The following table relates the two systems.

Verbal	Numerical
Equal	0
.3 ΔE in Zeta space → vvs	1-2
vs	3-5
s	6-11
Full	12-17
v Full	17-100*

*A designation of 100 represents an extreme mismatch.

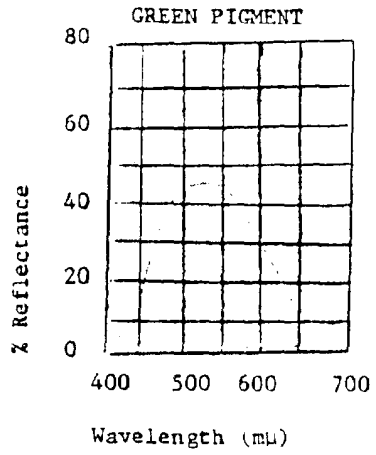
The term vvs is considered to be a "barely perceptable" difference. The term s is roughly 3 times the term vvs and is usually an acceptable commercial match. The verbal system is used when reporting tinctorial information to our customers. It has the advantage of being more descriptive than the numerical system. The numerical system finds use in estimating blending ratios to adjust tinctorial properties to match a standard. On occasion, numerical readings of over 100 are attempted but since the greater the color difference, the poorer the precision of the numerical estimate, such readings will have extremely poor precision and hence are of doubtful value.

Both the verbal and the numerical designations apply to the three color attributes previously described. There is another pigment property that relates to color but is not strictly one of the three color attributes. This is color strength. This is measured by mixing the colored pigment with a white pigment in some dispersing medium, usually a varnish ink. This is called an extension, or tint. If equal amounts of the colored pigment and the reference pigment are mixed with the white pigment and if visual inspections of the resulting tints give the appearance that the colored pigment tint contains more colored pigment than the reference tint, the colored pigment is said to be stronger. An adjustment in the relative weight of colored pigment is made until the color strength appears equal. The color strength is then designated as the relative weight of colored pigment required to match the reference, with the reference set at 100. For example, if it requires the relative weight of 115 to match the relative weight of 100 for the reference, the pigment strength is 115 which means that it is weaker than the reference by 15%. If the strengths are close, frequently no adjustment is made and the strengths are estimated directly without adjustment. This is a somewhat dangerous practice if hue and color intensity are important because changing the ratio of colored pigment to white can change both hue and color intensity, and the change need not be the same for the two pigments being compared.

III. INSTRUMENTAL COLOR MEASUREMENT

A. The Spectrophotometer

The spectrophotometer is the basic instrument for making color measurements. White light consists of light of many different wavelengths ranging from 400 to 700 nanometers (violet to red). When this light strikes a surface, a portion of it is absorbed and the remainder is reflected. A spectrophotometer measures the ratio of reflected (or transmitted) light to incident light as a function of wavelength. A colored surface obtains its characteristic color by reflecting some of these wavelengths more than others. A plot of percent reflectance versus wavelength is called a spectrophotometric reflectance curve as illustrated.



Without any calculation, a spectrophotometric curve will usually reveal certain characteristics about the color of the reflecting surface. The peak of maximum reflectance indicates the approximate hue or dominant wavelength. The overall height of the curve indicates whether the color is light or dark, and the sharpness of slope of the peak is an indication of the color intensity or purity.

A spectrophotometric curve, along with the specifications of a standard viewing light can be used to calculate the three basic color parameters in the C.I.E. color system. It is possible to equip some spectrophotometers with a computer to automatically make these calculations. For purposes of visualizing the three color parameters, they are imagined to make up a three dimensional grid. This is called a color space. The hue is given in cylindrical coordinates and comprises the hue circle. Color intensity is measured radially from the center of the circle, and lightness is measured vertically from the plane of the hue circle. Over the years many color spaces have been proposed, all employing the same basic

C.I.E. grid system. All such modifications from the C.I.E. color space have the one objective of creating a color space such that an incremental distance in some spot in the color space will have the same subjective color difference in any other spot in the color space. This objective has never been realized and hence the search goes on. In any event, color spaces, far superior to the C.I.E. system have been developed and two such colorspaces in current favor are the so called U* V* W* color space and the L a b color space.

B. The Color Difference Meter

Since the eye integrates the radiation it receives, producing a single color sensation that we describe in terms of three parameters, it is possible to design an instrument that will do the same thing. This is accomplished with the use of a specified light source, specified color filters, and a specified light sensing device. When properly combined, three numbers are obtained that can be related to any color designating system. Such an instrument is particularly useful in getting a measure of color difference between two colors that differ by a small amount. The ability of such instruments to detect small color differences exceeds that of current spectrophotometers and for many colors it compares favorably with the human eye. Unfortunately these instruments are on the defensive when dealing with dark or intense colors but instrumental research is active in this field and it is to be expected that this limitation will soon be removed. One such instrument is the DU COLOR designed by the DuPont Engineering Department and manufactured by the Neotec corporation. In addition to giving three numbers that may be used to calculate to any color space, the instrument will also read L, a, and b and will directly give color differences in L a b color space.

Two such instruments are available at Newark. One is in the Color Control Lab. and the other is in the Physics Lab. A plant project is under way to use the DU COLOR as a substitute for making visual color comparisons.

metameric pair – two pigments which look alike under one light, but different under different light

References

1. W. D. Wright - ''The Measurement of Color'' Van Nostrand- Reinhold Company (1969).

2. D. B. Judd - ''Color in Business, Science, and Industry '' - John Wiley and Sons Inc. (1963).

3. R. M. Johnson and M. Saltzman (Chairmen)"Industrial Color Technology"- Advances in Chemistry Series. American Chemical Society (1971).

4. F. W. Billmeyer Jr and M. Saltzman - ''Principles of Color Technology'' Interscience Publishers. Division of John Wiley and Sons (1966).

5. A. C. Hardy - ''Handbook of Colorimetry'' - The Technology Press. Massachusetts Institute of Technology (1936).

Revised by A. R. Hanke - 1975

COLOR MEASUREMENT AND TERMINOLOGY

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I - GENERAL PRINCIPLES OF COLOR MEASUREMENT

A. Three parameters are required to designate a color. In the Pigments Department these are as follows:

1. Light - Dark

   Relates to amount of radiation.

2. Intense - Dull

   Relates to purity of radiation.

3. Hue

   Relates to particular wavelengths present in the radiation.

B. The eye integrates the radiation it receives producing a single hue sensation, and this may correspond to a wavelength that is not actually present in the radiation.

C. Grassmann's Laws are the basis of all colorimetric measurement.

These laws state that color sensation can be added, subtractad, multiplied and divided without regard for their spectral composition.

II - COLOR MEASURING SYSTEMS

A. A color measuring system called the CIE (older terminology ICI) system is the most fundamental system in use today. It makes use of three parameters called "Tristimulus Values", X, Y, Z. After conversion to "Trichromatic Coefficients", x, y, the data are referred to a "Chromaticity Diagram". Color is usually designated as:

1. Dominant wavelength (relates to Hue)
2. Lightness (relates to "Light - Dark")
3. Excitation Purity (relates to "Intense-Dull")

B. The Munsell system is a classification of surface colors aimed at spacing the colors in subjectively estimated equal steps. The color is designated as:

Hue
Chroma (Intense - Dull)
Value (Light - Dark)

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C. To achieve a uniform color scale, the C.I.E. chromaticity diagram has been transformed to many other coordinate systems.

1. Judd's "Uniform Chromaticity Scale" (U.C.S.) is one of the earlier systems.

2. A more recent, improved, and widely used system is the Adams coordinate system which has the advantage of simplifying comparison with the Munsell system.

III - COLOR MEASURING INSTRUMENTS

A. A spectrophotometer measures the ratio of reflected (or transmitted) light to incident light as a function of wavelength. This constitutes a "Reflectance (or transmittance) curve.

Knowing the reflectance curve and the light quality (Illuminance A, B, C, etc.) incident upon the sample, is all that is necessary to calculate a complete designation of the color.

B. A Color Difference Meter uses appropriate color primaries to directly determine three parameters that relate simply to the difference in tristimulus values between surfaces of nearly the same color.

1. When these differences are expressed in terms of a uniform color system, a "color difference" (ΔE) can be assigned.

2. Unfortunately, there is no completely satisfactory uniform color system so for any given application it becomes necessary to investigate several systems or use a system that experience has shown to be satisfactory.

IV - NUMERICAL DESIGNATION OF COLOR DIFFERENCE

A commonly used color difference unit is the NBS (National Bureau of Standards) Unit. One of these units is about equal to the maximum color difference tolerable in rather critical commercial color matching.

One NBS unit is approximately equal to:

0.1 Munsell Value step.
1.5 Munsell Chroma steps.
2.5 Munsell Hue steps (Chroma/1). ← Mean Chroma = ~~~,

A. R. HANKE

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PARTICLE SIZE AND PIGMENT PROPERTIES

Pigment technologists must concern themselves not only with the chemical properties of pigments but also with their physical properties. A physical property of paramount importance and which influences most all pigment properties is particle size. In the size range of 30μm, texture effects are noted. As little as 0.1% of the pigment particles in the 30μm size range can produce a visual blemish in a high gloss paint film.

Rheological properties of pigmented systems are also affected by pigment particle size. As the particle size decreases, there is an attendant increase in specific surface, and such rheological properties as thixotropy and an increase in viscosity with time (reactivity) are accentuated. Another rather anomalous observation is that if the pigment exists initially as extremely small primary particles, these "cement" together to form large, hard aggregates; hence, pigments that start out with a very small ultimate particle size may, for this very reason, finish with aggregate particles that are too large. Pigment technology is concerned with obtaining some desired particle size, neither too large nor too small. In most cases, the difficulty lies not in getting the particles large enough but in getting them small enough and keeping them small. Factors tending to prevent the particles from staying small are flocculation, agglomeration, aggregation, and crystal growth.

All factors tending to change the effective particle size of the pigment will change the tinctorial properties. That particle size will have a marked effect on the coloring ability of a colored pigment can be readily appreciated in a qualitative sense by imagining a strong blue pigment, with a particle size as large as 0.1 mm dispersed in a white pigment. Such a mixture will not look blue. At best, it will make the white pigment appear speckled. The strong blue color, inherent in the pigment, will not manifest itself until the particle is decreased to a size well below 0.1mm. The size range of interest from the point of view of color properties is about 1.5μm to 0.02μm. The wavelength range of the visible portion of the spectrum is 0.7μm to 0.4μm; hence, it is apparent that the important pigment size range extends well beyond the visible wavelength range.

When light encounters a pigment particle, two things can happen. The light can be absorbed and it can be scattered. This discussion will dwell briefly with the theoretical aspects of the interaction of small particles with electromagnetic radiation and its application to pigment technology. Fluorescence and phosphorescence will be ignored but such phenomena can be accommodated by an extension of the general theory.

The general theory was first given expression some 70 years ago by Gustav Mie. He took Maxwell's electromagnetic radiation equations and derived equations describing the action of spheres of all sizes and colors on such radiation. It is

crystallite size + particle size may not be the same, x-ray line broadening due to small crystallites will not show the maybe large effective particle size made up of hard aggregates. x-ray line width can also be affected by degree of crystallinity.

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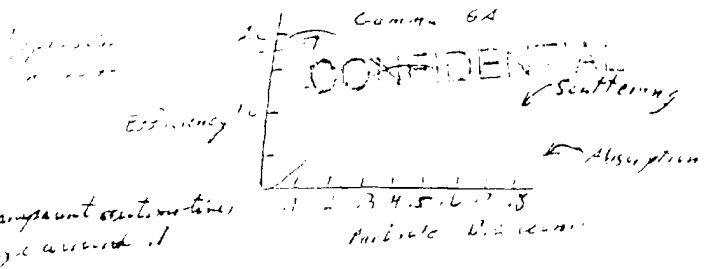
assumed that a photon incident upon a particle is subject to one or the other of two fates. It is either annihilated by absorption or scattered without change of frequency. The scattering efficiency is a measure of how effectively the particles scatter radiation and the absorption efficiency is a measure of how effectively the particles absorb radiation. These efficiencies are expressed as ratios of the effective cross section area to the geometric cross section. For spheres, it is obvious that the geometric cross section is πa^2 where a is the radius of the particle. One might ordinarily think that the upper limit for scattering efficiency would be unity because the effective scattering cross section could never exceed the geometric cross section. This is not true and, for small particles, the effective cross section is larger than the geometric cross section, which means it is possible to have efficiencies greater than unity.

Two intrinsic properties of pigments will influence the scattering and absorption efficiencies. These are the refractive index and the absorption index. In addition to these parameters, the wavelength of the radiation, the refractive index of the surrounding medium, and the particle size will influence the scattering and absorption efficiencies. It should also be pointed out that the values of the refractive index and the absorption index of colored pigments change considerably with wavelength. This behavior is to be contrasted with the behavior of colorless pigments (white) where the absorption index is essentially zero and the refractive index does not change very much with wavelength.

The need for including an absorption index when dealing with colored pigments makes the efficiency calculations considerably more complicated than when the absorption is zero. This complication arises from the fact that the refractive index terms in all the equations must now be replaced by a complex number that takes the form (n-nki) where n is the refractive index as usually defined and k is the absorption index. The development of high speed computers has made such calculations reasonable and it is now possible to theoretically examine how scattering and absorption will change with pigment particle size. All that is necessary is that the refractive index and absorption index be known as a function of wavelength. These parameters have been measured for some of our pigments using an ellipsometer. Such an instrument measures the characteristics of elliptically polarized light reflected from a smooth pigment pellet. These measurements, when made at different wavelengths, enable a calculation of both the refractive index and absorption index as a function of wavelength.

When scattering and absorption efficiency calculations are made, it is observed that as particle size decreases, scattering increases to a maximum and then decreases. The intensity of the scattered light will also vary with the wavelength; hence a variation in the selective light scattering brought about by a variation in particle size will alter the hue. In a masstone color, the light scattered by the pigment particles is the sole cause of ''lightness of masstone''. Particle size will have a very large effect on this property. It takes only a relatively small percentage of the pigment in the size range of maximum light scattering to markedly affect the ''lightness of masstone''.



It has already been mentioned that the light absorption efficiency will also change to a considerable extent with change in particle size. A plot of absorption efficiency vs. particle size in the wavelength region of maximum light absorption shows that when the particle size gets very small (approx. 0.06μ m), a further decrease in size does not contribute much additional absorption. In fact, if the refractive index is quite different from that of the surrounding medium, light absorption will also go through a maximum, although at a size smaller than that for maximum scattering. This particle size is so small that it is difficult to actually experimentally observe a decrease in light absorption with decrease in particle size, so that for all practical purposes, it is permissible to consider that a decrease in particle size will mean an increase in light absorption. Realize, however, that in the small particle size range, very little additional light absorption is realized by further decreasing the particle size. For larger sizes, however, a decrease in particle size will cause a considerable increase in absorption efficiency and hence in pigment strength.

From the foregoing, it becomes evident that because of light scattering and light absorption, particle size is a very important parameter in influencing the tinctorial properties of colored pigments. The theoretical treatment leading to these conclusions imposes certain conditions that are not realized in an actual pigment dispersion. These are worth noting. Mie theory assumes that all particles are far enough apart so that light scattered from one particle is not rescattered by another. Mie theory assumes that all particles are isotropic spheres. Pigment particles are neither isotropic nor spherical. These limitations will, to some extent, destroy the quantitative significance of calculations made using Mie theory but it is still possible to draw conclusions that are of practical value in pigment research.

The most serious limitation in the application of Mie theory is the assumption of "no particle interaction" that was previously mentioned. Most pigmented systems are so populated that considerable interaction occurs. A completely satisfactory treatment of this problem has not been accomplished. A widely used method is one developed by Kubelka-Munk. This theory assumes perfectly diffused illumination of and reflection from the pigmented sample surface. This is never realized but, in spite of this limitation, the agreement between theory and experiment has been sufficiently good to render this theory very useful in predicting the color and hiding power of pigment mixtures in any system.

The basic formula is,

$$\frac{C_1S_1 + C_2S_2 + \cdots C_nS_n}{C_1K_1 + C_2K_2 + \cdots C_nK_n} = \frac{S}{K} = \frac{2R_\infty}{(1-R_\infty)^2} = D = \frac{1}{\theta}$$

Cn = Concentration of a particular pigment designated by the subscript.

Sn = The Kubelka-Munk light scattering coefficient for the pigment designated by the subscript. This is considered a constant for a given pigment in a particular system.

K_n = The Kubelka-Munk light absorption coefficient for the pigment designated by the subscript. This is considered a constant for a given pigment in a particular vehicle system.

R_∞ = The diffuse reflectance from the surface of the pigmented system where the system is thick enough so that increasing the thickness will not cause a change in reflectance. In practice, the measured reflectance is corrected in a somewhat arbitrary manner to account for the surface reflectance due to the refractive index change that occurs at the interface.

S = The Kubelka-Munk scattering coefficient for the completely pigmented system.

K = The Kubelka-Munk absorption coefficient for the completely pigmented system.

An inspection of the equation shows that ''S'' is simply the sum of the individual S's for each pigment, weighted by the concentration of that pigment in the completely pigmented system. The same holds true for ''K''. The ratio S/K is the so-called, Kubelka-Munk function ''Ø'', and in some publications its reciprocal is designated as ''θ''. The numerical value for the individual coefficients are determined from reflectance measurements of simple pigment mixture of known concentration in the particular vehicle system. These coefficients are themselves functions of the wavelength; hence, it is necessary to calculate them from reflectance measurements at suitable wavelength intervals. This is the basic computational scheme that is used in computers designed particularly to calculate the proper amount of each pigment required to match a preselected color. Such a calculation usually does not give a perfect match because of errors inherent in the theory but with very few iterations, an acceptable match is obtained; hence, this method, even though based on imperfect theory, is finding practical application in color control for many pigment-using industries.

Revised by A. R. Hanke - 1975

REFERENCES

F. C. Chromey, ''Evaluation of Mie Equations for Colored Spheres'' J. Opt. Soc. Am., 50, 730 (1960).

A. Brockes, ''The correlation of Color Strength and Particle Size of Pigments According to the Mie Theory'' Optik 21, 550 (1964).

A. C. Cooper, ''The Refractive Index of Organic Pigments'' J. Oil and Colour Chemists' Assn. 31, 343, (1948).

Jenkins and White ''Fundamentals of Optics'', McGraw Hill Book Co. N. Y., 1950.

Born and Wolf ''Principles of Optics'', The MacMillan Co., N.Y., 1964.

Van de Hulst ''Light Scattering by Small Particles'', Wiley and Sons, N.Y., 1957.

D. R. Duncan ''The Colour of Pigment Mixtures'', Proceedings Physical Soc. 52, 390 (1940).

Revised by A. R. Hanke - 1975

PARTICLE SIZE REDUCTION METHODS

Most methods for the manufacture of the phthalocyanine (CPC) or quinacridone (QA) pigments, and many other organic pigments or dyes, yield a crude product directly from the synthesis whose ultimate particle size is far too large for pigment applications. Numerous size reduction processes are available. In general all of these, we now believe, consist of the initial reduction in the ultimate particle size of the pigment to a size below that capable of practical use, with subsequent growth and crystal perfection (by partial solubility) to the desired particle size, followed by an isolation procedure which avoids the agglomeration of these particles.

ACID PASTING

Acid Pasting is one of the earliest processes for recrystallization and purification of organic materials and has been practicized for many years in the industry. The pigment is dissolved, usually in concentrated sulfuric acid, and the solution of the pigment-acid salt is drowned into water, thereby reprecipitating the pigment by hydrolysis, in small particle size, usually with some purification resulting. The more rapid the regeneration (dilution), the smaller the ultimate particle size of the product. To achieve a product having good working properties, it is usually necessary to ''develop'' the poorly crystalline, very small particle size products in the diluted sulfuric acid by heating, or by adding a solvent for this purpose. This art is still of interest to the trade and is the subject of recent patent literature. Examples are tabulated below:

Ciba Geigy - Canadian 904276 - July 1972

Sun Chemical U.S. 3,713,857 - 1973 - Covers the acid pasting of organic pigments of improved heat stability and dispersibility by acid pasting in the presence of alpha naphthylene sulfonic acid or its salts.

Am. Cyanamid - U.S. 3,697,464 - July 1972 - claims production of β-phase QA by drowning a H_2SO_4/aryl sulfonic acid solution.

BASE PASTING

Since acid pasting is simply a recrystallization process, some attention has been given to processes in which the pigment a dyestuff is solubilized by strong alkali and subsequently drowned and recovered. Studies have been conducted along these lines on QA pigments.

TWO STAGE DROWNING

The acid pasting process can, in some cases, be combined with the isolation of the pigment from its synthesis medium, as in the acid flushing process. The CPC synthesized in kerosene can be dissolved into 98% H_2SO_4 (sulfuric acid), the acid solution decanted from the kerosene, and the H_2SO_4 solution then added to water. To achieve a small particle size, the regeneration is carried out under high turbulence conditions in two stages in a specially designed tube, the process being known as HT drowning.

Both acid pasting and acid drowning require some 10 parts per part of pigment with subsequent waste disposal problems.

ACID SWELLING (Permutoid Swelling)

The crude pigment is agitated in sulfuric acid of a concentration not quite sufficient to dissolve the pigment. Under these conditions, CPC is converted to exceedingly fine crystals of its sulfate salt. When the acid suspension of this salt is drowned into water, hydrolysis occurs and the CPC is regenerated in pigmentary size. Bill West's patents U.S. 3,326,918 and 3,362,957 are of interest in this connection.

PRE-MILLING (Dry Milling)

The acid swelling process can be markedly improved by dry milling or pre-milling the crude CPC. This process consists of grinding the crude CPC using ''Cylpebs'' (short steel rods) to a small particle-sized, but highly aggregated, product. These aggregates can be broken down by acid swelling, probably through the growth of the very small particle size CPC which forms the aggregates. Premilled crudes are quite old in the phthalocyanine art. Dupont has several patents on the subject:

Cooper - U.S. 2,857,400 - premill-solvent mill
Minnich - U.S. 3,017,414 1962 - Premill-aqueous mill
U.S. 3,051,720 1962 - Premill-acid swell
Wheeler - U.S. 3,051,718 1962 - Premill than acid swell
Braun - U.S. 3,267,116 1966 - Premill acid swell HCl

wherein the size reduced premilled crudes are superior to "as is" crudes in subsequent operation. Dupont's patent British 1,087,004 is very illustrative of the art.

VISCOUS SALT MILLING

β-phase CPC is usually made in this country by a process known as viscous salt milling. This operation requires high shear input equipment for which we have never been equipped. (WP mixers or Banbury mixers, Baker Perkins Mixers).

Large numbers of patents exist in this area involving viscous salt milling to either α or β-phase utilizing:

1) Inorganic salts such as NaCl or Na_2SO_4 and a phase converting solvent if β-phase CPC was desired. American Cyanamid pioneered in this area with two patents, U.S. 2,416,304 and U.S. 2,486,359 which dominated the β-phase CPC field for years. The economics of these patents seems highly uncertain by today's standards since they involved starting with acid pasted α-phase CPC and conversion to β by milling with NaCl/Xylene or Decalin mixtures followed by extraction.

This process type is still operated by many of our competitors and customers. The current variation seems to be dominated by U.S. 2,982,666 (Cal Ink-Tenneco) which grinds β crude at very high temperature and shear in presence of polyols (glycols, etc.)

VISCOUS ACID MILLING

A variation of viscous salt milling involves the grinding of CPC with H_2SO_4 and an aromatic solvent:

U.S. 2,930,796 GAF 1960 - Grinds CPC green crude/conc. H_2SO_4/xylene followed by drowning in water to recover pigment.

U.S. 3,080,375 GAF - is of similar type applied to CPC Blue or Green crudes and aromatic sulfonic acids.

This approach appears to be of importance to GAF since they patented these and similar approaches in Canada, Germany, and Great Britain.

American Cyanamid also has patents in this area.

SOLVENT BREACHING

This is an alternate means of deagglomeration of pre-milled crude in which an organic solvent for the pigment (o-dichloro-benzene, carbon tetrachloride, or Perclene) is used to separate the agglomerates by a crystal growth mechanism. The solvent is usually used as an aqueous emulsion and is subsequently removed by steam distillation before excessive growth of the particles occur. The degree of emulsification of the solvent appears to control the effectiveness of the process. An alternate means for obtaining a small particle size crude for solvent breaching is used in Green G (GG) processing where the crude is produced as an $AlCl_3$ complex, size-reduced by hydrolysis, and then developed by solvent breaching. Numerous competitive patents exist in this area - see U.S. 3,041,192 GAF 1962, German 1,125,574 Badische Aniline.

SOLVENT MILLING

Solvent milling utilizes simultaneous size reduction and solvent breaching and development and can be accomplished on a crude, but much more effectively on a pre-milled crude. In the latter case, the achievement of pigmentary particles, probably via solvent breaching, is much more rapid than the primary size reduction from a crude.

SALT MILLING

This process is conducted in a ball mill using salts such as Na_2SO_4, $Al_2(SO_4)_3 \cdot 14.5H_2O$, NaCl, etc. and gives initially an extremely fine particle size pigment in a highly amorphous form. The salt (about 80-85% of the charge) is then removed by aqueous extraction (usually dilute acid to remove any iron from the grinding medium) permitting the pigment to develop into a practical particle size and crystallinity. Under normal conditions, this procedure will give the least stable crystal modification with CPC.

This is also a very old art in the pigment and dye industry. Some of the pertinent patent references include the following:

U. S. 2,402,167 - Dupont
U. S. 3,119,835 - GAF - CPC NaCl mill+ liquid - β
U. S. 3,137,704 - Bayer CPC NaCl mill + Organic liquids- α

DISPERSION MILLING

If a phase-directing solvent is added to the salt milling (Perclene, etc.), it is usually possible to produce a more stable crystal modification. Dispersion milling has also been used successfully with many of the quinacridone and β CF-CPC, U.S. 2,556,728, U.S. 2,556,730 Dupont, U.S. 3,030,370 ($Al_2(SO_4)_3 15H_2O$-JJ)

HF MILLING

HF milling is a salt grinding (borax, etc.) in a highly viscous, usually aqueous medium using a Cowles type disc mill. The salt is removed by separating the highly dispersed aqueous pigment dispersion from the undissolved borax. It is particularly of interest where phase transformation problems are not encountered. Dupont's process is covered in U.S. 2,816,114, etc. A recent competitive patent is shown in U.S. 3,176,295 - 1965.

Suitable dispersion agents to assist in the size reduction and dispersion are also incorporated in the process. We use Blancol (sodium salt sulfonated naphthylene - formaldehyde complex) in this operation. This material is subsequently inactivated by an acid extraction and diphenylguanidine treatment.

The isolated presscakes are redispersed via homogenization in the presence of large percentages (10-25% of pigment toner weight basis) of nonionic or anionic type surfactants.

Renex 20 (polyethoxylated mixed fatty and resin acids).
Daxad 11 (sodium salt alkyl naphthylene sulfonic acid.

Revised - JJ - 1/76

LPH 0072386

α CPC is higher energy form of CPC formed from B if mill from solvent & mill, & goes to B in a good solvent in water & elevated temps.

PARTICLE SIZE REDUCTION METHODS

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ACID PASTING

α form of CPC produced when this process first used

The pigment is dissolved, usually in concentrated sulfuric acid, and the solution of the pigment-acid salt is drowned into water, thereby reprecipitating the pigment by hydrolysis, in small particle size, usually with some purification resulting. The more rapid the regeneration (dilution), the smaller the ultimate particle size of the product. To achieve a product having good working properties, it is usually necessary to "develop" the poorly crystalline, very small particle size products in the diluted sulfuric acid by heating or by adding a solvent for this purpose.

The acid pasting process can, in some cases, be combined with the isolation of the pigment from its synthesis medium, as in the acid flushing process. The CPC synthesized in kerosene can be flushed into 98% H_2SO_4 (sulfuric acid), the acid solution decanted from the kerosene, and the H_2SO_4 solution then added to water. To achieve a small particle size, the regeneration is carried out under high turbulence conditions in a specially designed tube, the process being known as HT drowning.

Problem is the 10 parts H_2SO_4 per part of pigment - ppt over.

ACID SWELLING (Permutoid Swelling)

The crude pigment is agitated in sulfuric acid of a concentration not quite sufficient to dissolve the pigment. Under these conditions, CPC is converted to exceedingly fine crystals of its sulfate salt. When the acid suspension of this salt is drowned into water, hydrolysis occurs and the CPC is regenerated in pigmentary size.

dry mill before acid swelling to greatly increase rate of acid swelling (by reducing particle size)

PRE-MILLING (Dry Milling)

The acid swelling process can be markedly improved by dry milling or pre-milling the crude CPC. This process consists of grinding the crude CPC using "Cylpebs" (short steel rods) to a small particle-sized, but highly aggregated, product. These aggregates can be broken down by acid swelling, probably through the growth of the very small particle size CPC which forms the aggregates.

pre-mill by putting in barrel with rods & short steel rods

Book by Wallen (consultant) on math treatment of particle growth after size reduction

CPC will agglomerate during grinding reducing strength

Viscous Acid Milling also used besides viscous salt milling

Solvents used to preserve or change phases of pigments during size reducing

SOLVENT BREACHING

This is an alternate means of deagglomeration of pre-milled crude in which an organic solvent for the pigment (o-dichloro-benzene, carbon tetrachloride, or Perclene) is used to separate the agglomerates by a crystal growth mechanism. This solvent is usually used as an aqueous emulsion and is subsequently removed by steam distillation before excessive growth of the particles occur. The degree of emulsification of the solvent appears to control the effectiveness of the process. An alternate means for obtaining a small particle size crude for solvent breaching is used in Green G (GG) processing where the crude is produced as an $AlCl_3$ complex, size-reduced by hydrolysis, and then developed by solvent breaching.

SOLVENT MILLING

Solvent milling utilizes simultaneous size reduction and solvent breaching development and can be accomplished on a crude, but much more effectively on a pre-milled crude. In the latter case, the rate of size reduction, probably via solvent breaching, is much more rapid than the primary size reduction from a crude.

SALT MILLING

a first changed to β in this process

This process is conducted in a ball mill using salts such as Na_2SO_4, $Al_2(SO_4)_3 \cdot 14.5H_2O$, NaCl, etc. and gives initially an extremely fine particle size pigment in a highly amorphous form. The salt (about 80-85% of the charge) is then removed by aqueous extraction (usually dilute acid to remove any iron from the grinding medium) permitting the pigment to develop into a practical particle size and crystallinity. Under normal conditions, this procedure will give the least stable crystal modification.

formation of CPC from acid ex enhances ease of size reduction

DISPERSION MILLING

grow up of size reduced material during this process, want to avoid this by getting rid of it like pinacone process as in CPC

If a phase-directing solvent is added to the salt milling (Perclene, etc.), it is usually possible to produce a more stable crystal modification. Dispersion milling has also been used successfully with all the quinacridones.

Dispersion & solvent milling very energy intensive (inefficient)

HF MILLING

HF milling is a salt grinding (borax, etc.) in a highly viscous, usually aqueous medium using a Cowles type disc mill. The salt is removed by separating the highly dispersed aqueous pigment dispersion from the undissolved borax.

used to make aqueous dispersion pigments that are anionic or non-ionic usually a more expensive process but maybe not so now

J. Jackson - salt milling by $AlCl_3$, $FeCl_3$, & CPC; ex forms then hydrolyses to CPC pigment

Salt milling appears to be more economical than ball milling

In β/ cubic crystals appears to be greener & more intense vs α tetragonal shape (▭ vs □)

EPL has small particles group

PARTICLE SIZE DETERMINATION

GENERAL COMMENTS

This will outline the methods used by Colors R and D for the determination of pigment particle size. Only those methods whose merits have been established by our actual experience and for which equipment is available here will be discussed. Other methods are mentioned briefly. Exclusion of a method does not necessarily mean that it is unsatisfactory or unsuited to our use but may indicate that we have had no experience with it.

DEFINITIONS

Definition of size and size distribution is critical to size distribution determinations and answers obtained can vary greatly with change in definitions, for the usual non-spherical particles. It is ordinarily necessary as a practical matter to define the size as a single parameter even though the particles (e.g., platelet or needle-shaped) are far from equidimensional. An attempt is made to select the parameter most relevant to the problem in question. Most frequently, the diameter of the "equivalent sphere" is used, but the projected area, maximum chord, etc., may be the preferred parameter in some instances. Distribution can be defined in terms of either the number or weight of particles within a given size range. The definitions to be used should be clearly understood before a size analysis is undertaken (References 1 and 5).

Generally, where an effective average diameter is reported by the Newark laboratory, it is the mean volume-surface diameter, when calculated from specific surface data; and, in the case of microscopic results, either a length average diameter or a particle size range (Reference 5).

ASTM suggests (ASTM D-1366-65 (Vol 20)) that in reporting particle size characteristics of pigment, report (a) particle size parameter (e.g. specific surface) (b) coarseness (size below which 99.5% falls, and (c) distribution parameter - show distribution curve on 3 phase log probability paper. usually straight lines for pigments

SELECTION OF METHOD

Selection of the method to be used for the size analysis is based principally on the purpose for which the information is to be used, the equipment available, and the ease and speed with which the measurements can be carried out. In the sections which follow, we define the various types of particles, discuss briefly the methods which have been used by Colors R and D, the size range covered, and indicate the facilities available for their use.

References 18 and 5 contain good reviews of methods of particle size methods.

TYPES OF PARTICLES

1. Primary Particles

Single crystals or crystals composed of crystallites.

2. Agglomerates

A relatively loose arrangement of primary particles or aggregates. Unlike flocculates, agglomerates do not spontaneously reform in fluid systems. Surface area is substantially the sum of surfaces of individual particles.

3. Aggregates

A tightly bound arrangement of primary particles attached at their surfaces. Surface area less than the sum of the areas of the primary particles.

4. Flocculates

A very loose arrangement of primary particles, agglomerates, or aggregates which can be disintegrated by the influence of a small shearing force but which tends to reform in fluids once the disruptive force is removed.

PARTICLE SIZE METHODS USED BY PIGMENT COLORS R AND D

1. Gas Adsorption (0.005 to ca. 5μm)

The classical BET method has been supplanted in our labs by the related ''Sorptometer'' procedure which is faster and much easier to carry out. (The ''Sorptometer'' instrument is manufactured by Perkin-Elmer). In the BET method, the number of molecules of gas (usually nitrogen) to give a monolayer is calculated from an adsorption isotherm. Area per gram of pigment (i.e., specific surface) is then calculated using area per molecule of adsorbed gas. The ''Sorptometer'' method involves adsorbing gas (nitrogen at liquid nitrogen temperature), desorbing the gas by heating, estimating the amount desorbed by reference to known quantities, and determining surface area using a reference curve based on amounts desorbed from samples of known area (from BET). The ''Sorptometer'' method is one of the principal surface area methods used in our colored pigments research (References 1 and 5). (Arrangements can be made to have BET measurements carried out for us at Central Research and Development Department laboratories, Experimental Station.)

2. Centrifugal Sedimentation (0.1 to 2.0μm)

A variety of centrifugal sedimentation procedures have been used successfully to obtain relative size distributions of pigment samples. The simplest, and the most extensively used method, involves centrifuging a sample in

Particle size Data { Parke + Zack 1974 p 1044-1049
Beresford, Carr etc., Joyce March 1965

an ordinary laboratory beaker-type centrifuge for a fixed period of time, and then separately collecting, drying, and weighing the sedimented pigment and that in the (decanted) supernatant liquid. By varying the speed of rotation, a size distribution curve may be obtained. Particle sizes are calculated assuming Stokes' Law holds, which law is valid only for very low concentrations, independent (non-flocculated) smooth spherical particles in viscous flow, without disturbing electrical effects. The simple method is very useful for lead chromate pigments; difficulty is encountered with the less dense and smaller organic pigments. Accurate quantitative results are not generally obtained because of departures from Stokes' Law requirements. Flocculation is a frequent problem.

A steam-driven continuous flow Sharples supercentrifuge is used for size-fractionation of organic pigments. Results are qualitative only (References 1, 5, 13).

A Joyce-Loebl disc centrifuge is useful for the pigmentary size range. (Ref 18). The equipment is not available within the Pigments Dept., but arrangements can usually be made to use that elsewhere in the company (e.g. J. Lab.).

Centrigual sedimentation results are greatly influenced by pigment dispersion and special precautions are required to measure primary particles.

3. Gravity Sedimentation (1.0-50μm)

This method has been extensively used in its simplest modification as a qualitative indication of particle size, to differentiate between samples and to separate coarser fractions. It has been little used here for quantitative determinations. In general, a pigment slurry is allowed to settle in a graduated cylinder or test tube and the quantity of sediment noted after various settling periods. Samples are drawn from a fixed position in the settling vessel after various settling times (References 14, 13). Andreasen Pipettes are available at the Newark laboratory and Central Research and Development offers particle size determinations by Andreasen Pipette.

Results are greatly influenced by state of dispersion (flocculation, etc.) in the slurry and special precautions are required to obtain a measure of primary particle size (References 1 and 5). Particle size calculations are based on Stokes' Law, which is ordinarily not strictly applicable (References 1, and 18).

4. X-Ray Line Broadening (0.001 to 1μm)

The mean dimension , D, of the crystallites composing a powder is related to the pure x-ray diffraction broadening, β, by the equation:

$$D = \frac{K \lambda}{\beta \cos \theta}$$

where K is a constant (approx. equals 1) related both to crystallite shape and the way β and D are defined. β is the pure breadth, free of all broadening due to the experimental method and is usually defined as the angular width at half-maximum intensity. It should be distinguished from the experimentally observed breadth B (frequently erroneously called "B 1/2"), which is the quantity ordinarily used in DuPont Pigment Colors Research as an empirical index of crystallite size (β is rarely determined). Values of B, obtained by simply measuring the width (in arbitrary units) at half-maximum intensity, of a suitably selected single x-ray diffraction peak, have proved to be very useful indices of relative crystallite size. The B values increase with decreasing size in the pigmentary size range. X-ray diffractometer records of powder samples are used. It should be noted that the line width is a measure of the crystallite (coherent domain) size which is not always the same as the particle size since a single particle may contain many crystallites. Despite these problems, the simplicity, ease, rapidity and significance of line breadth measurements have made them a principal particle size tool in our research (Reference 12).

5. Light Microscopy (0.2 to ca. 70μm)

Light microscopy is usually the preferred method for initial examination of pigment dispersions such as inks and paints. It is especially useful for the detection of oversize particles, estimating degree of dispersion, etc. For ordinary light microscopy, particles must be larger than about 0.5μ, which is generally the case with the usual paints and inks, even when primary particles are much smaller. Mounting techniques are very important; juxtaposed mounts are desirable in making comparisons since the overall impression is much influenced by specimen thickness. Equipment for optical photomicroscopy (Polaroid) is available at Newark. This is a valuable, widely used method. Various aids to counting are provided (References 1 and 4). Rapid electronic methods (see Quantimet) are now available within the company.

A special technique, "Millipore® Microscopy Mounts", has been developed at the Newport laboratory for preparation of mounts for use in determination of particle size distribution of flake pigments such as Afflair®, mica and aluminum by the Quantimet® instrument. Briefly, this involves preparation of an aqueous dispersion of known concentration of the pigment (using surfactant to aid dispersion), addition of an aliquot of the dispersion to a dilute sodium carboxymethyl cellulose solution (Na CMc), filtration of the resultant mixture on a Millipore® filter, attaching the filter to a microscope slide (with dilute NaCMc), drying the mount, and counting the sample with the Quantimet® instrument (Vol. 1).

ASTM (E-20-62T (Vol 30)) suggests counting at least 250 particles in each of three fields or method B indicating a frequency per 1000 particles.

6. Electron Microscopy (.001 to 10um)

Electron microscopy is required for observation of primary particles of most pigments which are below the resolving power of the light microscope. This technique is very useful and extensively used. Procedures are available for estimating hardness of particle clusters, determining particle shape, detecting surface coatings, etc. Film sectioning equipment is also available. This is one of the most valuable and widely used particle size methods for colored pigments research (References 15, 16, 17).

7. Particle Size Analysis by Electronic Analyzers

Various instruments to aid in determination of particle size distribution are on the market. (Vickers shearing eye-piece, the Zeiss TGZ-3 semi-automatic device and the Zeiss(Microvidiomat), Leitz (classimat), Vickers (quantimet), and Millipore (MIC) electronic image analyzers). A particle size analysis service, using a ''Quantimet'' image analysis computer, provided by Orchem, has been used for particle size analysis of Afflair® pigments. The ''Quantimet'' can be used to count and size particles either directly with a microscope or indirectly from photographs. The system of interest is scanned with a TV camera, and the image from the camera is converted into about 500,000 useable picture points in an internal computer. A particle is detected when the optical density of the picture points lying inside the image of the particle are sufficiently different from the background. For good analysis, each particle to be counted should not touch a neighboring particle and each particle must be sufficiently distinct in optical density from its surroundings to be distinguished by the instrument. Particles that touch are counted as a single feature. For small particles a minimum of about 1000 particles must be counted. For a reliable distribution more is desirable. The instrument yields directly:

(1) The total area scanned
(2) The total area of particles
(3) The maximum horizontal chord of each particle

From these data various size distribution can be generated by the computer, (a) not assuming spheres and (b) assuming spheres. The data can be summarized as size distribution plots, tables or both. (Ref. 11).

8. Particle Size Index (0.10 to 0.5μm)

A ''particle size index'', defined by

$$100 \times \frac{\text{Absorbance at wavelength of minimum absorption}}{\text{Absorbance at wavelength of maximum absorption}}$$

developed at the Newark laboratories has proved to be an extremely useful measure of relative particle sizes of colored pigment dispersions and has been used extensively. The method is applicable to even the smallest particles (References 6 and 7).

9. Light Scattering (0.01 to 10μm)

Intensity of scattered light varies with direction and depends upon wavelength, particle size shape, and refractive index. Procedures and equipment have been extensively developed and the method is widely used for polymers and the like. The method has not been extensively used for colored pigments because of equipment, experimental, and theoretical problems. Procedures have been developed in this laboratory for measurement of relative light scattering of samples based

on difference in transmission in the ''near'' and "far" positions in the GE or Beckman DK-2 spectrophotometers. From these results, a qualitative relative size relationship can be inferred (References 1,3,9).

10. X-Ray Scattering (0.002 to 0.1μm)

X-rays are scattered by particles in the size range from about 0.002 to 0.1μm. The scattering is at a maximum at angles only a few degrees from the forward direction of the radiation. A procedure has developed at Newark for use of the Norelco apparatus for x-ray scattering measurements. The method gives results which correlate with those of specific surface determinations and electron microscopy but this has not been used extensively because of the much greater convenience and general utility of x-ray line broadening procedures (References 10 and 11).

11. Sieving (+ 10μm)

Sieves are extensively used for determining the particle sizes of dry powders. The ultimate particle size of most colored pigments (exception: Afflair®) is far below the size range covered by sieves, so, in general, one is limited to measurements of aggregate or agglomerate sizes. Such size data are of considerable significance for pigment dispersion, as in nitrocellulose inks and plastics. Sets of sieves covering the size range above about 25μm are available at Newark as are various shaking devices (Rotap, etc.). A 3'' 5μm sieve is also available here. Air jet sieves are available at the Engineering Test Center. Procedures and precautions are given in ASTM standards (Reference 2 and 3).

12. Elutriation (1-100μm)

Air elutriation has been used occasionally at Newark to size fractionate pigment powders. A homemade apparatus of the ''Roller Analyzer'' type is used. Primary particles are not ordinarily separated but, rather, various particle clusters. Fractionated pigments are useful in studies of pigment dispersion (e.g., nitrocellulose inks), aggregation, etc. The equipment has not been kept intact but must be assembled for each study. At Newport equipment for size fractionation of mica is available.

OTHER METHODS

A comprehensive summary of particle size methods is given in References 1 and 18 and critical discussions of some methods are given in Reference 5. A chart issued by Stanford Research Institute also provides a concise summary of methods and their range of applicability. (Copies of the copyrighted chart are in the Physics Lab.). Among the more important methods which have not been used appreciably at Newark are the following:

1. Harkins and Jura Method (0.005 to ca. 5μm)

The sample is equilibrated with the saturated vapor of a liquid which wets it. Solid adsorbs a film whose outer surface has the same total surface energy as

the liquid itself. The heat developed on immersing the sample, with adsorbed film, in the liquid is a measure of the area of adsorbed film. The method is little used for routine measurements because of experimental problems (References 1 and 5).

2. Other Adsorption Methods

Adsorption of dyes, surface active materials, etc., from solution can be used for determining surface area. Calibration with standards is essential. The method has been little used in our colored pigments research (References 1, 5, and 18).

3. Permeability to Fluid Flow (0.5 to 50μm)

Specific surface data are calculated assuming certain relationships between rate of fluid flow, pressure head, viscosity, porosity of the powder bed, density, and specific surface of the powder. Either liquids or gases are used as fluids. The methods give useful comparisons between different samples of materials of the same type but anomalous results may be obtained if samples differ in size distribution. The Fisher Sub-Sieve Analyzer operates on this principle (Reference 1). This method has been used in the Newark laboratories to a limited extent, but the equipment is not now available. There is a Fisher Sub-Sieve Analyzer in the Engineering Department.

4. Absorption of Radiation

Except for the ''particle size index'', particle size methods based on absorption of radiation have been little investigated at Newark. Other methods, published in the literature (Reference 1) are based on the relationship between light absorption and projected particle area. Penetrating radiation such as x-rays or atomic particles may be used in place of light. For a truly random dispersion of particles on a microscope slide, surface area, determined optically in the light microscope, is theoretically four times the mean projected area.

5. Coulter Counter (0.5 to 300μm)

A suspension of particles in an electrolyte flows through a small aperture having an immersed electrode on either side. As a particle passes through the aperture, it changes the resistance between the electrodes, producing a voltage pulse proportional to the particle volume. The White Pigment Group has a counter which they used on TiO_2 suspensions. No work, to our knowledge, has been done in DuPont on colored pigments. The very small size of ultimate particles of most colored pigments poses difficulties (orifice plugging, etc.), as does the necessity for the use of an electrolyte as a dispersion medium (Reference 1).

REFERENCES

1. Analytical Methods Committee, Particle Size Analysis Subcommittee, ''Classification of Methods for Determining Particle Size''. The Analyst, 88, No. 1044, 156-187 (March, 1963).

2. ASTM Standard D-1366, ''Reporting Particle Size Characteristics of Pigments''.

3. ASTM Standard D-185-45. ''Coarse Particles in Paints, Pigments, and Pastes''.

4. ASTM Standard E-20, ''Recommended Practice for Analysis by Microscopical Methods for Particle Size Distribution of Particulate Substances of Sub-Sieve Sizes''.

5. Fisher, E. K., ''Colloidal Dispersions'', John Wiley and Sons, Inc., New York, 1950.

6. Hanke, A. R. , KN-51-43, ''A New Application of Light Transmission in Following Particle Size Reduction. I. Application to Copper Phthalocyanine'', File 144.

7. Hanke, A. R., KN-52-2. ''A New Application of Light Transmission in Following Particle Size Reduction. II. Application to Pigments other than CPC''. File 144.

8. Hanke, A. R., Physical Chemical Research Summary for February 20 - March 19,1959.

9. Bender, M., ''The Use of Light Scattering for Determining Particle Size and Molecular Weight and Shape''., Journal of Chemical Education, 29, 15 (Jan. 1952).

10. Marculaitis, W. J. KN-57-11, ''Small Angle X-Ray Scattering''. File 146.

11. Particle Size Analysis Using the Quantimet 720 . Memorandum to Users of Orchem's Particle Size Analysis Service from Rulon E. Johnson E335/13.

12. Klug, H. P. And Alexander, L. E., ''X-Ray Diffraction Procedures'', John Wiley and Sons, Inc., New York, 1954.

13. Lewin, S. Z., ''Instrumentation for Particle Size Analysis'', Journal of Chem. Ed. 40, A-257, A-349, A-423 (1963).

14. Manger, C. W., KN-54-29, ''Correlation of Particle Size of Dispersed Pastes with Filterability''. File MR-176-1.

REFERENCES

15. Hanke, A. R., KN-52-1, Particle Size Distribution of Pigmentary Alpha Phase Copper Phthalocyanine, 1/25/52, File 223.41.

16. Hanke, A. R., KN-51-32 "Particle Size Distribution of Pigmentary Beta Phase Copper Phthalocyanine, 4/19/51. File 223.41.

17. Braun, J. E., KN-65-5, "Particle Size of CPC Pigments", 8/20/65, File 223.41.

18. Collins, E. A., Davidson, J. A., and Daniels, C. A., "Review of Common Methods of Particle Size Measurement" - J. Paint Tech 47, 35, May 1975.

Revised by D. H. Perkins - 1975

E. I. DU PONT DE NEMOURS AND CO.
Pigments Department

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Newark, New Jersey
January 16, 1976

TO ALL TECHNICAL PERSONNEL
NEWARK - NEWPORT

SPECIFIC SURFACE VALUES OF COLORED PIGMENTS

The available specific surface values for our colored pigments are given on the attached sheets. The list includes both active and inactive codes and obsolete standards as well as current ones. The values were calculated from nitrogen adsorption data as determined with use of the Perkin-Elmer "Sorptometer." Pigments were degassed before nitrogen adsorption by storing the sorptometer tube, containing the pigment, in an oven at 100°C for two hours at atmospheric pressure. Significantly different results can be expected in many cases with marked change in degassing conditions. Most results can be repeated within 5% under the conditions used. "KROLOR" results are markedly affected by any free silica present. Severe aggregation can lead to low specific surface values.

We have appended to the list some specific surface values from the literature which are of possible interest.

The mean volume-surface diameter, d_3, (assuming spheres), can be calculated from the equation:

$$d_3 \text{ (in meters)} = \frac{6}{\text{pigment density} \times \text{surface area in square meters per gram}}$$

We have calculated d_3 values for some of the more important pigments. It is to be emphasized that no single measure of particle size meets all needs. The specific surface values, and the particle size, d_3, calculated therefrom, are frequently used. None of the pigments listed has spherical particles, so the d_3 values do not represent the true particle size. The d_3 values are generally useful, however, as relative measures of particle sizes of samples of the same pigment type.

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Discussions of pigment particle size and the precautions to be taken in use of data such as those listed here are given in standard tests, such as Fisher, "Colloidal Dispersions," John Wiley and Sons, Inc., New York, 1950, Chapter II, and Herdan, "Small Particle Statistics," 2nd Edition, Academic Press, New York, 1960.

Electron micrographs of most of the pigments are available at Newark. These provide a useful supplement to the particle size data tabulated here.

Additional copies are available on request.

B. H. PERKINS
R & D DIVISION

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LPH 0072399

SURFACE AREAS OF STANDARD PIGMENTS
DETERMINED BY NITROGEN ADSORPTION

I. NEWARK LAB DATA

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CODE	STANDARD	NAME	SPECIFIC SURFACE M^2/g	d_3 μm
RT-201-D	SL 61579	"MONASTRAL" Violet R	60.0	0.067
	TS 80907	" " "	64.0	0.063
RT-202-D	L 00007	Magenta	77.0	-
RT-203-D	L 00009	"MONASTRAL" Magenta	68.0	0.054
RT-209-D	PS 98808	"MONASTRAL" Maroon	49.0	0.081
RT-232-D	SD 91550	Toluidine Red	13.1	0.32
RT-386-D	SD 201	Toluidine Red Med.	8.6	0.49
	TS 87507	Toluidine Red Med.	9.0	0.53
RT-396-D	SD 89782	Red Toner	15.3	-
RP-410-D	SD 604	Mineral Violet	3.4	0.64
	SD 89964	Mineral Violet	2.3	0.95
RT-427-D	SD 48474	Parachlor Red	6.5	0.60
	SD 00472	Parachlor Red	9.0	0.43
RT-428-D	PS 00866	"Watchung" Red	58.0	0.057
RT-443-D	SD 95124	Duol Carmine	74.0	0.053 ←
RT-455-D	PS 82569	"Watchung"Red B	57.0	0.064
RT-500-D	SD 48461	Arylide Maroon	24.8	0.17
	SD 48035	Arylide Maroon	25.6	0.16
RT-525-D	PS 00465	Bon Red Dk	33.0	0.11
	PS 85445	Bon Red Dk	40.0	0.096
RT-531-D	PS 98463	Naphthanil Red Lt	20.0	0.21
	PS 91892	Naphthanil Red Lt	35.0	0.12
RT-533-D	TS 85852	Bon Maroon Lt	20.0	0.16
RT-539-D	SD 94929	Naphthanil Red Dk	60.0	0.066
RT-565-D	SD 89666	Bon Red Lt	27.0	0.12
RT-566-D	SD 86141	Arylide Maroon	32.3	0.13
RT-588-D	SD 85605	Arylide Maroon	52.8	-
RT-593-D	SD 00907	Pyrazolone	43.0	0.093
RT-608-D	SD 35342	Maroon Gold	95.3	0.036
RT-618-D	PS 98161	"Watchung" Red Y	32.0	0.094
	PS 92123	"Watchung" Red Y	45.0	0.067
RT-662-D	PS 90829	"Watchung" Red	64.0	0.049
RT-665-D	SD 767	Maroon Gold	94.8	0.036
RT-695-D	PS 84045	BON Red DK	24.0	0.15
RT-698-D	A-133	"Watchung" Red	63.4	0.055
	PS 92596	"Watchung" Red	74.0	0.052

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CODE	STANDARD	NAME	Specific Surface M^2/g	d_3 , m
RT-709-D	SD 94533	"Watchung" Rubine	47.0	0.070
RT-710-D	SD 00167	"Watchung" Maroon	44.0	0.088
RT-733-D	SD 00136	"Monastral" Violet R	62.0	0.063
RT-742-D	PS 00117	"Monastral" Red B	62.0	0.064
	Lot 43064	"Monastral" Red B	67.2	0.059
RT-759-D	PS 85480	"Monastral" Red Y	31.0	0.14
	TS 93111	"Monastral" Red Y	23.0	0.18
	PS 97846	"Monastral" Red Y	29.0	0.14
RT-761-D	SD 00699	"Watchung" Red	59.5	0.059++
	PS 91029	"Watchung" Red	58.0	0.061
RT-787-D	PS 29135	"Monastral" Scarlet	60.0	0.063
RT-790-D	PS 92154	"Monastral" Red B	50.0	0.085
	PS 97845	"Monastral" Red B	50.0	0.085
RT-791-D	SD 00162	"Monastral" Violet R	41.2	0.10
	PS 97187	"Monastral" Violet R	50.0	0.083
RT-792-D	SL 86979	"Monastral" Maroon	62.0	0.067
RT-795-D	PS 97189	"Monastral" Violet R	47.0	0.082
RT-796-D	PS 82146	"Monastral" Red B	50.0	0.080
	PS 82148	"Monastral" Red B	43.0	0.093
	PS 99143	"Monastral" Red B	52.0	0.077
RT-805-D	L 12887	"Monastral" Magenta	71.0	-
RT-819-D	TS 90647	"Monastral" Violet R	43.0	0.055
RT-837-D	PS 98665	"Watchung"Red B	70.0	0.054
RT-841-D	TS 87985	"Watchung" Red Y	38.0	0.088
	L 49834	"Watchung" Red Y	46.0	0.073
RT-846-D	PS 82588	"Watchung" Red	75.8°	-
RT-849-D	PS 90158	"Monastral" Marcon B	27.0	0.15
RT-867-D	L 85198	"Watchung" Red B	60.5	-
RT-879-D	SL 44319	"Monastral" Red A	23.0	0.19
RT-880-D	PS 85793	"Watchung" Red B	64.0	0.055
	PS 91997	"Watchung" Red B	64.0	0.055
RT-887-D	PS 81381	"Watchung" Red B	76.0	0.051
RT-899-D	PS 92376	"Monastral" Violet	52.0	0.079
RT-920-D	SL 59160	"Monastral" Maroon	53.0	0.076

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CODE	STANDARD	NAME	Specific Surface M^2/g	$d_{3,1,m}$
BT-172-D	SD 48428	CPC Blue Toner	33.0	-
BP-242-D	PS 83992	Blue Lake	36.0	0.11
BP-258-D	PS 00677	Blue Lake	48.0	0.069
BL-282-D	PS 98063	"Monastral" Blue BF	57.0	0.070
BT-283-D	SD 83044	Dianisidine Blue	57.0	-
BT-284-D	SD A-160	"Monastral" Blue B	62.8	0.060
	L-98090-1	"Monastral" Blue B	66.0	0.057
BT-297-D	SD 90497	"Monastral" Blue G	64.3	0.059
	98150	"Monastral" Blue G	72.0	0.053
BT-304-D	SD 00704	CPC Blue Toner	74.2	0.050
BP-366-D	PS 98149	"Ramapo" Blue BF	60.0	0.062
BT-383-D	SD 97732	"Monastral" Blue G	64.0	0.059
	SD 97732	"Monastral" Blue G	56.0	0.067
BT-391-D	SD 00556	"Monastral" Blue R	67.6	0.056
	PS 00120	"Monastral" Blue R	67.6	0.056
BT-413-D	98143	"Monastral" Blue BF	53.0	0.072
BT-417-D	PS 00052	"Monastral" Blue GF	58.0	0.065
BT-425-D	98076	"Monastral" Blue BF	64.0	0.060
BT-426-D	PS 00146	"Monastral" Blue GF	56.0	0.074
BT-427-D	TS 84165	"Monastral" Blue RF	65.0	0.060
BT-440-D	98453	"Monastral" Blue G	54.0	0.069
BT-449-D	97419	"Monastral" Blue B	67.0	0.055
BT-450-D	93064	"Monastral" Blue B	65.0	0.058
BT-457-D	Lot 34850	"Monastral" Blue RX	64.0	-
GT-486-D	SD 48421	"Monastral" Green GS	54.6	-
GT-674-D	SD 00121	"Monastral" Green B	47.7	0.062
GT-751-D	PS 89040	"Monastral" Green G	60.0	0.048
GT-805-D	PS 86509	"Monastral" Green Y	63.0	0.035
YO-38-D	SD 48448	Chrome Orange Dk	0.5	1.70
YE-421-D	PS 83027	Molybdate Orange	8.4	0.13
	PS 83027	Molybdate Orange	8.7	0.12
Y-433-D	PS 99782	Chrome Yellow Lt	8.0	-
Y-434-D	83387	Chrome Yellow Lt	12.0	0.088

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CODE	STANDARD	NAME	Specific Surface M^2/g	d_3
YT-445-D	SD 00137	Toluidine Yellow	34.0 - 30.0	0.12
YT-459-D	SD 00092	Diarylide Yellow	38.0	0.11
Y-469-D	TS 99984	Medium Yellow	9.1	0.12
	PS 89191	Medium Yellow	13.0	
Y-488-D	PS 98899	Primrose Yellow	15.0	0.073
Y-493-D	SD 86721	Shading Yellow	7.7	0.14
Y-539-D	PS 99104	Zinc Yellow	4.1	0.42
YT-553-D	PS 82439	Diarylide Yellow	59.0	0.068
YT-562-D	SD 48403	Green Gold	48.2	0.075
	PS 00051	Green Gold	61.0	0.059
YE-637-D	82739	Molybdate Orange	12.0 - 10.0	0.090
YE-698-D	PS 86582	Molybdate Orange	16.0	0.065
YT-714-D	PS 87683	Green Gold	61.0	0.062
YT-717-D	PS 22767	"Dalamar" Yellow	28.0	0.15
	PS 98538	"Dalamar" Yellow	23.0	
YE-721-D	PS 83062	Molybdate Red	10.0	0.10
	PS 83062	Molybdate Red	15.0	0.07
YT-729-D	SD 00167	Toluidine Yellow R	28.0	0.15
YE-735-D	TS 87425	Molybdate Orange	10.0	0.10
YT-748-D	PS 85295	"Monastral" Gold	71.0	-
YT-756-D	PS 85172	"Monastral" Orange	57.0	0.066
Y-758-D	PS 12839	Primrose Yellow	12.0	0.077
YE-758-D	PS 98878	Primrose Yellow	11.0	
YT-785-D	PS 89482	Diarylide Yellow	60.0	0.071
YT-793-D	SL 00067	"Monastral" Gold	89.0	0.044
YT-800-D	SL 95938	"Monastral" Orange	42.0	0.091
YT-805-D	L 12887	"Monastral" Green Y	71.0	-
YT-807-D	SL 97619	"Monastral" Orange	32.0	0.12
YT-808-D	PS 97870	"Dalamar" Yellow	10.0	0.42
YT-809-D	PS 97658	Green Gold	75.0	0.71
YT-812-D	PS 98860	Deep Gold	85.0	0.044
YT-815-D	SL C0277	Deep Gold	90.0	0.040
YT-820-D	SL 99217	"Dalamar" Yellow	6.0	0.71
YT-821-D	SL 99277	"Dalamar" Yellow	6.0	0.70
YE-765-D	PS 83420	Molybdate Orange	9.0	0.11

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CODE	STANDARD	NAME	Specific Surface M_2/g	d_3 μ
KY-781-D	PS 92779	"KROLOR" Yellow Lt	38.0**	0.039
	SL 86728	"KROLOR" Yellow Lt	31.0**	0.048
KO-786-D	SL 52197	"KROLOR" Orange R	23.0**	0.061
KY-787-D	SL 52569	"KROLOR" Yellow Medium	18.0**	0.10
KY-788-D	SL 90964	"KROLOR" Yellow Light	24.0**	0.070
KO-789-D	SL 90787	"KROLOR" Orange Y	13.0**	0.11
KY-790-D	PS 98244	"KROLOR" Primrose	19.0**	0.085
KY-795-D	SL 92400	"KROLOR" Yellow Medium	15.0**	0.10
Y-433-D	PS 99732	Chrome Yellow Light	8.0	0.14

* Low value for specific surface apparently owing to severe aggregation. Electron micrographs indicate primary particles considerably smaller than d_3 value shown.

** "KROLOR" specific surface values strongly influenced by any free silica present. Particle size of KY-781-D similar to that of Y-434-D

o Reported previously, through error, as 16.7

++ RT-742-D Lot 43064 BET Method(CR&D) 66.0, 68.3 10/10/68

LPH 0072404

II. SPECIFIC SURFACE DATA FROM LITERATURE

A. V. T. Crowl J.O.C.C.A. 46 171 (March, 1963)

Pigment		Spec. Surface(M^2/gram)
Titanium Dioxide	Rutile	8 - 10
	Anatase	9 - 10
Lithopone		2 - 4
Zinc Oxide		2 - 50
	Silver Seal	1.5
	Acicular	2
	White Seal	4
	Green Seal	5
	Colloidal	14
Precipitated Calcium Carbonate		30
Barytes		5 - 8
Blanc Fixe		3 - 10
Silicas		5 - 200
Iron oxides		3 - 50
	Indian Red	3
	Turkey Red	7
	Red oxides	7 - 40
	Black Iron Oxide	19
	Yellow oxides	15 - 20
	Umbers	100 - 130
Chromium oxide		4 - 5
Lead chromate		3 - 10
Brunswick Green		13 - 26
Prussian Blue		7 - 100
Ultramarine		3 - 20
Carbon Blacks		100 - 600
Phthalocyanine Blue		18 - 50
Arylamide Yellow		34 - 70
Benzidine Yellow		16 - 80
Toluidine Red		13 - 20
Organic Toners		20 - 60

II. C. Farbe Und Lack 80 1044-1049 (Nov., 1974)

Specific surface values for approximately 400 European pigments are given in this Farbe U Lack tabulation which also lists values for specific gravity, oil absorption, pH, covering power, lightfastness, chemical stability and thermal stability

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B. Beresford, Carr and Lombard (Ciba-Geigy) CONFIDENTIAL
J.O.C.C.A., 48, 301-307 (March, 1965)

Pigment				Specific Surface
Dinitraniline	C.I. Pigment Orange 5	Irgalite Red 2GA		9.2
Tetrazo Yellow (Benzidine Yellow AAA)	C.I. Pigment Yellow 12	Irgalite Yellow BO		42
Tetrazo Yellow (Benzidine Yellow OT)	C.I. Pigment Yellow 14	" "	BR	53.2
Tetrazo Yellow (Benzidine Yellow OA)	C.I. Pigment Yellow 17	" "	26F	48.3
Tetrazo Yellow (Benzidine Yellow OA)	C. I. Pigment Yellow 17	" "	2CP	91.5
Arylamide Ye-low 10G (Hansa Yellow 10G)	C. I. Pigment Yellow 3	Irgalite Yellow VG		7.5
Alpha CPC " "	Blue 15	Fast Brilliant Blue BCS		62.9
Beta CPC " "	Blue 15	" " "	GLS	51.1
Naphthol Red - Permanent Carmine	C.I. Pigment Red 5	Carmine FB		48.0
Naphthol Red - Arylide Red Lt.	C.I. Pigment Red 2	Red FBS		30.0
Arylamide Yellow 6 - Hansa Yellow G	C.I. Pigment Yellow 1	Yellow G		14.8
do	do	Yellow GTN		75.6
Arylamide Yellow 5G - Hansa Yellow 13G	C.I.Pigment Yellow 4	Yellow 5GG		21.0
do	do	Yellow 5GL		18.6
Tetrazo Yellow - Benzidine Permanent Yellow HR	C.I.Pigment Yellow 83	Fast Yellow BAR		49.1
Tetrazo Yellow - Benzidine Yellow MX	C.I.Pigment Yellow 13	Yellow BAW		56.2
Pyrazolone Red " "	Red 38	Fast Red FY		37.5
Calcium Lithol " "	Red 49	Red RLB		53.0
Titanium Dioxide Anatase				9.0 - 9.9
" " Rutile				9.4 - 10.6
Zinc Oxide Direct Process(Zincoli Silver Seal)				1.8
" " Metal Conversion Type				2.4 - 11.1
Lithopone (Normal multipurpose)				4.3
Blanc Fixe (B SS 1795 Grade)				3.4

LPH 0072407


12

Chestnut Run Training Manual #27

PIGMENT DISPERSION

Most pigments marketed in the dry form contain aggregates or agglomerates that are many times the ultimate particle size in diameter. These aggregates may be created by compaction during handling, cementing by some action of the soluble salts present when losing moisture (i.e. during drying), coalescence from fusion during calcining, or other causes. If a pigment is simply stirred into a vehicle, the forces applied may not be great enough to break the aggregates, and the resultant pigmented vehicle will be deficient in tinting, strength, tinctorial quality, hiding, suspension characteristics and gloss, among others. Most pigments are manufactured with an ultimate particle size designed to yield optimum hiding or transparency, tinting strength, and tinctorial quality; consequently, these basic properties will not be utilized to best advantage if aggregates remain in a dispersion.

The process of breaking up aggregates or the softer clumps called agglomerates on some sort of mill is often called "grinding", although discrete primary particles or crystals are seldom really ground in the sense of fracturing such solid particles.

The process of dispersing pigments in a liquid can be divided into three phases as follows:

1. Initial wetting as indicated by mix-in time. It is virtually impossible to disperse a material in a liquid that will not wet the surface of the material, e,g., aluminum stearate in water. However, most commercial pigments are fairly well wet by the vehicles used and differ appreciably only in their rates of wetting.

2. Breaking of aggregates and agglomerates as indicated by gloss, fineness, and tinting strength. The various types of pigments differ considerably in the toughness of the aggregates and agglomerates that they contain. The lumps in any one pigment are said to break up in a stepwise fashion as the shearing or impact stress on the particles increases. Because of the various combinations of weak and strong fractions in pigments, one pigment may yield superior fineness to another at low shearing stress but be inferior to it at higher shearing stress. For this reason, ratings at several different levels of shearing stress are required for a comprehensive evaluation of ease of dispersion.

3. Flocculation as indicated by hiding, suspension, consistency, shear-strength uniformity (partial-set rub-up of tints), and fineness under the microscope. The extent to which pigment particles group into soft clumps, or flocs, after grinding is primarily a function of the nature of pigment surface and the polarity of the vehicle. The particular mill used or the fineness of grind obtained does not seem to have any marked effect. Flocculation can be a potent

factor during milling because of its effect on the milling consistency, and hence on the fineness obtained, but flocculation is classified here as one phase of dispersion because a pigment is truly ''poorly dispersed'' when it is not subdivided to its ultimate size whether the lumps that are present consist of hard aggregates or soft flocculates. Since these two types of poor dispersion have quite different effects, a clear distinction should be made between them. Flocculation may have undesirable effects on hiding and gloss, but desirable effects on the suspension and sag resistance in a paint composition. With pigment colors, flocculation is more pronounced with organic colors, particularly more with the phthalocyanines than with the inorganic colors.

The classification described above is useful because experience shows that one pigment may differ from another in one or more of these steps of the dispersion process. However the three phases are not always taken into consideration by pigment users; consequently, a pigment is frequently described simply as ''poor in dispersion properties'' regardless of the specific phase in which it is actually deficient.

The most direct way of determining whether aggregates have been reduced in size to a desirable level is to measure the size of the particles in the finished product. This may be done with a fineness gage, a microscope, or one of several devices developed for fine particle size measurement. Fineness may be run on colors to indicate their texture, but degree of dispersion is most frequently determined by the tinting strength of the milled color.

With pigment colors, all properties do not develop simultaneously; hence reliance on a fineness gage alone could be misleading. The following chart shows a generalized order of property development:

Property	Controlling Aggregate Size*
Texture	Large
Gloss	Large - Moderate
Hiding Power	Moderate - Small
Tinting Strength	Moderate - Small
Hue	Moderate - Small
Intensity	Small
Transparency	Small

*Large: Greater than 15 microns; small: Less than 0.3 microns

It is obvious from the above that a good texture reading might not indicate whether the optimum in other properties has been obtained. The most significant property in terms of enduse requirements should be used as the criterion to measure degree of dispersion.

Some effects like low gloss and low tinting strength can exist at good fineness levels if sufficient flocculation is present. Probably the most common way of measuring relative flocculation in a series of paints is by noting the differences in the amounts and types of settling on shelf aging. Other methods, such as microscopic examination, can be used. With tints, rubbing the film lightly when it is partially set is common practice. A darkening indicates probable deflocculation of the color, while a lightening indicates probable deflocculation of the white pigment. No change would indicate that both pigments were probably well deflocculated before rubbing, but there is a possibility that both pigments may have been equally deflocculated by the rubbing. Flocculates seldon show as particles on a fineness gage because they are broken up by the shearing action of the scraper.

''A flocculation index'', calculated from spectrophotometric reflectance curves of sprayed, poured, and rubbed films of tints provides a quantitative measure of the effects and their characterization. (A.R.Hanke - KN-50-15,9/20/50)

For a description of dispersion equipment see ''Pigments Progress Report No. 27'' White Pigments (PIR File 160-1) Revision.

Revised by G. R. Aldridge - 1975

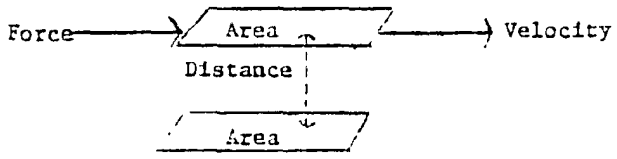
RHEOLOGY

Rheology is the science or study of flow. The terms flow, viscosity, and consistency pertain to the resistance of a material to deformation when a force is applied. Rheological information on a paint or on a coating is of value insofar as it can be translated into some property of practical significance such as reflow, brushability, sprayability, leveling, sagging, suspension, gloss, or transparency. Often it is easier to obtain these properties directly than to make the required rheological measurements, inasmuch as the translation of rheological data into practical properties is not too well understood.

TYPES OF CONSISTENCY

1. Newtonian

If, as indicated below, a force is applied to a thin layer of liquid a certain distance above a stationary layer of the same liquid causing the first layer

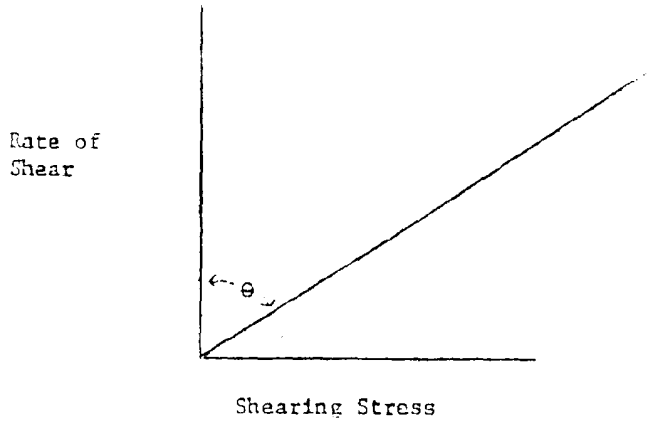


to move with a certain velocity, this velocity is a function of the resistance of the liquid to deformation and is defined as follows:

$$\eta \text{ (Viscosity)} = \frac{\text{Shearing Stress}}{\text{Rate of Shear}} = \frac{\frac{F}{A}}{\frac{V}{D}} = \frac{\frac{\text{dynes}}{\text{cm}^2}}{\frac{\text{cm/sec}}{\text{cm}}} = \frac{\frac{\text{dynes}}{\text{cm}^2}}{\frac{1}{\text{sec}}} = \frac{\text{dyne (sec)}}{\text{cm}^2}$$

A material is said to have a viscosity of one ''poise'' when unit force per unit area at unit distance produces unit velocity.

To demonstrate the flow properties of a material, the factors involved are often plotted as follows:

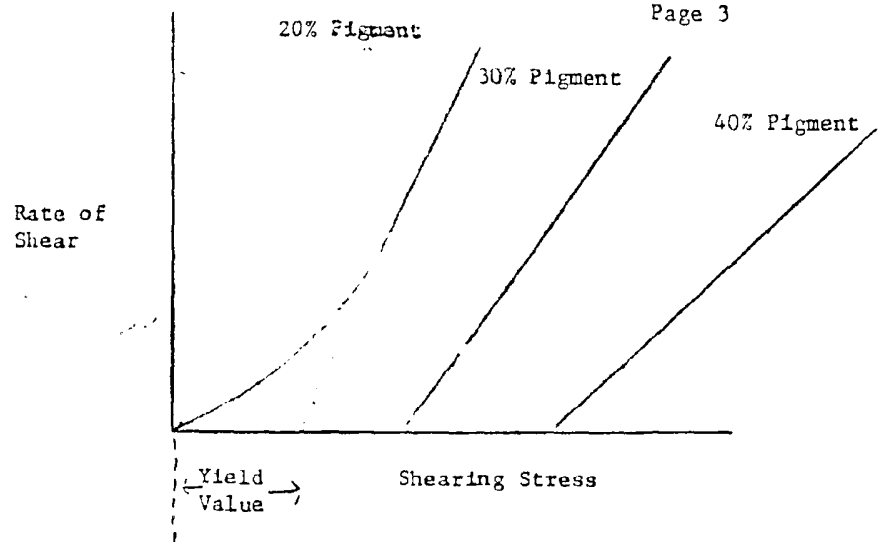


The curve shown is for a Newtonian liquid, that is one whose rate of shear (or flow) is directly proportional to the shearing stress applied, giving a straight line. Often rate of shear and shearing stress are not plotted in absolute terms but in some proportional factors such as rpm and torque. The plot for a so-called Newtonian liquid remains straight for only a limited range of rate of shear under most conditions. If the velocity becomes too high, laminar flow, the smooth sliding of one layer over another, ceases and turbulence occurs. In turbulent flow, the direct proportionality of rate of shear and shearing stress no longer exists. The slope of the curve, expressed as the tangent of the angle θ, is the viscosity as defined by the above equation.

Many materials, especially those consisting of only a liquid phase or even colloidal solutions like many paint vehicles, are Newtonian in character. Frequently, curves in the literature show a falling off in viscosity at higher shear rates for various liquids. More precise experiments indicate that this is often merely a lowering of the viscosity caused by heat build up in the material at the higher rate of shear.

2. Plastic

When liquid is pigmented, flow curves are likely to look something like the following:

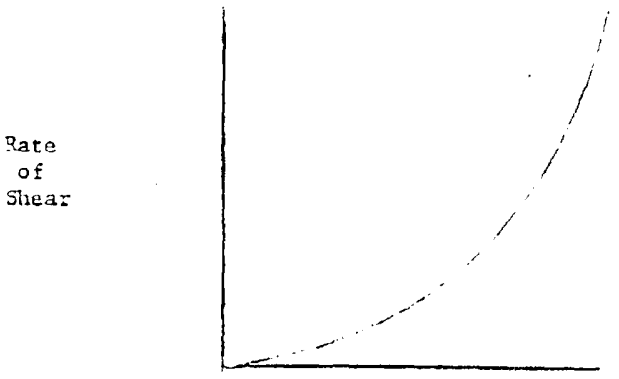


The flow curves tend to be straight only after a certain minimum shearing stress is reached. This minimum is called the ''yield value'' and is usually obtained by extrapolating the straight portion of the curve to the shearing stress axis. The slope of the straight portion of the curve as measured by the tangent of the angle shown above, is called the ''plastic viscosity''. The yield value is presumably the result of the attraction of the pigment particles for each other, and apparently a certain, relatively constant, force is required to hold the particles apart as long as the material is flowing. To that force over and above the yield value, the material acts like a true, or Newtonian fluid.

The difference between plastic and Newtonian flow may be demonstrated by the flow of mustard and honey through a funnel. Under atmospheric pressure, the mustard will not flow because of its yield value, but the honey will flow slowly through the funnel because it is a viscous but Newtonian fluid with no yield value. If more pressure is applied to the surface of the liquids by means of increased gas pressure, the mustard will flow faster than the honey, because once the force is great enough to exceed the yield value, the mustard will flow and it has a lower ''plastic viscosity'' than the ''true viscosity'' of the honey.

3. Pseudoplastic

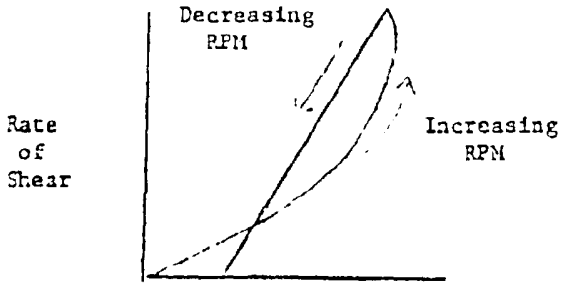
A material is usually classified as ''pseudoplastic'' when the slope of the flow curve varies continuously in somewhat the following manner:



Such a curve shows that the material becomes thinner as the rate of stirring increases. It is difficult to assign a single numerical value to the consistency of such a material, but sometimes the relatively straight portion of the curve is extrapolated to the shearing stress axis and the slope of this line is used as in materials with ''plastic'' viscosity. In this type of material, probably some sort of alignment of solid particles or molecules increases as flow is increased causing a reduction in internal friction, which is equivalent to a reduction in viscosity.

4. Thixotropic

When agitation reduces the consistency of a material, and this reduction is maintained for an appreciable time after the agitation ceases, the material is called ''thixotropic'' and gives flow curves something like the following:



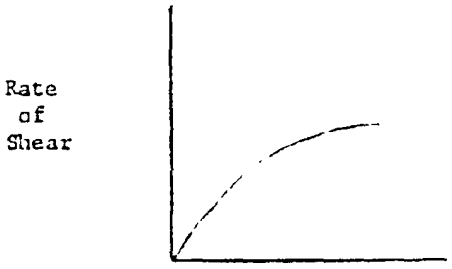
LPH 0072414

These ''hysteresis loops'' are sometimes run to indicate the degree of thixotropy present, but the results are quite dependent on the instrument and times involved and cannot be expressed in any fundamental units. Actually a ''pseudoplastic'' material can be considered a ''thixotropic'' material with a recovery time so fast that its body has been regained before another measurement can be taken at a lower rate of shear; consequently the ''up and down'' curves coincide.

Again this effect can be demonstrated by the flow of mustard through a funnel. If stirred, the mustard will flow at atmospheric pressure because it becomes thinner and loses its yield value for some time after stirring.

5. Dilatant

A material that increases in consistency as the rate of stirring is increased is known as ''dilatant'' and has a flow curve somewhat as follows:



No information is available at the moment of ''up'' and ''down'' curves on this type of material. The two curves would probably practically coincide, but visual observations indicate a matter of seconds for some materials to thin down after agitation has ceased.

This type of body is generally, if not always, the result of a well deflocculated solid dispersed at high concentration in a rather thin liquid. Dilatant effects can be obtained with sand and water and may be observed in the wet sand at the seashore. The theory is that the pigment packing arrangement changes with pressure from what is sometimes called ''maximum packing'' to ''cubical packing''. The latter type makes the material more rigid and more resistant to deformation, but has considerably more void volume than the type of packing when the material is not under stress. When the void volume is at its minimum there is

enough liquid to fill the voids and the mass is fluid. When the void volume is at its maximum there is not enough liquid present to fill all the voids and the mass becomes dry on the surface and very high in consistency because of the relatively dry pigment present. If there is sufficient liquid present to fill the voids at both their minimum and maximum value, there will be little or no dilatancy.

GENERAL

There are an almost infinite variety of flow curves. Even one material has more than one curve because of variations with temperature, the length of time of undisturbed rest preceding the determination, and other factors. Classification of materials into certain types, such as those mentioned here, is sometimes convenient but it can be misleading at times because it is a slight over-simplification. Most so-called dilatant materials, for example, are also thixotropic, in the sense that they show a definite thinning out action when first agitated after a period of rest.

INSTRUMENTS

Several types of instruments are in use at Newark for measuring paint viscosity. These include the ''cup'' types (Ford, Zahn, Parlin) which measure the time for a given volume of paint to flow through an orifice in the bottom of the cup, or the time when a break in the stream flowing from the cup is observed.

The Brookfield viscometer is electrically driven, with four speeds and four or more spindles, and with a spring scale to indicate torque on the rotating member. Results are reported as poise values at the various speeds available. At least theoretically, this value is a rating that is often termed ''apparent viscosity'', that is, the poise value that a Newtonian liquid would have for the same instrument readings.

The Krebs Modified Stormer Viscometer employs a paint can and a rotating paddle driven by the torque produced by weights on a string. The results are usually expressed in Krebs' Units which are determined from a chart supplied with the instrument.

More detailed information on these and other viscometers can be obtained from the Sales Technical Manual, Section 19.

Edited by B. H. Perkins - 1975

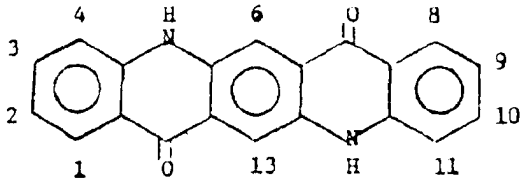
PHOTOCHEMICAL STABILITY AND HYDROGEN BONDING

One of the basic requirements for a high quality pigment is photochemical stability or lightfastness when dispersed in a vehicle. Despite the obvious importance of photostability, it is probably the least understood of pigment properties and consequently the most difficult to predict or build into a potential pigment. Even the great surge of activity in the field of photochemistry over the last decade and a half has failed to increase our knowledge of pigment photochemistry appreciably. This is due primarily to the emphasis put on gas phase and solution studies with solid state photochemistry getting only sparse attention.

The approach currently used to understand pigment photochemistry has been simply the extrapolation of basic concepts generated in solution phase studies to the solid state. This approach has suffered, however, for two reasons:

1. It neglects the significant effect of molecular interaction on deactivation processes in the solid state, and
2. It does not take into account the likely possibility that normally even minor and poorly understood photochemical pathways become important in the solid state.

The photostability of a molecule is governed by a competition between the rates of chemical reaction from the excited state and deactivation back to the ground state. To achieve the high degree of stability exhibited by pigments such as quinacridone (quantum yield for decomposition ~10^{-7})(1) the total rate for chemical reaction must be six to seven orders of magnitude slower than the deactivation processes. This spread in rates can be achieved by limiting the number of reactive centers in the molecule, by increasing the rate of excited state deactivation or both. Most pigments that show a high degree of photostability in the solid state have combined a relatively unreactive chromophore (as judged by solution studies) with a very efficient solid state deactivation step. Quinacridone (I) is a good example.



I

From a photochemistry standpoint QA is quite stable in DMF, having a quantum yield for decomposition of ~10^{-4}. This means that the QA molecule has a 99.99% efficiency

of returning to the ground state before a photochemical reaction occurs. Nearly 35% of this deactivation occurs via fluorescence. In the solid state, however, quinacridone exhibits no fluorescence at all and decomposes only slowly (ϕ_D-10^{-7}. These observations suggest the advent of some new radiationless deactivation process peculiar to the QA solid state. The nature of this new deactivation process has been well defined through detailed X-ray crystal structure determinations and empirical observation of substituent effects and involves effective intermolecular hydrogen bonding between pyridone groups in adjacent molecules. In fact the QA crystal is composed of networks of these hydrogen bonded molecules with each quinacridone bonded to four different neighbors. It has been shown that effective intermolecular hydrogen bonding and, consequently, photochemical stability, requires the absence of any sterically interfering groups in the immediate vicinity of the bonding atoms. Thus, 2,9-disubstituted quinacridones are invariably more photochemically stable than the corresponding 4,11-disubstituted counterparts. Within the 4,11-disubstituted series, photochemical stability goes down and solubility goes up as the steric bulk of the substituents goes up. Even 4,11-difluoroquinacridone is considerably less photochemically stable than

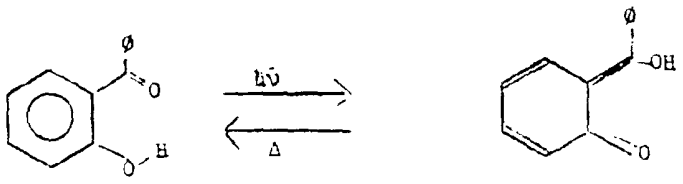
4,11-disubstituted Quinacridones	Photochemical Stability	Solubility
Diflouro	↑	↓
Dichloro		
Dimethyl		
Dibromo		
Bistrifluoromethyl		

quinacridone. The fluorine atoms appear to affect intermolecular hydrogen bonding as shown by solubility, and also the color, showing a hypsochromic shift relative to quinacridone. Of the two effects, the former appears to be of paramount importance as far as photostability is concerned. 4,11-Dichloroquinacridone, which is about the same color as the 4,11-difluoro compound, is inferior in photostability, presumably because of less effective intermolecular bonding due to the greater steric requirements of the chlorine substituents.

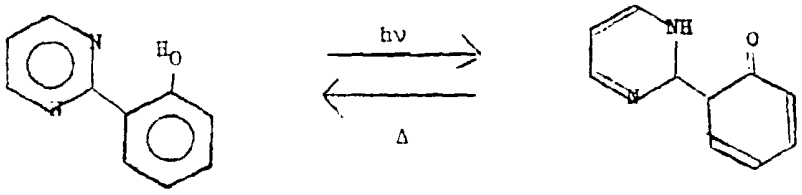
The effect of the 2,9 substituents seems to be mainly electronic. Electron donating substituents seem to have a slight beneficial effect on lightfastness while withdrawing substituents have a slight adverse effect. No doubt the strength of the hydrogen bond is involved.

The ability of a hydrogen bond to aid in the deactivation of excited states has been well established. Movement of the hydrogen between the two bonding centers very likely catalyzes crossing of the molecule from the excited state potential surface to an upper vibrational level of the ground state. Facile vibrational

deactivation completes the molecules' electronic decay. Complete hydrogen transfer does not have to take place to catalyze this deactivation process. In fact, with intermolecular bonding, hydrogen transfer could lead to photoreaction. However in some intramolecularly bonded molecules, hydrogen transfer does take place to form a tautomeric molecule which undergoes facile thermal reversal and thus a net deactivation. Thus an ortho hydroxy substituent on benzophenone stabilizes that system towards photoreduction, presumably via photoevolization followed by thermal reversal[2].



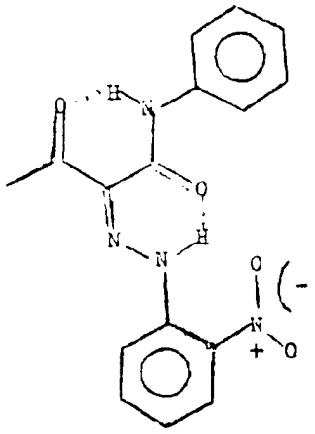
A similar stabilization nas been preposed for the effect of an orthohydroxy group in 2-phenyl pyrimidine [3].



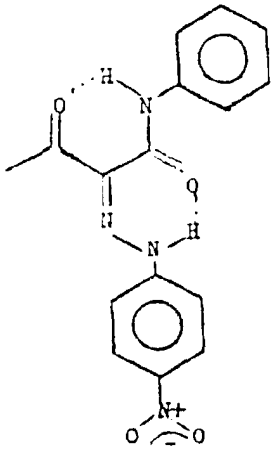
The importance of intramolecular hydrogen bonding in the photochemical stability of some pigments has been demonstrated by the substantially greater photostability of amides derived from 1-amino-anthraquinone relative to those derived from 2-aminoanthraquinone. Only the former are capable, and infrared spectra confirm the presence, of intramolecular hydrogen bonding.

Automotive grade pigs have quantum yield of only ~ 10^{-7} photoreactions studied are usually $> 10^{-4}$ ∴ pig can not have any obvious photo-reactive centers, & must have strong interactions in crystal to allow fast deactivation (unless molecule already has good internal deactivation)

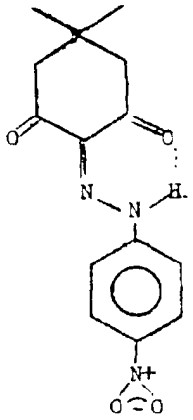
The fact that intramolecular hydrogen bonding increases the rate of excited state deactivation and thus increases photostability is beyond question. The effect is observed in some of the Hansa yellows. Thus, in solution, II is more stable than III and both are much more stable than IV. Quantum yields for



II



III



IV

decomposition of II in solution are on the order of 10^{-4}, very similar to QA. However, on going to the solid state, no dramatic increase in stability is observed with II, presumably because no strong interaction exists between the molecules in the crystal.

It is the strong interactions between molecules in the solid state, such as hydrogen bonding in QA, capable of effectively catalyzing radationless decay of excited states that will lead to the type of photochemical stability required of a high quality pigment. Needless to say, at this point our knowledge of solid state chemistry is not broad enough to be able to build this type of interaction into a pigment crystal.

Revised by P. A. Wriede - 1975

REFERENCES

1. A. R. Hanke - KN-70-14.

2. N. C. Yang and C. Rivas, J. Am. Chem. Soc. 83, 2213 (1961)

3. J.-E.A. Otterstedt, Orchem. RD-65-199.

Stabilization of Pig

energy traps (solid soln.) } deactivation
vibrational deactivation } of excited states
electron transfer

surface quenchers - screen or deactivate excited states

photo- bimolecular rxn
reduction
oxidation
addition
disproportionation

Deactivation of excited states

1. Reversible intramolecular rxn (eg. H transfer
2. Intramolecular H bonding (no H transfer)
3. Energy transfer $A^* + O \rightarrow A + O^*$ (quenches)
4. Bimolecular complexation
   a) electron abstraction
   b) exciplex formation

$$A^* + B \rightarrow [A \cdots B]^* \rightarrow A + B$$
$$\hookrightarrow RXN$$

Photoreaction occurs between pig. & vehicle components usually at defect sites on surface (an energy well)

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15

SURFACE ACTIVE AGENTS IN PIGMENT TECHNOLOGY

Most pigments manufactured today contain auxiliary organic or inorganic components which are not pigmentary in character. These components are an essential part of the pigment composition and they markedly affect the tinctorial properties in the end-use systems as a result of the alteration of the surface characteristics of the pigment.

These components may have been added for one or more of the following reasons:

1. During processing to control dispersion, i.e., surfactants used to make dispersed pastes.

2. During processing to aid in the control of particle size, shape, and distribution, i.e., surfactants are used in coupling of azos, in dispersion milling, or acid-drowning operations, and the subsequent pigment extraction procedures.

3. During processing to reduce chemical reactivity of the colored pigment in end-use systems, i.e., petroleum sulfonates in chrome yellows.

4. During processing to control dispersibility, flocculation, and rheology in end-use systems, i.e., sodium citrate, sodium phosphates in chrome yellows, and molybdate oranges for manufacture of aqueous dispersions.

5. During process, to control particle adhesion which may occur during drying operations, i.e., calcium Staybelite treatment of many organic pigments.

The organic vehicle systems being used in the paint, ink, rubber, and plastics industries vary in chemical composition and rheology. It requires a considerable effort to make a minimum number of pigments from a single chemical type which will be readily dispersible by conventional mixing and grinding equipment into these diverse systems.

Utilization of surface active agents frequently makes it possible to adapt a primary colorant particle to a new industrial use, i.e., a new vehicle system, without making it necessary to develop a new colorant. These agents drastically alter properties such as particle size, ease of dispersion, and rheology which have marked effects on the tinctorial properties and durability of a pigmented system.

It is quite obvious that the surface of the particle is the primary interface concerned in this dispersion operation. This interface is affected first by the physical chemistry of the pigmentary particle and secondly by the chemistry of the contacting substances.

The dispersion of a pigmentary solid into a liquid medium involves a change in interface from

solid - solid (pigmentary particles in contact)
solid - air (adsorbed air film)
solid - water (adsorbed water film)
to solid - liquid (organic system)

thus involving the spreading of the organic liquid over the solid surface with the resultant displacement of adsorbed gases or wetting of the solid surface. Capillary effects to assist in separating solid-solid interfaces are also important.

The mathematics of these situations are well understood and can be referred to in the attached list of references (1,2,3,4,5).

Surface active agents, substances which alter the conditions prevailing at the interfaces, have been obtained from natural products by extraction or modification, from prehistoric times. Examples of these are soaps, water-proofing agents such as greases and tallows, and dispersants such as glue, egg white, and natural gums.

In the last 50 years, an enormous industrial expansion to manufacture synthetic surfactants has been accomplished, along with a corresponding growth in the understanding of the physical chemistry of these agents in aqueous and, to a much lesser extent, in non-aqueous systems. This lack of basic theory in the non-aqueous situations frequently makes surfactant choice an art rather than a science. (See References 5-13).

1. Water-Soluble Surfactants

Most of the interest in surface chemistry has centered about the behavior of surfactants in aqueous systems. Thousands of compounds have been synthesized for use in wetting, foaming, anti-foaming, emulsification, demulsification, detergency, corrosion inhibition, flotation, and numerous other applications involving the use of water. These water-soluble surfactants are generally classified according to four types:

a. Anionic surfactants ionize in solution, with the long chain carrying a negative charge.

b. Cationic surfactants ionize in solution, with the long chain bearing a positive charge.

c. Nonionic surfactants do not ionize in solution.

d. Amphoteric or ampholytic surfactants ionize in solution with the long chain ion carrying either a positive or negative charge, depending upon the pH of the solution.

Each of these types finds application in our pigment technology dependent upon:

a. The pigment type being treated, i.e., CPC, QA, chrome yellow.

b. The vehicle or end-use system, i.e., alkyd paint, acrylic enamel, aqueous flexographic ink, etc.

Choice of a suitable surfactant for a given application is largely an art, but considerations which are likely to favor adsorption on the pigment surface due to chemical similarity, structural similarity or chemical or electrical fixation, coupled with knowledge of the vehicle system, its solids, solvents, and etc., frequently lead to striking results.

The effects achieved are often markedly affected by small differences in surfactant structure (see Reference 12).

A typical problem involving surfactant chemistry might be the improvement of a CPC dispersed paste (Reference 13). Here the end-use involves a dispersion of the pigment into an aqueous emulsion of vehicle solids, TiO_2, viscosity controller (Methocel), etc. The surfactant of choice in such a situation must be hydrophilic and preferably nonionic so as to minimize sensitivity to electrolytes or charged particles in the paint systems.

Another example of a problem solved by suitable choice of surfactant may be seen by studying Reference 14. Here the color characteristics of a chrome yellow in a printing ink system (Vaposet) were markedly affected by slight changes in the chemistry of the yellow pigment and a change in surfactant from an anionic to a nonionic type.

The use of surfactants in size reduction studies of CPC pigments is illustrated in Reference 15.

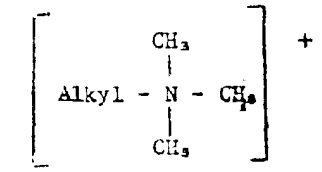
2. Hydrophilic Surfactant Groups

Anionics such as ionized - sulfonates
- sulfonated naphthylene-formaldehyde
- phosphates
- carboxyl
- dioctylsulfosuccinate
- citrate
- stearate

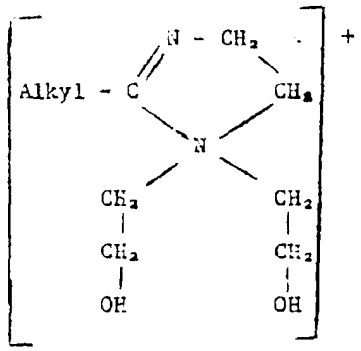
form the basis of many anionic surfactants. Products of this type, i.e., Daxad, Blancol, Polyfon, etc. (see Reference 6) are used as aids in the size-reduction of

CPC crudes with water, and a water insoluble salt such as borax, in our HF-milling operations.

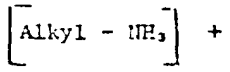
3. Hydrophobic groups such as



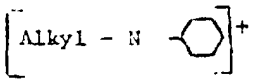
Armour ''Arquads''



National Aluminate
''NalQuat''



Armour ''Armeen'' Salt

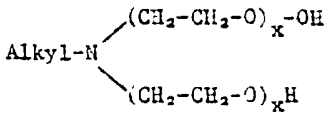


lauryl pyridinium

form the basis of many cationic agents.

Examples of the use of such products are involved in our dispersion milling operations on phthalocyanine or quinacridone pigments. Typical nonionics frequently encountered include:

$C_{13}H_{27}(O-CH_2-CH_2)_x-OH$ Polytergent J500 Mathieson



Ethomeen-Armour

Alkyl phenoxy poly (ethyleneoxy) ethanol Igepal (Antara)

As previously mentioned, these products are of use where a lesser sensitivity to electrolytes is essential.

1. Fischer - ''Colloidal Dispersions'' - Wiley, 1950 - Chapter 3.

2. Adamson - ''Physical Chemistry of Surfaces'' - Interscience, 1960, Chapter VII, X .

3. Osipow - ''Surface Chemistry, ACS Monograph No. 153 Reinhold, Chapters 2,10.

4. Bikerman - ''Surface Chemistry'' Academic Press, 1958, Chapter V .

5. Mollie-Collie and Black - ''Surface Activity'' Van Nostrand, 1962, Chapter 3.

6. ''Detergents and Emulsifiers'' - J.W.McCutcheon, Inc. (Useful for identification of proprietary names and chemical compositions.).

7. Sisley and Wood - ''Encyclopedia of Surface Active Agents'' - Chemical Publishing Company.

8. Schwartz-Perry and Berch - ''Surface-Active Agents and Detergents'', Interscience Pub.

9. Schick - ''Non-Ionic Surfactants'', Dekker.

10. ''Technical Manual - Pigment Colors'', Du Pont, Chapter 13.

11. Jackson KN-57-8, DuPont ''Finishing of Phthalocyanine Pigts. XII''

''Aqueous'' Milling of Premilled Phthalocyanine Crudes'' .

12. Jackson KN-59-9, DuPont ''Finishing of Phthalocyanine Pigts. XIV''. ''The Role of Surfactant Structure and its effect on Pigment Properties.

13. Jackson KN-66-9, DuPont ''BW-461-P Counteroffering for Hilton Davis' Super Seatone Phthalo Blue''.

14. Jackson KN-64-17, DuPont ''Y-751-D Counteroffering for Imperial's X-2904''.

15. Jackson PTC-60-2, DuPont ''Stronger BT-383-D Pigments''.

PIGMENT PURIFICATION (RESEARCH)

Many pigment properties including intensity, bleed characteristics, chemical and photochemical stability can be significantly affected by the presence of impurities. In the course of research work, therefore, it is useful and sometimes essential to prepare analytically pure pigments, for purposes other than chemical characterization.

The method of purification which can be applied to a given pigment will depend on its properties, including its solubility in various solvents. The solubility of commercial organic pigments in organic solvents varies over a wide range. Even among pigments which are used in automotive finishes and which are, therefore, considered to be essentially non-bleeding or insoluble in the vehicle, the differences in solubility are quite substantial. For example, quinacridone dissolves to the extent of 84 mg/liter in boiling α-chloronaphthalene (264°C.) while anthrapyrimidine yellow shows a solubility of 120 g/liter at 250°C. in the same solvent. Thus, if a pigment is sufficiently soluble in such solvents as α-chloronaphthalene, nitrobenzene, dimethylformamide and others, purification can be accomplished by conventional recrystallization either with or without charcoal.

High quality pigments, by definition, are either insoluble or very sparingly soluble in organic solvents, and consequently do not lend themselves to purification by conventional recrystallization techniques. Many pigments, however, are bases with respect to concentrated sulfuric acid by virtue of some heteroatoms which are part of their chromophores. Such pigments, including copper phthalocyanine and quinacridone, are soluble in concentrated sulfuric acid. Provided the pigment is chemically stable in cold concentrate sulfuric acid, this solubility can be a decided asset and is the basis of a purification method called "acid recrystallization". This purification method involves the selective precipitation of the pigment sulfate or hydrosulfate from a sulfuric acid solution of the pigment. Most, but not necessarily all, impurities possess sulfates of greater solubility. Controlled addition of water to a cold solution of the pigment in sulfuric acid causes the pigment sulfate to precipitate at a given acid concentration while keeping most of the impurities in solution. The sulfate is separated by filtration and subsequently washed with sulfuric acid of about 5% lower concentration than the acid concentration at which the precipitation occurred. The washed sulfate is hydrolyzed with ice and water, and ammonium hydroxide if necessary. The liberated pigment is filtered and washed acid or base free. If necessary, the procedure can be repeated. This is an effective and very useful method of pigment purification.

Another purification method which can be applied to highly insoluble pigments is sublimation under vacuum. Although in some cases an effective method, it is not as convenient as the "acid crystallization" procedure, particularly when purifying large (20-50 g.) quantities of pigment.

Reviewed by H. Matrick - 1975

Certain pigments, particularly chelates such as Green-Gold (see Section 22) are nearly completely insoluble in organic solvents and are also unstable in cold concentrated sulfuric acid. The purification of such pigments, if required, can be accomplished either by sublimation or, if thermally unstable, by repeated extraction with boiling solvents.

It is apparent from the above discussion that the selection of a purification method depends not only on the solubility but also on the chemical structure of the pigment.

Reviewed by H. Matrick - 1975

X-RAY DIFFRACTION

INTRODUCTION

X-ray diffraction is an indispensable tool of pigments research. Its usefulness resides in the fact that the interatomic distances in most all crystalline materials are of the order of magnitude of the wavelength of x-rays. This enables the ordered arrangement of atoms in a crystal to act as a three dimensional grating for the diffraction of x-rays. Since most all solids possess some degree of internal order (even so-called amorphous materials), x-ray diffraction can yield information about the internal structure of all of our pigments.

Here, at Newark, a Philips Electronics x-ray diffractometer is available. This includes copper and cobalt x-ray tubes with appropriate filters to achieve nearly monochromatic x-radiation. For those applications where a more nearly monochromatic source is required, properly cut crystals of sodium chloride and fluorite are available. By means of scintillation detectors and recorders, x-ray diffraction charts are automatically obtained plotting diffraction angle (2θ) vs. x-ray intensity. In addition to this, we have a Debye-Scherrer camera that gives a photographic strip record of diffraction angle. X-ray intensity is simply estimated by eye. Both of these methods use the powder diffraction technique where a small amount of pigment powder, with random orientation of the individual crystallites, is exposed to the monochromatic x-ray beam. We also have a Buerger Precession Camera which gives a photographic record of the diffraction angles from single crystals. This enables a determination of the dimensions and symmetry of the unit cell of the crystal and in some cases can lead to a fairly detailed determination of the crystal structure.

SPECIFIC APPLICATIONS

1. Polymorphism

Most all of our pigments, both organic and inorganic, exhibit polymorphism. This is the ability of a solid material to exist in more than one orderly arrangement of the units making up the internal structure of the solid. In the case of inorganic pigments, such as chrome yellow, the unit is the atom or ion. In the case of organic pigments, the unit is the molecule. Changes in internal arrangement, i.e., polymorphism, should not be confused with changes in crystal habit. Crystal habit deals with the external appearance of the crystal. To be sure, the habit is influenced by the internal arrangement of the structural units but, in many cases, the same polymorph can be made to exhibit different crystal habits.

X-ray diffraction serves to distinguish between the different crystal phases by virtue of the fact that each polymorph has a characteristic set of diffraction peaks that serves as a "finger-print" for the particular polymorph. Mixtures of polymorphs can also be recognized and, to some extent, the relative

Polymorph → α I – CPC
Polytype

polymorph differs in 3 dimensions
polytypes differ in 1 dimension

peak heights serve as a means for estimating the relative amounts of each phase. The lower limit for such an estimate is in the order of magnitude of 5% but, in some cases, somewhat less than this can be detected.

Crystal habit can also be assessed by x-ray diffraction. If the crystal shape is that of a needle or plate, an x-ray diffraction mount will have more of the crystals lying in the plane of the mount than would be expected from a purely random orientation. Such preferred orientation will emphasize certain diffraction peaks resulting in a change in relative intensity as compared to that obtained using a different mounting technique.

2. Solid Solution

Pigment technology has many examples of solid solutions. When two materials have an internal order that is not too different, substitutional solid solution can form. For such a solid solution, a well-ordered lattice results but the lattice points are occupied in a random manner by the units of each of the components in the solid solution. Even as an individual compound can exhibit polymorphism, so can a solid solution. For example, lead chromate can crystallize in an orthorhombic or monoclinic phase, and lead sulfate can enter either lattice as a solid solution. Solid solutions are not confined to binary systems. In theory, any number of components can enter into solid solutions provided that their crystal lattices are compatible. For example, ''Monastral'' Orange, YT-756-D, is believed to be a quaternary solid solution of QA, QAQ, 4,11-Cl_2QA, and 4,11-Cl_2QAQ. Solid solutions have limits of solubility even as do liquid solutions. Situations exist where component A can dissolve up to some limit in component B while maintaining the internal crystal configuration of B, but very little, if any, component B will dissolve in component A. An example of this is the solid solution of $PbCrO_4$ in tetragonal $PbMoO_4$. It is possible to get up to around 30 mole percent of $PbCrO_4$ into the tetragonal $PbMoO_4$ lattice whereas a solution of $PbMoO_4$ in either monoclinic or orthorhombic $PbCrO_4$ has not been established. Supersaturated solid solutions can also exist. Such solutions can be made to break down into a two phase system in which one phase represents a solid solution containing less solute and the other phase is the solute phase in its stable crystal configuration.

X-ray diffraction is ideally suited for the study of solid solutions. Any change in the lattice parameters brought about by the solid solution will cause a shift in the positions of the diffraction peaks. The shift will be more pronounced in the large 2θ region than in the small 2θ region but the general appearance of the diffraction record of the solid solution will be very like that of the pure component whose lattice is being modified. The extent of the shift in the diffraction peaks is a measure of the amount of solute in the solid solution but the shift is not necessarily proportional to this amount. Furthermore, the inclusion of the solute in the lattice of the solvent will not necessarily cause a proportionate change in the dimensions of the unit cell. This means that some diffraction peaks will change their position more than others and, in some cases, the direction of the change may be reversed. It should also be pointed out that, in some cases, a solid solution can be formed with lattice

parameters so nearly like that of the solvent, that it is difficult to observe any change in the position of the diffraction peaks. X-ray diffraction can still be useful in these cases by observing the disappearance of solute diffraction peaks under conditions where they would be observed if there were no solid solution. Such an observation plus the observation that the suspected solid solution has pigment properties other than those of the simple mixture is usually sufficient to establish the existence of a solid solution.

3. Degree of Crystallinity

Because x-ray diffraction results from an internal order, it follows that x-ray diffraction will be useful in studying variations in this internal order. The term ''degree of crystallinity'' encompasses two different factors. One is the deviation of the actual internal order from the ideally perfect order, and the other is the crystallite size. The internal arrangement of the units making up the crystal can be considered as varying from a perfect arrangement to no arrangement at all (amorphous). When the coherent domain,which can be considered as being the distance one can move through the crystal before reaching a lattice defect,is of the order of magnitude of approximately 0.2μm or smaller, the x-ray diffraction record will be influenced by a broadening of the diffraction peaks. This broadening is usually determined by measuring the peak width at the position of half-maximum intensity. When this width is corrected for line broadening introduced by instrumental effects, it is called β 1/2. When the coherent domain is related to the crystallite size rather than to internal deviations in the lattice structure, the β 1/2 relates to the average crystallite diameter, ''D'' by the formula,

$$D = \frac{K\lambda}{\beta\ 1/2 \cos\theta}$$

D = Degree of Crystallinity expressed as a crystal diameter.
λ = Wavelength of the monochromatic x-radiation
K = Constant approximately equal to unity and relates both to the crystallite shape and to the way β 1/2 and D are defined

It should be recognized, however, that both internal crystal defects and crystal size affect x-ray diffraction line broadening and the term ''degree of crystallinity'' is meant to encompass both. In those cases where ''degree of crystallinity'' is due primarily to crystallite size, good correlation between crystallite size and line broadening will result. If, on the other hand, crystal defects are the major cause of line broadening, correlation between crystallite size and line broadening will not be good. For all applications of x-ray diffraction line broadening to colored pigments research, this limitation should be borne in mind and line broadening should be considered to have only an eimpirical relationship to crystallite size. Fortunately, this has not limited its usefulness and many examples exist where degree of crystallinity has related

to crystallite size.

This correlation can be carried a step further if the crystallite size is the pigment particle size. When this condition obtains, x-ray line broadening can be related to particle size. Such a relationship will be reliable, however, only for fairly large crystalline, non-aggregated pigments. Pigments in the very small crystallite size range with a tendency to form hard aggregates will have their particle size determined by the size of the aggregates and not by the crystal size.

INTERPRETATION OF X-RAY POWDER DIFFRACTOMETER RECORDS

1. Pertinent Features of a Diffractometer Record

   a. Relative peak heights
   b. Peak widths
   c. Peak position (2θ)

2. Factors Affecting Relative Peak Height

   a. Crystallite Size and Shape

If size is less than about 0.2μm for any of the crystallite dimensions, the diffraction peaks tend to broaden as size becomes smaller.

   b. Crystal Strain and/or Distortion

Any deviation from a regular ordered structure will result in diffraction peak broadening.

   c. Preferred Orientation of Crystals in the Mount

Flat or needle-like crystals will tend to lie in such fashion as to favor certain interplanar spacings over others resulting in changes in relative intensity. Mounting technique becomes extremely important for such cases.

   d. Number of Crystals in X-ray Beam

If sample is small or crystallites are large, insufficient crystallites will be properly oriented for each of the diffracting sets of planes resulting in a non-statistical distribution of diffracted beam intensities.

   e. Temperature

The higher the temperature, the broader the diffraction peaks. This effect becomes most noticeable at the melting point where the peaks disappear completely.

f. Chemical Nature of the Material

Materials made of large atomic-numbered elements diffract most strongly.

g. Primary and Secondary Extinction

At the diffraction angle, the incident beam intensity is decreased as it passes through the crystal by an amount greater than the normal absorption, in order to supply diffracted beam intensity. The magnitude of this effect is maximum for large perfect crystals.

h. Instrumental

i. Time constant, rate of scan, and amplification factor, all affect relative peak height. When properly controlled, the variation will be well under 5%. A weak peak must amount to at least 5% of full scale intensity for good quantitative work.

ii. The non-linear Geiger tube response can introduce errors of 20% or more at counting rates exceeding 800 counts per second if linear response is assumed. This error is minimized by using a set of standards. Our present detector is a scintillation counter that is linear up to an extremely high number of counts hence this limitation is no longer a factor.

i. Percentage of Components

Peak intensity can be used to determine percentage composition. Under ideal conditions, it is possible to obtain an accuracy of about 5% of the amount present for quantities in excess of 5%.

The organic solids with which we commonly work, such as the QA's and CPC's, are far from ideal. The lower limit of detectability of one crystal phase in the presence of another is between 5 and 10%. Working curves derived from synthetic mixtures should be used. These mixtures should be as nearly like the unknown with regard to the nature of the crystallite as is possible. Uniformity in sample mounting and instrument operation should be maintained. The crystallite size should be less than 5 µm. This last requirement is met by most all of our organic pigments. A possible exception is crystal unstable CPC that has been allowed to convert to the β-phase through solvent action.

FACTORS AFFECTING 2θ

1. Solid Solution

The lattice parameters of the crystal will change slightly causing the 2θ angle to change slightly. Generally speaking, any change in lattice parameters will change 2θ.

2. Foreign Components

Two components having peaks close together can sometimes yield one unresolved peak with a slightly different 2θ value. A possible example of this is the position of the peak at around 6.4° 2θ for mixtures of α and γ QA.

3. Instrument Misalignment

The instrumental 2θ value is set by reference with a standard material. Slight differences will be observed between different instruments if proper alignment is not maintained.

4. Instrument Operation

Changing the rate of scan and time constant can allow the recorder to lag behind the scan by a varying amount.

5. Variation in X-ray Beam Absorption

The exact point in the sample mount where the diffracted beams emanate with maximum intensity depends on the characteristic absorption of the sample and on the sample thickness. A variation of the position of this point with respect to the axis of rotation of the detector causes a slight variation in 2θ.

6. Incorrect Sample Mounting

This is probably the most important factor of all and is related to item 5 above. If too much sample is placed in the holder or too little, the axis of rotation of the detector will not be properly located in the sample. Such improper mounting can easily cause differences of 0.2° 2θ.

COMPARING X-RAY PEAKS FROM NEWARK DIFFRACTOMETER

Finding Ratio of Peak Intensities from Two Different Scans

The counts per minute for a peak are related to chart parameters by:

$$CPM = (\text{height-baseline}) \times \left(\text{range} \times \frac{\text{multiplier}}{\text{attenuator}}\right) = (H-B)(RM/A)$$

The height and baseline are measured from the chart, the other parameters are found in the chart heading, which is ''pulse cutoff voltage/range x $\frac{\text{multiplier}}{\text{attenuator}}$ /time constant''. To find the ratio of the height of peak A on one chart to the height of peak B on a second chart with different range values, use the formula:

$$\frac{\text{peak A}}{\text{peak B}} = \frac{(H_A - B_A)}{(H_B - B_B)} \frac{(R_A M_A / A_A)}{(R_B M_B / B_B)}$$

This assumes that the x-ray generator kilovolts and milliamps are set at the same values for both runs and that the samples are similar in character and thickness for both runs. The x-ray operator uses standard values of kilovolts and milliamps for each run and packs all samples in a standard way; so these assumptions are generally good. There are other conditions more complex to define that are also held constant from run to run.

R.D.Nelson 5/13/77

LPH 0072436

REFERENCES

Klug and Alexander, ''X-ray Diffraction Procedures'' Wiley, N. Y., 1954

A. J. Kitaigorodskii, ''Organic Chemical Crystallography'' Consultants Bureau, N.Y., 1961.

G. J. Clark, ''Applied X-rays'', McGraw Hill, 1940

M. J. Buerger, ''X-ray Crystallography'', Wiley, N. Y., 1942

M. J. Buerger, ''Crystal Structure Analysis'' Wiley, N. Y., 1960

J. M. Robertson, ''Organic Crystals and Molecules'', Cornell Press, N. Y. (Ithaca), 1953

Revised by A. R. Hanke - 1975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ELECTRON MICROSCOPY

INTRODUCTION

Since all pigments are composed of ''particles'' which vary in size down to ◀ 0.1 micron diameter, the only way most of them can be observed directly is in an electron microscope. Clusters of primary particles or crystallites in the form of aggregates or agglomerates can also be observed in an optical microscope if they are greater than ca. 0.5 microns.

Electron microscopy has been a valuable tool in pigment research at Newark since ca. 1947 and considerable experience in sample preparation and interpretation has been gained. Considerable information can be obtained from electron micrographs regarding the particle size, shape, or habit, and dispersion of pigments, using as little as a few milligrams of sample.

PRINCIPLE

The electron microscope produces images by processes which are basically the same as those of the light microscope. An electron beam is used instead of light, and magnetic or electrostatic fields take the place of glass lenses. The final image is observed on a screen coated with a phosphor which emits light under electron impact. A permanent record may be obtained on a photographic plate exposed to the electron beam. Enlargements can be made photographically.

EQUIPMENT AT NEWARK

The electron microscope currently at the Newark Laboratory is the JEOL JEM 100B(Japan Electron Optics Laboratory Co, Ltd). This microscope is capable of ca. 20Å° resolution and magnifications up to ca. 1,000,0000X. Facilities for selected area electron diffraction are built into the electron microscope. The instrument is also provided with a goniometer stage and an accessory for scanning electron microscopy.

Two vacuum evaporators, an SC-3 (Kinney Division, N.Y. Air Brake Co.)(ca. 1958) and a JEOL JEE-4C are used for: (1) preparing carbon films for use as substrates for electron microscopy specimens, (2) shadowing with heavy metals, and (3) evaporation of certain pigments onto glass slides, etc., e.g.,CPC, QA's, etc.

A well-equipped darkroom is used for developing electron microscope plates and for making enlarged prints. The most common enlargements are on 8 in. X 10 in. paper. Enlargements up to 11 in. X 14 in. can be made for special purposes, etc.

A Porter-Blum Microtome and a Dupont Diamond Knife is available for cutting sections down to <0.1 micron thick, of paint films, plastics, etc. for observing dispersion in actual films.

TECHNIQUES AND APPLICATIONS

Since the electron microscope operates under vacuum (ca. 10^{-5} Torr) and the sample is exposed to a somewhat "hot" beam, the sample preparation is very critical and restrictive. Normally, pigment samples are dispersed in some medium and applied to an electron-transparent film supported on a metal grid (usually 200 mesh). Among the techniques used at Newark, the following are the most widely used:

Transmission Electron Microscopy

1. Dry pigment is mixed with a solution of nitrocellulose in isopropyl acetate using a spatula on a suede-finished glass plate. With particles well below 0.5 microns diameter, the best dispersion is obtained by rubbing vigorously with the spatula after most of the solvent has evaporated. The residue is reincorporated into additional solvent and then rubbed again with the spatula one or more times. If the particles are capable of being fractured, the samples should not be rubbed vigorously, since this is a severe technique. The final dispersion is either sprayed or dropped on to a carbon film (on a grid), washed with solvent, and then examined in the microscope. Exposures are made on plates at suitable magnifications, usually of selected fields which are as representative as possible. Prints are made of the plates. This procedure is capable of giving the best possible dispersion of particles from a dry pigment sample.

2. The dry pigment is mixed with "Petronate", a sodium petroleum sulfonate, in a small mortar with a pestle, and the mixture diluted with toluene and sprayed or dropped on a carbon film. The Petronate is washed out with toluene before viewing the microscope.

3. Masstone rubout inks are thinned with toluene or other innocuous solvent, sprayed or dropped on a carbon film, washed with the solvent, and viewed in the microscope. This technique shows the degree of dispersion in the ink.

4. Paints and fluid inks can be thinned with suitable solvents, sprayed on carbon film, washed free of vehicle, and viewed in the microscope. This also shows the degree of dispersion obtained. Electron micrographs of paint samples represent the state of pigment dispersion as it leaves the spray gun.

5. Replicas of surfaces such as paint films, etc. can be made by coating with something like polyvinyl alcohol (PVA) aqueous solution. After drying, the film is stripped, shadowed with a heavy metal, coated with carbon, the PVA dissolved away, and the carbon replica viewed in the microscope.

6. Particles on a carbon film can be ''shadow-coated'' by evaporating a heavy metal, such as Pt/Pd alloy, at an angle in the vacuum evaporator so as to leave, in effect, a ''shadow'' on the side of the particle opposite the source. From the length of the shadow and the angle, the height of the particle can be calculated.

7. To obtain a three dimensional view of particles, aggregates, etc., it is possible to make electron micrographs 5° or 10° either side of normal viewing and then to observe a pair of enlarged prints through a stereo viewer.

8. Sections of paint films, plastics, etc., less than 1 micron thick can be cut on the microtome to determine pigment dispersion, etc.

9. Pigment particle size distribution can be determined from electron micrographs by measuring and counting several hundred particles and plotting frequency vs. size.

10. To observe coatings such as in Krolor® pigments, magnifications >100,000X are desirable.

SCANNING ELECTRON MICROSCOPY

The EM-ASID high resolution scanning device is used in conjunction with the electron microscope. The specimen (ordinarily coated in a vacuum evaporizer with a metal to render it electrically conducting) is placed in the objective lens magnetic field and scanned with an electron beam much as in television, the scanning image being displayed on a CRT. A high resolution secondary image of better than 100Å and a transmission image of better than 30Å are obtained.

''PITFALLS'' IN ELECTRON MICROSCOPY

Because of the nature of the electron microscope and the techniques used in sample preparation, certain artifacts occur occasionally, as follows:

1. Because of an occasional ''hot'' beam, certain organic pigments, such as CPC or QA, can sublime in the microscope usually leaving a residue and ''feathery'' condensed particles.

2. Certain inorganic pigments, e.g., containing lead carbonate, can decompose and leave a skeleton-type residue.

3. Since toluene and other solvents are used in several techniques, crystal growth and/or phase conversions of certain pigments, e.g., α-phase chlorine-free CPC, are possible during sample preparations.

4. Although the operator tries to photograph representative fields of each mount, this is impossible when there are many particles much greater than 1 micron diameter. In such cases, it may be desirable to prepare photomicrographs at 100 to 500 diameters. In cases where pigment dispersion is of interest, a preliminary study with the optical microscope is recommended.

Revised by B. H. Perkins - 1975

EVALUATION OF EXPERIMENTAL PIGMENTS

Pigments are used for a variety of purposes, principally to impart color, hiding, decorative effects, reinforcement or corrosion inhibition. The initial step in a pigment evaluation is to decide whether usage as a colorant, in other types of application, or in both colorant and non-colorant applications, is of interest. In general, our interests are primarily in color, decorative effects, and properties related to colorant usage but other types of uses must be considered as, for example, film-fortification and metal-protection. This discussion, which covers evaluations only within the Research and Development Division, emphasizes applications basically dependent upon color and decorative effects and does not include tests for other pigmentary applications, (e.g., metal-protective paints, flakes or non-pigmentary uses which, however, should always be considered. (e.g., Biochemicals Department agricultural and insect screening tests).

A preliminary screening evaluation should be made by the chemist before submitting a sample to the Evaluation Group for end-use tests. Much time and money can be saved by the chemist's critical examination at this stage.

PRELIMINARY EXAMINATION (BY THE CHEMIST)

1. Rubout

In general, a rubout (TF-7001-10) or a flushout comparison with the nearest commercial pigment is the recommended initial test. Great care should be taken that the test material is of pigmentary size and that it is properly dispersed. Dispersion problems resulting from aggregation or drying can generally be avoided by flushing the pigment or by dispersing freeze-dried material. A quick light microscopic examination of the rubout ink will show the measure of dispersion insofar as large particles are concerned; grit visible to the unaided eye is an obvious warning. If still in doubt, get an electron micrograph of the ink. Mounts should be made of the masstone, skindown and drawdown over hiding power paper (black areas and white areas). Tint and masstone Fadeometer exhibits should also be made.

2. General

Note oil absorption, dispersibility (grit), wetting behavior, rheology, (heavy, thixotropic, etc.) , reactivity (gelation, etc.), finish, bronziness, soak-through on the paper, any color which migrates into the paper at the edge of the rubout and general appearance.

3. Masstone

The masstone shows the color obtained with the pigment by itself (i.e., no extender pigment present) in a film thick enough to give complete hiding. A highly transparent pigment will show complete hiding only in a very thick film. (Note if your exhibit hides.) Examine the exhibit both before and alter drying. Expensive organic pigments are not much used alone as masstones.

4. Skindown

The skindown gives some indication as to how the pigment will appear when used alone in a printing ink and is obtained by drawing down the masstone to a very thin film with a blade. Examine the exhibit both before and after drying. Note color, hiding, gloss, bronziness, grit, flocculation, changes on drying, etc. Intense color, good hiding, freedom from bronze (bronze can usually be corrected) , low oil absorption, high 'finish' and high gloss are generally considered desirable in pigments for most inks. For foil inks, transparency is generally desirable.

5. Drawdown on Hiding Power Paper and on Clear Plastic

Transparency is important as it influences the metallic paint properties, 'two-tone' effects and related characteristics. It can vary greatly depending on particle size insofar as the latter affects light scattering. The desire for transparency conflicts in some cases with the need for high hiding power so as to minimize the cost of a paint film which 'covers'. Hiding can generally be obtained by the addition of other pigments (e.g., aluminum flake) but an opaque pigment cannot effectively be made transparent by blending with other pigments.

6. Strength

As noted previously, special attention should be given to complete dispersion and the presence of undispersed particles. In case of doubt, absorptivity measurements should be made. Pigment strength is important as it influences cost, color and pigment loading in the vehicle. Generally, high strength is desired in pigments for tints, metallics, and printing inks. It permits the use of the minimum amount of pigment for a given color (cost) and facilitates the attainment of color without excessive pigment loading which may give rise to poor working properties. However, poor strength, as measured by rubout, is not necessarily a fatal defect, nor is outstanding strength of significance for all uses. For example, the weaker, redder type of molybdate orange is preferred to the stronger, yellower one

for many application. RT-759-D, a relatively weak quinacridone, is extensively used because of compensating virtues, although stronger quinacridones are available.

Polymorphism in the case of organic compounds is not a critical factor with respect to inherent pigment strength inasmuch as light absorption is determined primarily by the properties of the molecule rather than by their arrangement in the crystal.

7. Lightfastness

Masstone and tints should be exposed in the FadeOmeter. It is desirable to examine the exposures at 24 hour intervals until a 'break' (color change) occurs. Note whether the color fades, darkens or changes hue.

At the present time, completely reliable accelerated tests are not available. Poor lightfastness behavior in the FadeOmeter test has generally been predictive of poor performance on outdoor exposure, but good results by the FadeOmeter test do not necessarily mean good behavior outdoors. A table of conversion of FadeOmeter results to outdoor exposure has been published by the Technical Services group.

The FadeOmeter results are only a qualitative guide, and experimental pigments which show slightly inferior lightfastness relative to controls by this test should not be summarily discarded. The importance of purity, particle size, and the dispersion medium should be considered. A more durable vehicle, larger pigment particle size, or the use of certain additives may improve the lightfastness but are not likely to overcome very poor lightfastness.

Accelerated test by WeatherOmeter (on paint films, not on rubouts) are also useful indicators of lightfastness, but are not ordinarily carried out as part of the chemist's preliminary evaluation. The WeatherOmeter test should not be used for gloss retention studies. Chalking, film deterioration, etc. influence WeatherOmeter results. WeatherOmeter results do not always correlate with outdoor exposure results and in the case of experimental pigments must be evaluated with great care. Different pigmented systems in the WeatherOmeter show different degrees of correlation with outdoor exposure results so that unless the correlation is known for a specific system the validity of WeatherOmeter results is subject to question.

As a general guide, pigments which do not actually show poor behavior by these accelerated tests are usually placed on outdoor exposure if other test results are favorable.

8. Absorptivity (extinction coefficient)

Light absorption measurements on a solution of an organic pigment in 1-chloronaphthalene, dimethylformamide and similar solvents give a useful measure of the inherent pigment strength, even though the measurement in solution does not apply strictly for the solid. A very low absorptivity at λ max (use the values for known pigments as a reference) may be taken as an indication of poor inherent tinting strength as a pigment.

9. Solubility

A quick test for solubility in 1-chloronaphthalene and in dimethylformamide can usually give an indication of the bleed properties. Appreciable bleed is a serious handicap, especially for automotive type pigments. Note, however, that bleeding pigments ('Green-Gold', toluidine, red lake C) are used in some applications. A table of pigment solubilities is available in the Physics Lab data book. Low solubility and good thermal stability suggest a potential application in high temperature plastics systems.

10. Toxicity

Consideration should always be given to the possible toxic properties of any experimental products. Du Pont's Haskell Laboratory can assist in assessing toxicity.

CONCLUSIONS FROM THE CHEMIST'S PRELIMINARY EVALUATION

The results of the preliminary evaluation should be analyzed carefully before undertaking further work. Beyond this point, evaluation expenses may mount rapidly because of the cost of outdoor exposures, etc. The following, in addition to obvious instability of the pigment, etc., would appear to warrant terminating the evaluation.

Serious bleed in solvents commonly used in paints and inks.
Very poor lightfastness by accelerated tests. (But make certain it's not an inpurity which is responsible for the change.)
Very poor strength, for a pigment which is to be used principally for its color.
Inferiority to available commercial pigments of equal or lower cost which will meet the need in question. Liaison with Marketing can prove useful in this respect.

LPH 0072445

TEST BY PIGMENT EVALUATION GROUP (NEWARK)

Evaluation of a pigment, even for use only as a colorant, involves the consideration of many properties other than color; namely, chemical composition, chemical stability, mechanical strength of the particles or aggregates, and collodial properties, etc. These characteristics influence two major aspects of pigment technology; durability (resistance to light, heat, weather, solvents, chemicals), and working properties. The term 'working properties' refers to the influence that the pigment has on the fluidity or consistency of the vehicle. The surface area of a pigment, the shape of the particle, and the various forces acting between the pigment particle and between the pigment and vehicle at these surfaces are the principal determinants of the work properties. The properties of a pigment cannot be deduced from its gross chemical composition alone. Some properties are quite closely related to composition and others are determined by physical characteristics, such as

1. crystal geometry and phase
2. particle size
3. amount and type of inpurities
4. presence of special modifying agents
5. type and amount of surface coatings.

The principal end-use evaluations conducted by the Evaluation Laboratory concern (1) paints, (2) inks, and (3) plastics.

1. Paint

Dispersion of the pigment by sand milling is the preferred method in industry. Where this is not possible, two-roll chipping is used. These dispersion methods can be carried out in the Evaluation Laboratory but because of convenience, the initial test in most paint systems is usually a ball-mill grind in an automotive type paint vehicle. This test requires relatively small amounts of pigment and allows generally adequate evaluation of color, gloss, overstripe bleed, chemical resistance, heat resistance, working properties, shelf-storage properties (settling and reactivity) and lightfastness and durability by both accelerated weathering unit and outdoor exposure. (Sand mill and two-roll chip dispersions are also prepared where the need is indicated.) The choice of paint system depends on the pigment chemical type and also the characteristics as determined in the preliminary evaluation. The more durable colors are used in exterior paints, particularly in automotive finishes.

SERVICE WORK

PHYSICAL LABORATORY

Much of the work of the Newark Pigments Research Group involves particle size, shape, crystal phase, surface area, optical characteristics, and related properties. Instruments for the determination of pertinent physical parameters are maintained in the Physics Laboratory. Measurements will be carried out by the Physics Laboratory staff upon request or, in general, the chemist concerned may make arrangements to do the work, with assistance of the Physics Laboratory staff as needed. (For safety reasons, operation of x-ray equipment is restricted to personnel specifically authorized by the Laboratory Director.) The Physics Lab staff will also assist in planning. Arrangements can ordinarily be made with Central Research and Development or other Company groups for measurements or use of equipment not available at Newark.

Equipment is currently available in the Physics Lab for the following measurements:

1. X-Ray Diffraction

This technique is extensively used for the determination of crystal phase, identification and characterization of polymorphs, estimations of relative crystallite (coherent domain) size from x-ray line broadening (''B 1/2'') measurements, and also to identify unknown materials. A brief memo on the interpretation of x-ray diffractometer records is attached.

a. Equipment

Norelco (Philips) wide angle x-ray diffractometer. Two goniometers and recorders. Scintillation detectors. (Geiger tubes also available.) Powder camera for photographic recording. Weissenberg and Precession cameras for structure determination. ASTM x-ray file (books and IBM cards).

b. Principal Applications in Pigments Research

For the interpretation of x-ray diffractometer records, see separate section on ''X-ray Diffraction''.

i. Determination of phase composition of pigment samples.

Relative peak intensities (heights) vs. known mixtures and ''valley parameters'' are the principally used indices of the phase composition of mixtures.

ii. Identification and characterization of pigment polymorphs.

iii. Particle size. Relative crystallite (coherent domain) sizes in small particle region (ca. .1μm)by x-ray diffraction line broadening. Relative particle size from low angle x-ray scattering. Valley parameter may be used where there is no suitable single peak but a doublet is available.

iv. Identification of unknowns. Position and relative intensities of diffraction peaks.

v. Crystal habit. Relative intensities of different peaks in a pattern provides a useful index of crystal habit. Anisotropic particles tend to show preferential orientation which is reflected in peak intensities in some cases. A special sample holder is available to permit packing a sample in more than one way for the observation of orientation effects.

2. Surface Area

Surface area by nitrogen absorption is one of the most useful single measures of particle size.

a. Equipment

A Perkin-Elmer 212B Sorptometer with printing integrator. In this instrument, nitrogen gas mixed with a nonadsorbable carrier gas (helium) is passed over a weighed sample of degassed pigment at liquid nitrogen temperature. The quantity of nitrogen adsorbed is determined by warming the sample and determining the amount of adsorbed nitrogen released. The area under an automatically plotted desorption curve (integrated by the printing integrator) is proportional to the quantity of nitrogen evolved. This is converted into pigment surface area/gram (specific surface), by reference to a ''desorption'' curve with a known amount of nitrogen and comparison with a calibration curve obtained with samples of known specific surfaces.

b. Applications

Although a useful quantitative measure of particle size of colored pigments, the results are influenced by the method of degassing, and also by the surface treatments on the pigment. Tightly bound aggregates such as are formed, for example, by the drying of RT-849-D, are not penetrated by nitrogen molecules, so, in such cases, the surface area of the aggregates is obtained. Some samples, e.g., mica, may give difficulty. The method does not, by itself, provide a measure of particle-size distribution.

The results agree with those of the classical BET method which was used with the samples for the calibration curve. A combination of surface areas and x-ray line-broadening results can be especially useful in some cases as indicating aggregation, etc.

3. Electron Microscopy

a. Equipment

A JEOL (Japan Electron Optics Laboratory, Ltd.) Model 100B electron microscope with scanning attachment. Variable KV. Operating voltage (20,40,60,80, 100 KV), resolution 2A. Equipped for selected area electron diffraction. Has a high resolution universal goniometer which permits tilting the sample $\pm$ 30° and rotating it 360°. This is useful for structural determination and 3-dimensional work. Equipment for shadowing mounts with metal (length of shadow gives measure of size). Microtome with diamond and glass knives for sectioning paint films, etc.

b. Applications

Manifold applications to Pigments Research. Observation of size, shape, degree of dispersion, etc. in favorable cases. Surface coatings on pigment particles may be observed in some instances. Comparison of mounts at minimum and maximum work very helpful in some cases to evaluate aggregation, flocculation, etc. Particle size distribution can be obtained but requires many fields and the counting of a large number of particles. The greater depth of field of the electron microscope offers a considerable advantage. Results are influenced by the method of preparing mounts and the general necessity for dilution of the pigmented systems. Selection of a representative field is critical to avoid misleading results (microscopist does this). Care must be taken to avoid being misled by electron microscopy which deemphasizes large particles outside the usual microscope range.

4. Light Microscopy

a. Equipment

Bausch and Lomb "Dypnotic" (binocular eyepiece) research model. Circular stage. Polarizers, filters, illuminators, counting chambers, etc. Polaroid MP-3 set up for photomicrography in either black and white or color.

b. Applications

Light microscopy is generally the first choice in the initial investigation of pigment dispersion in paints, ink and the like, for the study of particle size in dry pigment powders and in all those instances which involve particles or objects in the size range easily covered by the light microscope. With pigment dispersions (ink, paints, etc.) it is well to note any large particles by light microscopy before proceeding to electron microscopy.

Many other possible applications of light microscopy to pigment research (e.g., crystallography, optical characteristics of crystals, etc.) are described in standard reference works on microscopy.

The ease and simplicity of photomicrography with Polaroid film favor its use in conjunction with the light microscope.

5. UV and Visible Spectrophotometry

a. Equipment

A Beckman DK-2 Ratio-Recording Spectrophotometer covers the range from about 200 nm to approximately 2500 nm. Deuterium and tungsten lamp sources. Reflectance and transmittance measurements. Quartz and glass cells and other accessories.

A Beckman DU spectrophotometer (non-recording) is located in the Research Analytical Lab.

A Cary Model 14 recording spectrophotometer with reflectance attachment is located in No. 2 lab, No. 23 building.

b. Applications

Color measurements. Analytical (absorption spectrophotometry) etc. Of special interest are particle size index measurements (KN-51-43, 52-2), light scattering measurements (differences between transmittance results between "near" and "far" positions of sample)and instrumental evaluation of pigment flocculation and flooding phenomena.

6. Colorimetry

A Neo-Tec DuColor Colorimeter, with remote head accessory and "selected" electronics for greater sensitivity, is available. As described in section on, "Color Measurements", the instrument gives direct color readings in the L,a,b system and readout of color differences.

7. Infrared Spectrophotometry

a. Equipment

Perkin-Elmer Models 21 and 137 ("Infracord") infrared spectrophotometers. Various accessories including ATR (attenuated total reflection) equipment.

b. Applications

In addition to the usual applications, it is especially valuable in pigment identification; detection, identification, and characterization of pigment polymorphs; and detection of impurities in pigments.

8. Emission Spectrometry

a. Equipment

DuPont emission spectrometer. Sensitivity an order of magnitude greater than that of commercial instruments (1965). Sample (liquid, solid, or gas) irradiated by 2537A° Hg line (other ''Pen-light'' source can be obtained) and emission spectrum is automatically recorded.

b. Applications

Photochemistry. Knowledge of emission spectra of great assistance in study of pigment fading, etc.

9. Nuclear Magnetic Resonance Spectroscopy

One of the most significant new tools for organic chemists, NMR spectroscopy is finding many uses in pigments research. Although generally limited to dissolved species, the ready availability of deuterated solvents such as dimethyl sulfoxide, trifluoroacetic acid and sulfuric acid extends its application to most organic pigments.

a. Equipment

At Newark is a Perkin-Elmer R-12B 60 MHz NMR equipped for proton resonance and decoupling. Higher resolution and multi-nuclear instruments are accessible at the Experimental Station.

b. Application

Identification of unknown pigments. Qualitative and quantitative analysis of pigment intermediates.

10. Freeze Drying

a. Equipment

Virtis freeze dryer with accessories.

b. Application

Study of pigment aggregation on drying, preparation of easily dispersible samples for special uses (IR spectra, etc).

11. Miscellaneous

Vacuum equipment (pumps, gauges, etc.).

EVALUATION LABORATORY

The Evaluation Laboratory examines experimental products to determine their utility in pigment end-use applications. Paints, inks, plastics, paper, floor coverings are among the end-use applications studied. Durability tests for pigments is another responsibility of this group.

a. Equipment

Various devices for preparation of pigment dispersion: ball mills, 2-roll mill for plastic, rubber, linoleum, and chip dispersions, a 3-roll ink mill, shaker mills, sand mills, Hochmeyer ''Discperser'' mill, ''let down'' equipment for use with chip dispersions, a heated platen press for press polishing plastic chips (polyethylene, polystyrene, etc.), spray booths, paint spraying equipment, and ovens for preparing painted panels, gauges for assessing degree of pigment dispersion in paints and ink, Brookfield, Ford, and Zahn Cup viscometers for measuring rheology of paints and inks, Gardner, Hunter, and DuPont (F and F) glossmeters, Hunter Multipurpose Reflectometer (and colorimeter), equipment for measuring pigment bleed, equipment for testing (controlled sanding and heating) reflow properties of paints, two Atlas WeatherOmeters and three FadeOmeter for accelerated exposure testing, raw materials (solvents, pigments, vehicles, driers, etc.) for the preparation of paints and enamels.

b. Applications

The largest single area of pigment evaluation at Newark is in automotive finishes, both lacquers and enamels. Plastics, industrial finishes, and nitrocellulose inks are other areas of extensive evaluation.

Procedures used in the evaluation of pigments are described in ''TF'' methods, copies of which are available in the Evaluation Laboratory and in the Research Office.

Descriptions of the principal areas of pigment application and discussions of the effects of pigment properties on their commercial utility appear in outline elsewhere in this manual, and in considerable detail in the ''Sales Technical Manual''.

ANALYTICAL LABORATORY

The Research Analytical Laboratory carries out analyses to assist Pigments Research. All types of analytical work are done, but an attempt is made to avoid any routine analysis (e.g., chromate in N-S solution) which is handled by the Plant Analytical Lab. In addition to elemental analyses, including determination of C, H, N, and Halogen, other work includes identification of unknowns, determination of pigment purity, identification of surfactants, development of methods, and consulting. The staff provides liaison with other Company analytical groups and commercial analytical laboratories whose services are sometimes used. Mass spectrometry, EPR, emission spectrographic analyses, and the like, are carried out for us by Central Research and Development or by Pigments - Experimental Station.

a. Instruments

In addition to the usual chemical analytical equipment, the equipment includes the following:

Coleman Automatic Nitrogen Analyzer
Coleman Carbon and Hydrogen Analyzer
Hewlett-Packard (F and M Model 810) gas chromatograph with programmed temperature controller and integrating recorder. Accessories include a solids injector.

b. Applications

The Analytical Staff assists in planning analyses to aid R and D, in addition to carrying out actual analyses.

Revised by EHP - 1975

RESEARCH EQUIPMENT AND FACILITIES AT THE EXPERIMENTAL STATION

The ''Index to DuPont Analytical and Physical Test Equipment'' (latest edition: July 1974) is the most complete listing of instruments and apparatus in use throughout DuPont. Copies are in the hands of analytical supervisors and can be ordered from Miss Mary Lou Mancuso, Information Systems Department, Extension 8-4004.

The following describes easily accessible equipment and services at the Pigments and the Central Research and Development (CRDD) Departments. Requests for service work in other departments should be best made through analytical supervisors or the technical man involved.

Pigments Department (T. D. McKinley, L. J. Matienzo)

Inorganic wet analysis
Atomic absorption for small inorganic quantities
Optical microscopy
Electron microscopy
Electron microprobe - elemental surface and bulk analysis of solids for elements >B
Emission spectroscopy - semi-quantitative analysis for elements
Spectrofluorimetry - fluorescence exitation and emission spectra
Infrared spectroscopy - including ATR technique for surfaces
UV/visible spectroscopy - including reflectance of solids
Differential Thermal Analysis (DTA)
Thermogravimetric Analysis (TGA)
BET surface area
Porosimetry
X-ray diffraction - powder camera and diffractometer
X-ray fluorescence - qualitative and quantitative for elements >Al

CRDD Spectroscopy Division (W. E. Mocha)

Optical Spectroscopy

Infrared (4000-200 cm^{-1}) - including ATR, micro techniques, polarized IR, digitized data output
Far infrared (400-10 cm^{-1})
Raman (He-Ne and Ar lasers)
UV/visible (→ 186 nm) - including reflectance
Optical Rotation
Fluorescence - excitation and emission (200-800nm)
Phosphorescence
NMR - 1_H, 13_C, 19_F, 31_P, 11_B, etc.
Homonuclear and heteronuclear spin decoupling
Fourier transform for 1_H, 13_C, 31_P

Relaxation measurements for 1_H, 13_C
C-1024 Time Averaging Computer for ^{C}signal enhancement
NMR spectral analysis - including computer simulation, double resonance, multiple frequencies, etc.
Quantitative analysis - isomers ratios, concentrations of some functional groups, mixtures
Broadline NMR of Solids

Gas Chromatography

Gel Permeation Chromatography

Molecular size distribution and molecular weights
Preparative for IR, UV, NMR

Mass Spectrometry

Available with coupled GC and computer data acquisition
Time-of-flight
Special techniques - chemical ionization
field desorption
field ionization
metastable ions
low voltage ionization
appearance potentials

X-ray Diffraction

CRDD Physical and Analytical Division (E. C. Dunlop)

X-ray photoelectron spectroscopy (ESCA)
Ion scatter spectroscopy
Electrochemistry - elemental analysis, structure determination, pulse and differential pulse modes
Zone refining
Crystallization
Distillation
Physical properties - density, specific gravity, refractive index (liquids, solutions, films) conductivity, dipole moment, dielectric constant, ASTM tests: flash point, etc., surface tension, vapor pressure vs. temperature
Molecular weight determinations - ebullioscopic, cryoscopic, vapor pressure, osmometric techniques
DTA/TGA
Differential scanning calorimetry - specific heats (solids), purity analysis, special transition temperatures

Microscopy - optical, electron, scanning electron
Particle size - sieve, Andreasen pipet, light scattering
BET surface area
Sorptometer pore volume
Microchemical analysis - C, H, N, O
Analysis by spectroscopic methods - atomic absorption, arc and spark excitation (emission) X-ray fluorescence
Activation analysis
Inorganic elemental analysis
Liquid chromatography - analytical, preparative
Organic analysis - functional group determinations: carbonyl, hydroxyl, carboxyl, amine, ester, unsaturation, hydrazine, hydroxylamine, mercaptan, peroxide, oxirane, oxygen, isocyanate; amino acid analysis, determination of water, pK_a and pK_b, solubility in specific solvents

CRDD Computer Division (E. A. Abrahamson)

A variety of scientific capabilities available on time-sharing basis via teletype-telephone, also for outside locations.

CRDD Special Services Lab (H. D. Carlson)

Electron and light irradiation

Resonant transformers delivering 2 Mv electron beam at 1 ma current.
High current radiation unit with 300 kv, 175 ma electron beam over a large area (49''x10'') for surface treatment or reactions in films and coatings (lower penetration);
High intensity light radiation source - Linde plasma arc with UV, IR and visible radiation

Unit operations and scale-up

Molding Lab

Compression and injection molding for thermoplastics
Processing of thermosetting resins
Film casting
1-inch extruder (lab size)
Rubber mills 2''x6'' and 6''x12''
Banbury mixer for 100g batches
Ball mills, tumblers, bottle rollers

CRDD Pressure Research Lab (Paul H. Mehne)

Autoclave reactions at 3-5000 atm
Tetrahedral anvils for extreme pressures

Prepared by P. A. Wriede - 1975

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PIGMENT CLASSIFICATION - GENERAL

The prime white pigment industry is characterized by relatively few chemical types, chiefly, titanium dioxide, zinc oxide, white lead, zinc sulfide and antimony oxide. In marked contrast, the pigment color industry deals with hundreds of chemical types. Accordingly, systematic classification can be of considerable value in reviewing the field in its entirety.

Classification of hue is that used by the Technical Division of the National Paint and Coatings Association in the RAW MATERIALS INDEX. More helpful classifications, from a technical viewpoint, are those based on chemical structure. Pigments may be classified grossly as inorganic or organic and the following table shows a modification of such a classification publicized by Mattiello (Volume II) with some variations and additions.

CLASSIFICATION OF PIGMENT COLORS

1. Inorganic

    a. Chromates

        1. Chrome yellows
        2. Chrome oranges
        3. Molybdate oranges
        4. Zinc chromates

    b. Ferrocyanides
    c. Mixed chromate - ferrocyanides
    d. Sulfide and selenides
    e. Oxides
    f. Phosphates and silicates
    g. Coated micas
    h. Coated chromates
    i. Metal flakes

2. Organic

    a. Basic and acid dye types
    b. Azos

        1. Pigment dye types
        2. Metallized types

    c. Nitroso
    d. Phthalocyanines
    e. Anthraquinones and vats
    f. Quinacridones

Except for the earth colors, most all of the pigment colors of commerce are synthetic.

The generalized properties which, with exceptions, characterize the organic pigments as compared to the inorganic are as follows:

1. Solubility - Inorganic pigments are generally insoluble (non-bleeding) in organic solvents. Many organic pigments show slight solubility in these solvents.

2. Cost - Organic pigments are generally more expensive than the inorganic.

3. Tinctorial strength - The generally higher strength of the organic pigments tends to offset their higher cost.

4. Hiding power - Inorganic pigments are usually opaque in contrast with the more transparent organics.

5. Specific gravity - The inorganics generally exhibit higher specific gravity than the organics.

6. Heat resistance - The inorganics are generally more heat-resistant than the organics.

7. Color intensity (Munsell Chroma) - The organics usually exhibit greater color intensity.

Newark capacity
~ 30 M lbs.
~ 7 M M. Evolve

INORGANIC PIGMENTS

CHROMATE COLORS

LEAD CHROMATES

Lead chromate pigments fall into three distinct groups:

- Chrome yellows - lead chromate precipitated alone or with lead sulfate.
- Chrome oranges - basic lead chromates.
- Molybdate oranges - lead chromate coprecipitated with lead molybdate and lead sulfate.

In the manufacture of these products, water solutions of the reactants are mixed in large, agitated tanks where the color is ''struck''; i.e., precipitated under carefully controlled conditions of temperature, pH, and agitation. The resulting crystalline precipitate is filtered, washed, dried, pulverized, and packed. Although historically a batch process, chrome yellows are now made at Newark by a continuous process in which a ''strike'' tank and a series of small overflow vessels replace the large reaction tank, centrifuges are substituted for the high labor, high cost filter presses, and drying is carried out in a continuous, automatic feed, belt drier.

Variations in color and properties are obtained through control of crystal structure, particle size, chemical composition, and the use of surface treating agents. As a general rule, the larger the particle size, the redder and weaker the product. Uniformity of particle size is desirable for maximum color brilliance (intensity).

1. Chrome Yellows

a. Medium yellow is the reddest and strongest of the chrome yellows; it consists essentially of monoclinic lead chromate ($PbCrO_4$) made by the reaction of lead and chromate ions.

b. Light yellow is also a monoclinic lead chromate but is lighter, greener, and weaker than the ''medium'' shade as a result of being coprecipitated with 20 to 40% of lead sulfate ($PbSO_4$) to form a solid solution.

c. Metastable yellows - These are yellows of about the same chemical composition as the ''medium'' and ''light'' yellows but which are stabilized in the rhombic crystal form and/or in a very small particle size range to produce a greenish-yellow hue. Immediately after precipitation, the rhombic particles begin to grow in size and change to the more stable monoclinic form. The arresting of either or both of these transformations is usually accomplished in one of three ways, the procedure being associated with the following pigment names:

We do not make pre-reduced $PbCrO_4$ (5% treated) in chrome yellow lt. pre-reduced is as lightfast as the non-reduced silica coated. Introducing also helps prevent product turning chrome yellow med.

- Primrose yellow - coating the crystals with alumina or titania hydrate.
- Phosphated or lemon yellow - introducing an irregularity into the crystal structure, such as the hexagonal-shaped lead phosphate crystal.
- Shading yellow for greens - treatment with inorganic salts (antimony or tin) to obtain small particle size of good lightfastness.

2. Chrome Oranges

Chrome oranges are basic lead chromates of tetragonal crystal structure. The basicity of the product controls the shade of the orange, e.g., extra light, medium, extra dark. Very light shades have the approximate composition $PbO.2PbCrO_4$ (74% $PbCrO_4$), whereas very dark shades approach $2PbO.PbCrO_4$ (42% $PbCrO_4$) in composition. The darker oranges are blue and weak in tint.

3. Molybdate Oranges and Reds make OK-straight - ½ time (076) blend to get low content

Molybdate lead chromates (molybdate oranges) are lead chromate/lead molybdate compositions with monoclinic crystal structure, different from that of either lead chromate or lead molybdate. The crystal structure characteristic of molybdate orange is most strongly evident at 90 mol% lead chromate/10 mol% lead molybdate, where maximum redness is attained, but is also detectable in compositions containing as little as 60-75% lead chromate. Commercial pigments also contain lead sulfate in addition to lead chromate and lead molybdate. The molybdate oranges are much stronger and brilliant than the chrome oranges.

By virtue of their sumilarity in composition, lead chromate colors have the following properties in common:

- High specific gravity (tendency to settle)
- Low oil absorption
- Soft texture (danger of over-grinding chrome and molybdate oranges)
- Poor soap and alkali resistance (except dark chrome oranges which are already basic)
- Sulfide darkening
- Moderately good resistance to acids except at low pH (chrome oranges inferior to the others)
- Non-bleeding
- Good bake resistance.

There are also some significant differences in properties among these pigments; namely,

- Color - Aside from hue differences, which are apparent from the pigment name, the chrome oranges are less intense than the chrome yellows and molybdate oranges.
- Gloss and gloss retention - The chrome oranges, particularly the darker shades, are decidedly inferior in this respect.
- Tinting strength - Strength increases appreciably as the chrome yellow shade changes from ''Primrose'' to ''Light'' to ''Medium''. The lighter shade chrome oranges have about the same strength as the ''Medium'' yellow, and strength decreases as the shade becomes darker. The molybdate oranges are much stronger than either the chrome yellows or oranges; their strength decreases with increasing redness.
- Opacity - This property varies in the same manner as tinting strength for these pigments, e.e., opacity increases with tinting strength. The molybdate oranges are much more opague than either the chrome yellows or oranges, although their opacity decreases with increasing redness.
- Lightfastness - All of these pigments darken on exposure; however, the chrome yellows, particularly the metastable varieties, e.g., ''Primrose'' and ''Lemon'', are generally inferior to the chrome and molybdate oranges in this respect. ''Pre-reduced'' medium chrome yellow is adequate in lightfastness for some automative finishes use.

The inferior lightfastness of the chrome yellows and the low gloss of the chrome oranges restrict their outdoor use principally to applications where these properties are of secondary importance, such as in finishes for rail cars, trucks, fleet cars, road markings, signboards, implements, tanks, and bridges. Red-shade molybdate oranges, on the other hand, are finding widespread use in automotive and industrial finishes in blends with organic reds to make bright, low-cost, non-bleeding reds of fair to good durability. These blends have already displaced many cadmium and toluidine red formulations. Similarly, blends of yellow-shade molybdate orange with chrome yellow compete with chrome orange formulations on the basis of improved cost and gloss properties with little sacrifice in lightfastness.

The shade of molybdate orange used in these blends is important for two reasons:

- Color clash normally is minimized by using the orange closest in hue to the pigment with which it is to be blended.

- The closer the orange is in color to the pigment with which it is to be blended, the more of it that can be used in a formulation to obtain a color match. This can result in reduced formulation costs (provided the orange is lower in cost per unit volume) and/or improved performance. The tinting strength and opacity of the orange must also be considered in such blends. The lower the orange is in tinting strength, the greater the amount used in a given blend. On the other hand, weakness in molybdate orange is generally accompanied by low opacity; hence, a compromise in properties is sometimes required.

A lack of good soap and alkali resistance is the major weakness of these molybdate blends; however, these deficiencies are minimized in some vehicles. Because they contain lead, none of the lead chromate pigments can be used in non-toxic finishes, e.g., toy enamels.

Low cost, opacity, and brightness of color are major factors contributing to the large use of chrome yellows and molybdate oranges in printing inks. Low reactivity and good flow are of particular importance here; ink pigments are frequently designed with emphasis on these properties. The chrome yellows and molybdate oranges also find use in the paper, rubber, and plastics industries.

4. ''<u>Krolor'' Colors</u>

In 1967, some modified chrome yellow and molybdate orange pigments, the ''Krolor'' colors, were introduced to the trade. These pigments have superior heat and chemical resistance. In many cases, the heat resistance is sufficiently good to permit them to replace cadmium colors at a considerable reduction in cost. (See under ''Krolor'' Pigments.)

Can use press-cake for ~~the~~ chrome yellow lt. & molys. but doesn't work for primrose & med. Med modified by adding some [illegible] to [illegible] -ous press-cake workable.

LPH 0072462

ZINC AND STRONTIUM CHROMATES

Two types of zinc chromate yellow are made:

- Zinc yellow, a zinc potassium chromate, having the empirical formula $4ZnO.4CrO_3.K_2O.3H_2O$.
- Basic zinc chromate the approximate composition of which can be expressed as $4.5ZnO.CrO_3.4H_2O$.

1. Zinc yellow is greenish-yellow, low in chroma and tinting strength, and semi-transparent. It is non-bleeding in organic solvents and resins, slightly soluble in water, moderately easy grinding, and resistant to acids; however, it has poor resistance to alkali and soap. Athough it is only fair in masstone and tint lightfastness, this performance is masked to a considerable degree when blended with blues and greens. In fact, this is about the only use where its color and low strength can be used to particular advantage. Surprisingly attractive, low cost, lightfast light grees can be made in blends with phthalocyanine or chromium oxide pigments.

Zinc yellow is a corrosion-inhibitive pigment and finds major use in metal protective primers. Properties of zinc yellow which make it useful here are:

- Availability of soluble chromate ions for passivation of the metal.
- Mild alkalinity, capable of neutralizing acid-corroding agents, such as might be formed in the oxidation of drying oils.
- Low specific gravity (3.4), leading to improved working and packaging characteristics.
- Compatibility with fast drying, snythetic resins; e.g., absence of significant reactivity.

2. Basic zinc chromate differs from zinc yellow in two important properties:

- It is virtually insoluble in water.
- It is lower in strength and much duller in color (practically a brown).

The major use of this pigment is in a ''wash primer' which is essentially a solution of polyvinyl-butyral resin, alchol, and phosporic acid. The primer offers good adhesion, toughness, and abrasion resistance on a variety of metal surfaces.

3. Strontium chromate is used as a rust-inhibitive pigment, bein more stable than zinc chromate in some paint vehicles. A growing use is in electrodeposated primers, for which zinc yellow is not satisfactory. It also finds some use in vinyl plastic formulations. (Zinc causes polymer degradation.)

IRON FERROCYANIDES (IRON BLUE)

Iron blues are complex ferric ferrocyanides containing an alkali metal or ammonia $Fe(NH_4)\ Fe(CN)_6$. They can be classified as:

1. Milori - easiest to disperse, least reactive and reddest in masstone.

2. Chinese - jet and intense in masstone, greenest in tint; other properties generally intermediate to Milori and Prussian.

3. Prussian - jet in masstone, reddest in tint, hardest to disperse, most reactive; commonly referred to as toning blue.

Iron blues are characterized by the following properties:

- Good lightfastness in masstones and deep tints, slight bronzing, fade in light tints.
- Very sensitive to alkali, resistant to acids.
- Non-bleeding
- Moderate to hard texture.
- Tendency to absorb moisture.
- Very dark in masstone, fairly transparent.

SULFIDE AND SELENIDE PIGMENTS

The following are included under this classification:

1. Cadmium sulfide
2. Cadmium sulfoselenide
3. Cadmium - mercury sulfides

Cadmium sulfides and sulfoselenides are available as both pure pigments and as pigments extended with barium sulfate. Extended products are more widely used than pure pigments and are commonly called cadmium lithopones.

Cadmium sulfides vary in hue from a light primrose yellow to light orange shade. In the light shade (primrose and lemon), small amounts of zinc sulfide are present along with the cadmium sulfides. In orang and redder shade yellows, some selenium is used.

The basic reaction for preparing cadmium yellow lithopone is:

$$CdSO_4 + BaS \longrightarrow CdS + BaSO_4$$

The cadmium sulfate and barium sulfide are coprecipitated to give cadmium sulfide and barium sulfate. This material is filtered, calcined in an inert atmosphere, quenched, wet ground, dried, and pulverized.

In making cadmium red lithopone, metallic selenium is dissolved in the barium sulfide liquor prior to precipitation or is mechanically mixed with the precipitate prior to calcination. The larger the quantity of selenium used, the deeper the shade obtained.

Pure cadmium colors are made by reacting cadmium sulfate or chloride with an alkali metal sulfide or hydrogen sulfide and following the same procedure as given above. Again, in the case of the reds or maroons, metallic selenium is either dissolved in the alkali metal sulfide prior to precipitation or is mechanically mixed with the precipitate prior to calcination.

The cadmium colors have the following properties:

Advantages	Disadvantages
1. Lightfast (fair to excellent)	1. Low strength
2. Non-bleeding	2. Somewhat difficult to grind
3. Heat stable	3. Low color intensity in tints
4. Resistant to alkalies	4. Decomposed by dilute acids
	5. Susceptible to overgrinding

These pigments find their broadest application in paints, plastics and rubber systems. In automotive paints, cadmium reds and maroons show a tendency to water-spot and have poor gloss retention. In vinyl systems, care must be taken to eliminate lead from the formulations to prevent the formation of black lead sulfide.

Historically, there has been a supply problem with cadmium reds and maroons because of their dependence on the availability of selenium. It was because of this supply situation that Imperial developed the so-called Mercadium pigments. These products vary in shade from an orange to a fairly deep maroon. They are considered to be solid solutions of cadmium and mercury sulfides. Although originally reported to be fully equal to the cadmium reds, the Mercadiums have been shown to have poorer lightfastness and poorer resistance to water spotting than the cadmiums.

In vinyl, Mercadiums are more intense in full shade and offer better money value than the cadmiums.

OXIDE PIGMENTS

The following synthetic hydrous oxides and oxides are used as pigments. In the iron oxide category, many natural products (umbers, siennas) not discussed here, are available.

1. Yellow hydrated iron oxide
2. Brown hydrated iron oxide
3. Red iron oxide
4. Venetian red
5. Precipitated black iron oxide
6. Chromium oxide
7. Hydrated chromium oxide (Guignet's Green)
8. Red lead
9. Orange mineral
10. Cuprous oxide
11. Mercuric oxide

1. Yellow Hydrated Iron Oxides

These pigments vary in hue from a light lemon yellow shade to a deep orange. Many different processes are used in preparing these pigments although all processes are based on the principle of precipitating hydrated iron oxide from a ferrous salt by means of an alkali, with subsequent oxidation.

The yellow iron oxides ($Fe_2O_3.H_2O$) are low in cost, have excellent opacity, excellent lightfastness, and are not affected by weak acids or alkalies. They do not possess the strength nor color intensity associated with the chrome yellows or chrome oranges.

The yellow iron oxides are used in paints where high baking temperatures are not encountered; however, they have relatively low initial gloss and poor gloss retention on exposure.

Some use is made of the yellow iron oxides in the plastics and floor covering industries. Again, because they are hydrated products, excessive temperatures limit their usage.

2. Brown Hydrated Iron Oxides

These products are made by precipitating the hydrated oxide from an iron salt solution and partially oxidizing.

The Pigments Department has manufactured two products which may be classed as brown hydrated iron oxide. The first of these, Auric Brown, F-4-P, now obsolete, was a ''special'' sold principally to the F and F Department. This was a presscake which was flushed by the customer to give a relatively transparent red shade brown which can be metallized.

Auric Brown, F-113-D, is sold as a dry pigment. Some comparable competitives include Midas Gold (available only as a dispersion) and Refined Gold (available as a dispersion and a mix-in powder). Generally, Auric Brown is considered to be a paint pigment, although some use has been made in vinyl floor covering. Ordinarily, F-113-D is not recommended for vinyl applications because of the degradative effect of iron on the polymer.

3. Red Iron Oxide

The red iron oxides are made by calcining copperas ($FeSO_4.7H_2O$), precipitated hydrated ferric oxide or precipitated black iron oxide. They vary in hue from light red to dark red and are used in paints, plastic, and rubber. They have high opacity but are relatively low in chroma and tinting strength. They are much more stable to heat than yellow iron oxides and,hence, have wider applications in plastic systems.

In paints, they have low initial gloss and poor gloss retention. They chalk to a considerable extent on exposure.

4. Venetian Reds

The Venetian Reds are usually calcium sulfate base iron oxide pigments. They are manufactured by calcining a mixture of iron sulfate and hydrated calcium oxide which results in the simultaneous formation of red iron oxide and anhydrous calcium sulfate. These pigments vary from light to dark and are used principally in barn paints.

5. Precipitated Black Iron Oxide

Pure black iron oxide is a precipitated ferro-ferric oxide (Fe_3O_4). It is used primarily in metal protective paints. It produces tough, non-porous, elastic films of excellent durability. It can be used in combination with zinc chromate or red lead in long-life paints suited for the protection of steel structures and equipment.

6. Chromium Oxide

Chromium oxide is manufactured by roasting potassium or sodium bichromate in a kiln with a reducing agent or in a reducing atmosphere. By analysis, this product is 97 to 99.5% Cr_2O_3.

Chromium oxide is available in only a very limited shade range, has low chroma and low tinting strength. It is, however, very lightfast and heat-stable and resists both acids and alkalies.

Although its color tends to limit its use, chromium oxide is used in paints where ultimate durability and not color is the controlling factor. It also is used in some printing ink applications where lightfastness and alkali resistance are of prime importance.

Rather wide usage is made of Cr_2O_3 in rubber because of heat stability (it stands any type of cure), lightfastness, and the fact that it does not cause rubber to embrittle. These pigments are also used in plastic systems where high processing temperatures are encountered.

7. Hydrated Chromium Oxide (Guignet's Green)

This pigment is made by calcining a bichromate compound with boric acid and hydrolyzing the fused mass while it is being washed. The reactions may be written as follows:

$$2Na_2Cr_2O_7 + 32H_3BO_3 \rightarrow 2Cr_2(B_4O_7)_3 + 2Na_2B_4O_7 + 48H_2O + 3O_2$$

$$Cr_2(B_4O_7)_3 + 20H_2O \rightarrow Cr_2O(OH)_4 + 12H_3BO_3$$

This pigment is more intense than chromium oxide and is almost as fast to light.

LPH 0072468

Being a hydrated product, it is not as heat-stable as the chromium oxide. It is alkali resistant but it is several times more expensive than the chromium oxide. Use is limited to certain transparent lacquers.

8. Red Lead

Red lead is trilead tetroxide (Pb_3O_4). Commercial products contain some litharge (PbO). Common grades of red lead have from 85 to 98% Pb_3O_4.

Red lead is manufactured by heating litharge (PbO) in a reverberatory furnace in an oxidizing atmosphere. The heating time controls the degree of conversion of PbO to Pb_3O_4.

Use of red lead is confined mainly to protective priming paints. The color itself is not light stable and on exposure will go to a white or a pink.

The remaining oxides- orange mineral, cuprous oxide, and mercuric oxide - are of only limited interest. Orange mineral has the same composition as red lead (Pb_3O_4) but has a higher Pb_3O_4 content (above 95%). Cuprous oxide is used in antifouling marine paints for both steel and wood. It is also used as a fungicide and in some ceramic applications. Mercuric oxide finds very limited use in marine paints and then usually in combination with cuprous oxide.

PHOSPHATE AND SILICATE PIGMENTS

1. Phosphate Pigments

The best known of the phosphate pigments is Mineral Violet, which is also known as manganese violet, Permanent Violet or Nurnberg Violet. It is a manganese ammonium phosphate having the following formula:

$$(NH_4)_2MnO_2(P_2O_7)_2$$

It is used as a toning agent in paint and some plastic systems. It is relatively hard to disperse, very weak, relatively transparent and sensitive to alkalies. "Monastral" Violet has displace this pigment to a marked extent.

Another phosphate type pigment manufactured and sold by the Pigments Department is Film Fortifier, A-133-D, which is an iron pyrophosphate. This material is essentially colorless and in baked alkyd systems shows definite film fortification. One major disadvantage of A-133-D is that it retards drying in air-dried systems and is not recommended, therefore, for such applications.

2. Silicate Pigments

The only pigment type in the silicate group is ultramarine blue which is manufactured by calcining mixtures of china, clay, silicate, soda ash, sodium sulfate, sulfur, and a reducing agent, such as wood, charcoal pitch, or rosin in fire clay crucibles or muffles in the absence of air. The color is believed to be due to sulfur trapped in cavities of the alumino-silicate lattice.

The composition of ultramarine blue pigments is as follows:

	Percent
SiO_2	37-50
Al_2O_3	23-29
Na_2O	19-23
S	10-14
Balance	1-2

The ultramarine blues have very high color intensity and vary from a greenish-blue (low silicate) to a reddish-blue (high silicate) not mateched with any other pigment or pigment combination. They have low opacity and tinting strength, and are sensitive to acids. These products show varying degree of lightfastness, depending upon the system in which they are used. In paint, they generally show a distinct fade at low concentrations. In vinyl systems, however, the ultramarine blues at low concentrations sometimes outperform the phthalocyanines. Because of their heat stability, they are also used in such plastics as polystyrene, polyethylene, polyesters, and phenolics.

AFFALIR© FLAKE PIGMENTS

Afflair© is the trade name applied to a type of colored, nacreous flake pigment . The Afflair© pigments are chemical and heat-resistant, non-bleeding, non-migrating, noncrocking, and have excellent lightfastness. The pigments also disperse readily in most systems, usually by simple mix-in techniques. The products are presently offered as a sparkling off-white powder exhibiting pronounced color effects which are produced by light interference rather than by the conventional color absorption.

The Afflair© pigments are composed of non-opaque platelets upon both surfaces of which is coated a thin, adherent, translucent layer of a metal oxide (titanium dioxide). Variation in the thickness of this metal oxide coating changes the optical thickness, thereby changing the interference color ranging from silver through gold, red, blue to green. This interference color can also be supplemented with an absorption color. For example, the deposition of chromium or iron with the titania produces a deep gold pigment. Currently, there are five colors of Afflair© pigments being produced: Pearl, Gold, Deep Gold, Green and Blue.

The individual particles of Afflair© are flat platelets with irregularly shaped peripheries. Thickness of the platelets is in the range of 0.1 to 3 microns, while the flat surface is 5 to 40 microns. The most suitable flake substrate is water ground muscovite mica having a specific surface in the range of 2 to 7 square meters per gram.

The titania coating is applied by adding an acidic solution of titania to a water slurry of mica flakes and boiling this mixture to hydrolyze the titania on the mica surface. The final product is filtered, washed, and calcined in air at

950°C. to develop the necessary high refractive index (2.5) and the light stability of anhydrous titania. The calcined flakes are then air-classified into the desired size fraction. The final products find application in cosmetics, paint, plastics,and ink systems.

AFFLAIR® MANUFACTURE

Afflair® manufacture consists of five unit operations including hydrolysis, filtration, calcination, air classification and blending.

The process is a batch operation for the hydrolysis and filtration steps, continuous for the calcination and air classification steps, and batch for the product blending step.

All facilities are at Newport, except for the calcination step which is at the Edge Moor plant.

1. Hydrolysis

The equipment used in the hydrolysis step consists of a titanium sulfate concentrate (obtained from Glidden/Durkee or NL Industries sulfate TiO_2 process), solution storage tank, a mix tank, head or measuring tank, and the hydrolysis tank. All tanks have been designed to handle sulfuric acid, and are equipped with heating coils (except the mix tank) and agitators. Centrifugal pumps are used to transfer solutions from one tank to another.

Hydrolysis is generally carried out by adding mica to water in the hydrolysis tank and bringing the vessel to a prescribed temperature. Only water-ground mica has been used in Afflair® manufacture.

A measured volume of titanium concentrate is pumped to the head tank and brought to a specified temperature. The strike is made by adding the concentrate to the agitated mica slurry and immediately heating the solution to the boil at a fixed rate.

The hydrolysis slurry is held for three hours and then quenched to 60°C by the rapid addition of cold water.

2. Filtration

Two wood presses fed by one of the transfer centrifugal pumps via plastic (acid proof) pipe, and a facility to charge 55-gal. drums with water-washed presscake comprise the filtration facilities.

The cool hydrolysis slurry is transferred to the two presses in approximately three hours. No filtration problems are encountered, and the filled presses are washed with cold water to a prescribed level of conductivity in the filtrate.

The presses are air blown to reduce the moisture content. The discharged presscake ranges from 55 to 65% solids when properly pressed and air blown.

The presscake is charged to 55-gal. drums and shipped to Edge Moor for calcination. If improper pressing and air blowing occur, free water is noted in the drum at Edge Moor and affects that operation .

3. Calcination

The calcination equipment consists of a presscake feed station, the kiln and a hot kiln discharge station. The auxiliary equipment includes a stack recycle system (to minimize losses and avoid air pollution).

Presscake is fed to the kiln at the rate of 140 lbs/15 min. interval. The kiln temperature is adjusted by inspection of product samples against standard. The normal calcination temperature is 950°C.

4. Air Classification

The classification equipment consists of a feed hopper to the mikro-pulverizer, a ''Hurricane'' air classifier, an air cyclone and finally a Pulse-aire bag filter unit.

Three principal products are obtained. The ''21s'', the coarse product from the ''Hurricane''; the ''11s'', the coarse product from the air cyclone; and the ''31s'', the dust from the air filter unit. The ''21s'' are normally recycled through the mikropulverizer and the three fractions are then called ''26s'', ''16s'', and ''36s'', respectively.

All of the above fractions are drummed out in fiber drums (approximately 100 lbs. net) and identified.

5. Blending

The blending facility consists of a Patterson double cone blender with loading and unloading facilities and a drumout station with scales.

Lots are blended by dividing the various numbered classified drums into groups up to 2400 lbs. The composition is predetermined by laboratory testing using a plant standard for each grade.

The lots produced are identified by date, Afflair® type, lot number and part number (first, second, third blend).

Present commercial grades of Afflair® are:

NF-103 Gold	NF-144 Coating Gold
104 Pearl	145 Green
108 Pearl	146 Autopearl
109 Pearl	148 Autogold
134 Pearl	149 Blue
135 Satin	152 Flash
137 Pearl	154 Pearl
138 Pearl	155 Satin
139 Gold	157 Ultraluster Deep Gold
140 Deep Gold	158 Ultra Hi-Luster Satin
142 Glimmer	
143 Coating Pearl	

Grades formerly made and/or not commercial at present include:

1. NF-105-D, Deep Gold
2. NF-106-D, Large Flake
3. NF-113-D, Automotive Gold
4. NF-123-D, Satin
5. NF-128-D, Dark Gold Automotive
6. NF-129-D, Silver Automotive
7. NF-132-D, Gold Automotive
8. NF-133-D, Deep Gold (Heavy Metal-Free)
9. NF-156-D, Glimmer

$$TiO^{++} + SO_4^{=} + H_2O \xrightarrow[20\%\ H_2SO_4]{90^\circ C} \underset{12\%\ occluded\ TiOSO_4}{TiO_2\ (gel)} + H_2SO_4$$

$$SnCl_4 \cdot 5H_2O \xrightarrow[H_2O]{90^\circ C} SnO_2\ gel + 4HCl + 3H_2O$$

BIBLIOGRAPHY

1. KN-61-4
2. PT-KN-62-3 (NF-103-D and NF-104-D)
3. PT-KN-63-16
4. PT-KN-64-2
5. PT-KN-64-4
6. KN-64-13 (NF-106-D)
7. PT-KN-64-24 Pearl
8. KN-67-2 (NF-128-D)
9. Information circular, Bureau of Mines No. 8125, "Mica---A Material Survey", Milford L. Skow, 1962.

Genl Inorganics - Revised by B. H. Perkins - 1975
Afflair® - Revised by O. E. Ringwald - 1975
Organic - Revised by E. E. Jaffe - 1975

KROLOR® PIGMENTS

Krolor® is the trade name applied to a group of lead chromate pigments that have been coated with an inert skin which imparts greater chemical resistance, heat stability, and lightfastness to the lead chromate. Specifically, the coating is primarily silica, applied by adding to a water slurry of the pigment, a dilute solution of sodium silicate and sulfuric acid. The addition is carried out over a prolonged period of time at elevated temperatures (90°C) and under alkaline conditions. To develop the best pigment properties, the starting pigment must be well dispersed. This is achieved by passing the slurry through a homogenizer.

However, at present it appears that 20% silica is needed for multi-purpose Krolor® codes (plastics and automotive finishes) with the exception of KO-786-D which contains 16% silica. Listed below are the current Krolor® codes and pertinent information concerning manufacture.

Base*	Krolor® Code	Color	SAA	% Silica	End Use
Y-434-D (YC-3)	KY-781-D	Light Yellow	-	20	Plastics
Y-434-D (YC-3)	KY-788-D	Light Yellow	10% CaSx	13	Plastics, alkyd finishes
Y-469-D (YC-2)	KY-795-D	Medium Yellow	1% Emery-Igepal	20	Automotive finishes
Y-469-D (YC-2)	KY-787-D	Medium Yellow	10% CaSx	20	Alkyd finishes plastics
YE-698-D	KO-777-D	Red-shade Molybdate Orange	-	5	Plastics
YE-698-D	KO-786-D	Red-shade Molybdate Orange	-	16	Plastics, automotive and alkyd finishes
YE-421-D (YC-1)	KO-789-D	Yellow-shade Molybdate Orange	1% Emery-Igepal	20	Plastics, automotive and alkyd finishes

*No surfactant on base - given YC code No.

The first two codes developed (KY-781-D and KO-777-D) were strictly plastics codes. Extension of the line to all colors including primrose is now complete and Krolor® is used in alkyd and automotive finishes as well as plastics. It affords better chemical resistance than the base and gloss levels are very close to those of the base at the same P/B. KO-786-D, KO-789-D, and KY-795-D are the primary automotive codes and are "humidity resistant".

The above mentioned Krolor® codes are used in high temperature plastics (polystyrene, polyethylene, etc.) where they undergo considerably less darkening than the conventional chrome yellow and molybdate orange pigments when processed over the temperature range 400-600°F. All products achieve excellent heat stability even when subjected to abrasive action while in a dry state such as may be experienced during long, dry blending cycles.

KROLOR® MANUFACTURE

Krolor© manufacture involves several batch operations including the dispersion of an aqueous slurry of the substrate (chrome yellow or molybdate orange), deposition of a silica coating, filtration, drying, pulverization and blending, if needed. All of the facilities are located at the Newark Plant.

1. Dispersion

Dispersion of the starting pigment, prior to silica coating, is accomplished by homogenization. In each case, the starting pigment is slurried in water and a small amount of sodium silicate added to aid dispersion. The slurry is then pumped through a Manton-Gaulin homogenizer, first at a 2000 psi pressure drop and then a 5000 psi pressure drop into the strike vat.

2. Coating

After heating the homogenized slurry to 95°C., the silica coating is deposited by simultaneously adding (two metering pumps with a single motor are used) dilute sodium silicate solution and dilute H_2SO_4 solution over a four hour period. Following the silica addition, there is a pH adjustment and, for some products, a surfactant treatment.

3. Filtration, Washing, and Drying

Following coating, the slurry is pumped into a plate and frame filter press and then washed to 2000 or more ohms. The presscake is loaded onto dryer pans and dried (roughly 16 hrs.) in a forced air dryer at 220°F.

4. Pulverization

After drying, the products are mikropulverized at high speed (3555 rpm) using standard hammer mills. In each case, the product is packed out in 50 lb. bags.

ORGANIC PIGMENTS

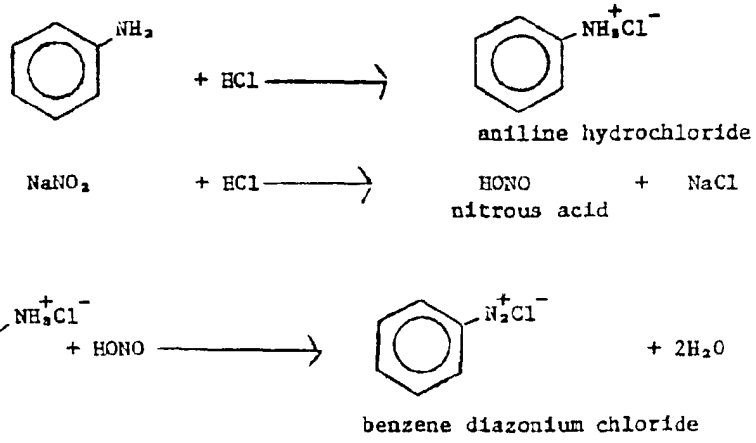
The large, diverse group of organic pigments may be classified into two large classes, namely, the azo and non-azo pigments. Representative pigment types in each of these classes, with appropriate subdivisions, are described. It is not intended that the listing be complete.

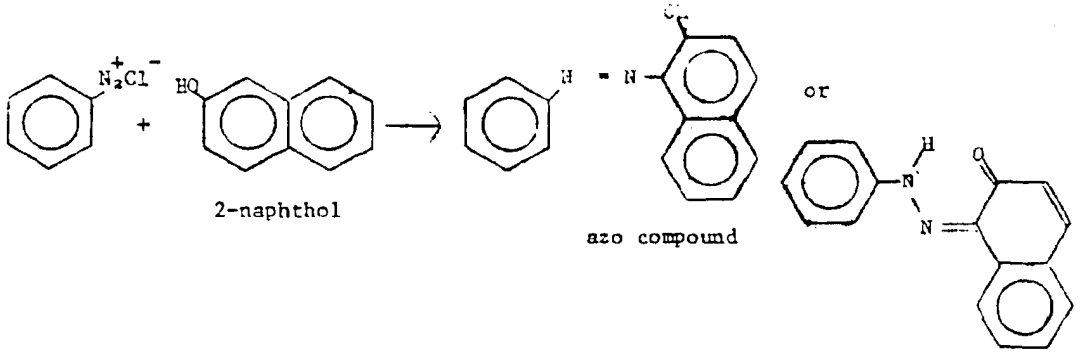
AZO ORGANIC PIGMENTS

The azo compounds have contributed more products to the pigment industry than any other chemical type, due in large part to the diversity of the chemical raw materials which can be utilized, the simplicity and flexibility of manufacture, and low cost. These considerations permit the preparation of products of varied type and color, with a variety of chemical and physical properties which extend their use into practically all areas of pigment application.

Azos are formed by the successive chemical processes of diazotization and coupling. A primary aromatic amine, usually referred to as the first component, is dissolved or suspended in a dilute mineral acid and sodium nitrite is added whereby the nitrous acid formed reacts (diazotization) with the amine to give the diazonium salt. The reaction is usually run at low temperatures. The coupling is effected by reacting a solution or suspension of the second component directly with the diazonium salt without isolating the latter. Second components include such chemical types as β-naphthol, arylides (arylamides) of 3-hydroxy-2-naphthoic acid (also referred to as beta-hydroxynaphthoic acid or BON), arylides of acetoacetic acid, and pyrazolone derivatives. The specific conditions of temperature, pH, rates of addition, presence of auxiliary agents, and even agitation, can appreciably affect the tinctorial and other pigmentary properties of the product.

The series of reactions to form an azo compound can be represented as follows using aniline as the first component and 2-naphthol as the second component.





Controversy still surrounds the structure of the azo coupling product shown above. Recent evidence supports the keto hydrazone structure, particularly in the solid state. Azo pigments contain one (monoazo) or two (disazo) chromophore groups and are subdivided for convenience into two types, viz., ordinary pigments and the precipitated azo pigments. The former include those products which are insoluble in the aqueous reaction medium directly on formation, and hence require no metal or other means to effect precipitation. The precipitated azo pigments include those products which contain salt forming groups, principally sulfonic acid or carboxylic acid, which are precipitated by being rendered insoluble by the use of metal salts. The salts most commonly used include those of calcium, barium, strontium, and manganese.

LPH 0072478

The generalized properties which characterize each of these two types of azo pigments are as follows:

Pigment Dyes	Precipitated Azos
1. Some solubility in organic solvents and vehicles. Poor bleed resistance.	1. Good to excellent bleed resistance.
2. Good acid and alkali resistance.	2. Poor acid and alkali resistance.
3. Good lightfastness in deeper shades. Poor tint lightfastness.	3. Fair to very good lightfastness in deeper shades. Poor tint lightfastness.

Included in the category of pigment dyes are such products as toluidine red, the para reds, arylide reds and maroons, and the Hansa and benzidine yellows. Among the precipitated pigments are lithol red, lithol maroon, lithol rubine, lake red C, pigment scarlet, and azo bordeaux.

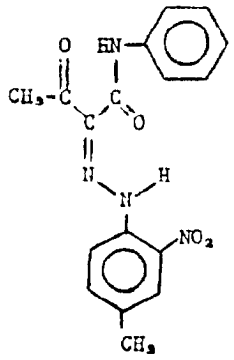
REPRESENTATIVE AZO PIGMENTS BY COLOR GROUPS

1. Azo Yellows

Reference to azo yellows is a misnomer since recent evidence supports hydrazone rather than azo structures for these pigments. However, the designation "azo" for pigments of this and similar types is associated with a long tradition and will be continued in this manual.

a. Toluidine Yellows*

Two important yellow pigments are the Toluidine yellows and the benzidine yellows, the former being monoazo pigments and the latter disazos. The following is a representative Toluidine yellow.



*Frequently referred to as "Hansa" Yellows

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The Toluidine yellows have been prepared in red to green shades and some of the more commercially important are formed by the couplings shown below, in the order of increasing greenness:

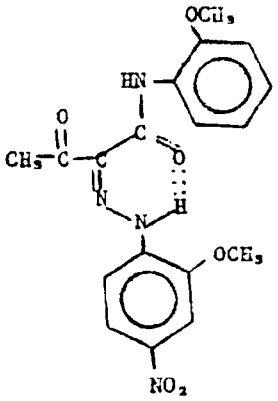
Toluidine Yellow

R	2,5-dichloroaniline	3-methyl-1-phenyl-5-pyrazolone
GR	4-chloro-2-nitroaniline	acetoacet-m-xylidide
G	2-nitro-p-toluidine	acetoacetanilide
3G	4-chloro-2-nitroaniline	acetoacetanilide
5G	2-nitroaniline	acetoacetanilide
10G	4-chloro-2-nitroaniline	o-chloroacetoacetanilide

The Toluidine yellows are bright pigments with high tinting strength, which show good lightfastness in dark shades (masstone) but poor tint lightfastness. Toluidine Yellow G is particularly lightfast in masstone. They are relatively transparent (semi-opaque) and, therefore, find little use where opacity or high hiding power is required. Although they bleed in most paint solvents, they show good chemical resistance to alkali and acid. The Toluidines are relatively sensitive to heat and show high oil absorption. The tinctorial strength of the Toluidine Yellows is less than that of the benzidine yellows but greater than the inorganic chrome yellows. The latter, however, exhibit greater hiding power. The Toluidine yellows find extensive use in emulsion paints, paper coating compositions, linoleum and in toy enamels where non-toxic, lead-free pigments must be used.

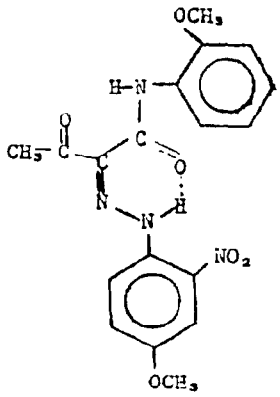
b. Dalamar® Azo Yellows

The coupling product derived from diazotized 2-amino-5-nitroanisole and acetoacet-o-anisidide is a greenish shade yellow of relatively poor tint lightfastness but high extinction coefficient, being almost twice the strength of ordinary monoazo pigments of equal particle size.



On deliberate growing of very small particle size pigment to an average particle size (calc. from specific surface) of about 0.4µm, a redder, substantially weaker but more opaque yellow pigment is obtained which shows excellent outdoor durability in aqueous emulsion paints and alkyd trim systems. Like most monoazo pigments it shows relatively poor bleed resistance.

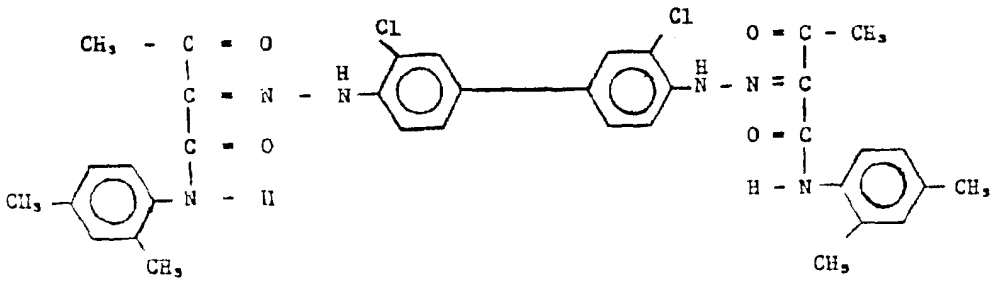
A still redder shade yellow which is a considerably weaker pigment at comparable particle size is an isomer of the following structure.



This pigment also finds application in aqueous emulsion paints.

C. Benzidine Yellows

The formula for a typical benzidine yellow is as follows:



Benzidine Yellow GR

The same chemistry is involved as with the Toluidine yellows except that the first component amine, benzidine or a benzidine derivative, has two amino groups, each of which is diazotized to give the diazonium salt grouping, the resulting compound being referred to as a tetrazonium salt. The latter then couples with two molecules of the second component to give the disazo benzidine yellow.

Some typical benzidine yellow couplings are as follows:

1st Component	2nd Component[1]
3,3'-dichlorobenzidine	acetoacetanilide
3,3'-dichlorobenzidine	acetoacet-m-xylidide
3,3'-dichlorobenzidine	acetoacet-o-toluidide
3,3'-dichlorobenzidine	acetoacet-o-anisidide

[1]Two moles used

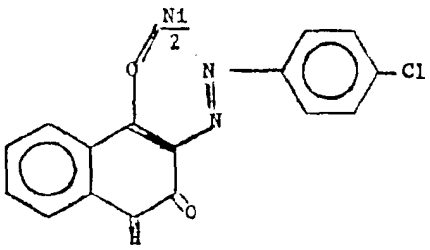
Other first component amines which are employed in benzidine yellow manufacture include dianisidine and toluidine.

Generally, the bright benzidine yellows offer greater tinctorial strength than do the Toluidine yellows, in addition to superior bleed and heat resistance. They exhibit minimum bleed in alcohol, water, and paraffin wax. They are generally inferior in lightfastness to the Toluidine yellows though they show good lightfastness in dark shades, but poor tint lightfastness. They exhibit good chemical and bake resistance, but also low hiding and high oil absorption, when the pigments are optimized for strength by virtue of small particle size.

D. Nickel Azo Yellow (''Green-Gold'')

This greenish-yellow, chelated nickel azo pigment of relatively recent

development is superior in permanence to any other azo yellow pigment, offering excellent lightfastness in masstone (dark shades), tint and metallic formulations, together with good bake resistance. This pigment shows lightfastness in tints up to the phthalocyanine pigment standards. The product is the nickel chelate of the azo dye derived from the coupling of diazotized p-chloroaniline and 2,4-dihydroxy-quinoline.

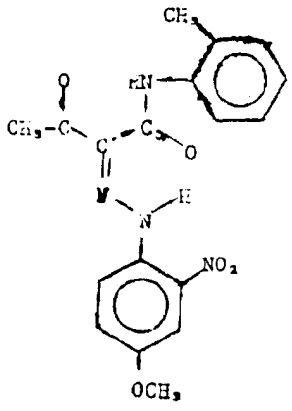


Nickel Azo Yellow

The nickel in this compound forms coordinate bonds with the azo nitrogens of two ligand molecules. Although good in chemical resistance, it is subject to dematallization under highly acid or alkaline conditions resulting in color drift, poorer lightfastness, and solvent-bleed. The pigment shows excellent transparency, which together with its superior durability has resulted in its wide acceptance by the automotive finishes industry.

2. Azo Oranges

a. Azo Orange

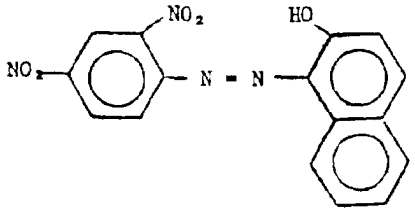


Azo Orange

LPH 0072483

Azo orange (Orange 3G) is an intense, high strength color of good lightfastness in dark shades and good chemical resistance. When prepared in small particle size, it is low in hiding power and shows poor tint lightfastness. The pigment shows poor bleed-resistance, and is sensitive to heat.

b. Dinitraniline Orange

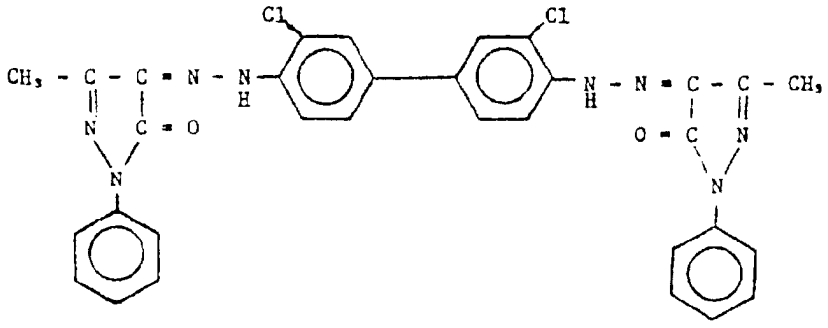


Dinitraniline Orange

Dinitraniline orange is prepared by coupling diazotized 2,4-dinitroaniline with β-naphthol. It is a bright, high strength pigment, superior in the latter respect to the inorganic molybdate orange which it approximates in masstone shade. It is low in hiding and shows good lightfastness in dark shades but poor tint lightfastness. Although good in chemical resistance, it has poor bleed resistance and only fair bake resistance.

c. Benzidine Orange

Benzidine orange is a disazo pigment prepared by coupling tetrazotized 3,3'-dichlorobenzidine with two moles of 1-phenyl-3-methyl-5-pyrazolone.

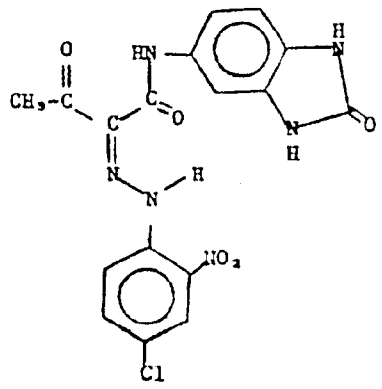


Benzidine Orange

When prepared in small particle size, it is a bright, intense color of high strength with good lightfastness in dark shades but poor tint lightfastness. It has good bake and chemical resistance, but is low in hiding, and shows only fair bleed resistance.

d. Benzimidazolone Orange HL

Azo pigments of much improved bleed resistance and lightfastness properties are derived from acetoacetarylides, which are in turn synthesized from 5-aminobenzimidazolone. Orange HL is an orange of the following structure:

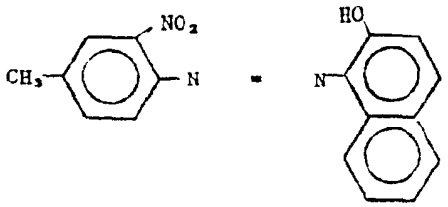


3. Azo Reds and Maroons

a. Toluidine Reds

Toluidine red prepared from diazotized 2-nitro-4-methyl aniline coupled to β-naphthol is one of the most popular red pigments for industrial enamels. This high color intensity azo pigment shows excellent masstone (dark shades) lightfastness but poor tint lightfastness. It exhibits good bake and chemical resistance and good hiding power, but shows poor bleed resistance in many solvents. It produces enamels of excellent film durability. Toluidine reds of several different shades

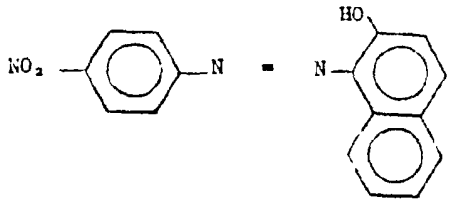
are available. Although widely used, toluidine red is being displaced by other, more bleed-free reds.



Toluidine Red

b. Para Red

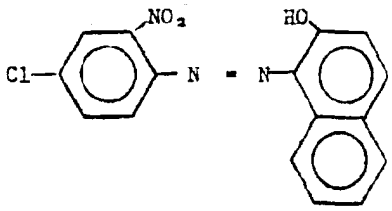
Para Red is a low cost, bright red offering good hiding and chemical resistance. Lightfastness, especially in tints, is poor, as is the bleed and bake resistance. The para reds are darker and bluer than the toluidine reds, and are less lightfast. They are made by coupling diazotized 4-nitroaniline with β-naphthol.



Two types of para red are in use, the lighter and yellower para Y, and the darker and bluer para B. The latter is obtained by substituting a portion of the β-naphthol with an accessory agent. The prior usage of the para reds is in industrial finishes, but their overall use is limited by their poor bleed resistance.

c. Chlorinated Para Reds

There are two different chemical types of chlorinated para red, one prepared by the coupling of diazotized 2-chloro-4-nitroaniline with β-naphthol and the second which uses the 4-chloro-2-nitroaniline as the first component and which is shown below.

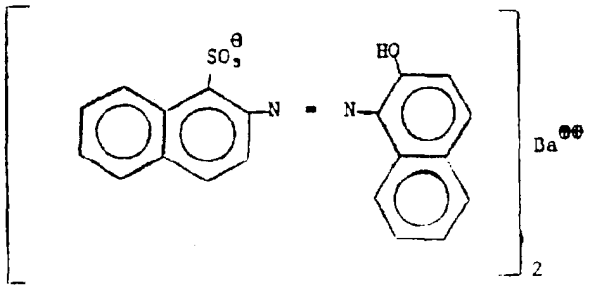


Parachlor Red

The chlorinated para reds are bright, very light yellowish reds, almost orange, pigments. The parachlor red is significantly superior in both tint and masstone lightfastness to the 2-chloro-4-nitroaniline product, being excellent in dark to medium shades and good in light shades. It is more transparent than the 2-chloro isomer which shows good hiding. These properties vary as a function of particle size. Both isomers exhibit poor bleed and bake resistance. Parachlor red has good chemical resistance and is probably one of the most lightfast azo pigments.

d. Lithol Reds

The lithol reds (Lithol Red R) are among the more important of the precipitated azo pigment dyes. They comprise a family of the metal salts (sodium, barium, calcium, strontium) of the coupling product from diazotized Tobias acid (2-naphthylamine-1-sulfonic acid) and β-naphthol. Bright reds of increasingly darker shades are obtained by using the metals in the order shown above, the barium and calcium being the most popular. The barium pigment is shown below.



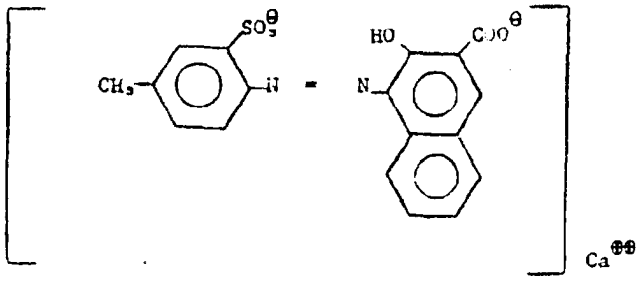
The lithol reds are used widely where brightness, hiding power, bleed resistance, and low cost are of primary importance. They are generally poor in lightfastness and are not satisfactory for outdoor use. As typical precipitated azo dyes, they show poor chemical resistance. Bake resistance is also poor.

The lithol reds are the most economical of the organic red and maroon pigments and find wide application where good durability is not required.

e. BON Reds and Maroons

The BON red and maroons derive their name from the use of beta-hydroxynaphthoic acid (BON) as the second component in the coupling of the various diazotized amines containing salt forming groups. Insolubilization is obtained by the use of such metal ions as calcium, barium, or manganese to give pigments varying from a toluidine red shade to a dark maroon.

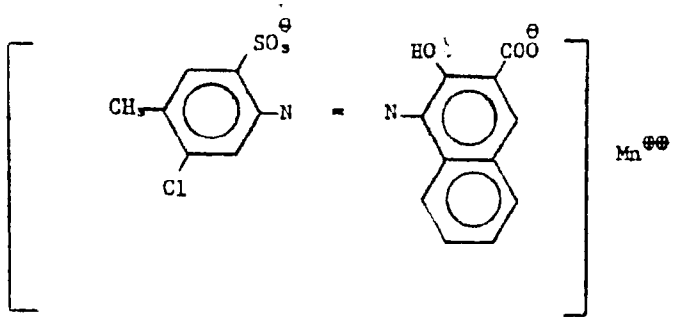
i. Lithol Rubine is the calcium salt of diazotized 4-aminotoluene-3-sulfonic acid coupled to beta-hydroxynaphthoic acid. It is a dark red and is usually resinated to enhance the brilliance and depth of color. Lithol rubine shows good bleed and bake resistance but poor alkali and soap resistance. Although it has relatively poor lightfastness, it produces in blends with molybdate orange a wide range of bright shades suitable for interior industrial enamels. As a self-color, it is used where a high degree of exterior durability is not required.



ii. Permanent Red 2B

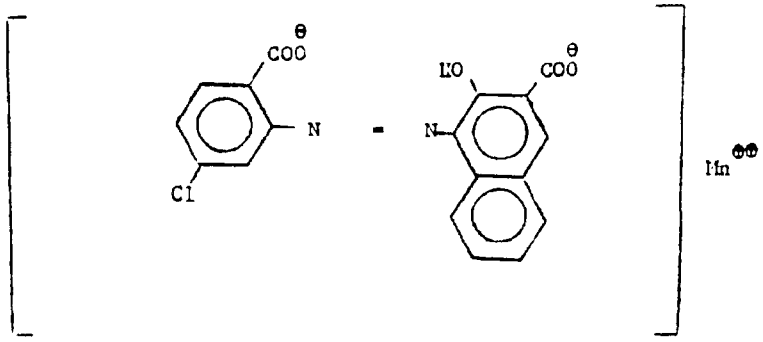
The calcium, strontium or barium precipitated salts of the coupling product from diazotized 2-chloro-4-aminotoluene-5-sulfonic acid with beta-hydroxy-naphthoic acid are bright pigments which exhibit excellent bleed and bake resistance, but which are poor in chemical resistance and in lightfastness.

The manganese salt (manganese BON red) has significantly better masstone lightfastness and is used in automotive and other high quality industrial enamels where durability is a prime consideration. It exhibits good bleed resistance but only fair bake resistance. Poor lightfastness and chemical resistance is obtained in tints. The manganese BON reds can be blended with molybdate orange to give a wide hue range of intense, durable reds.

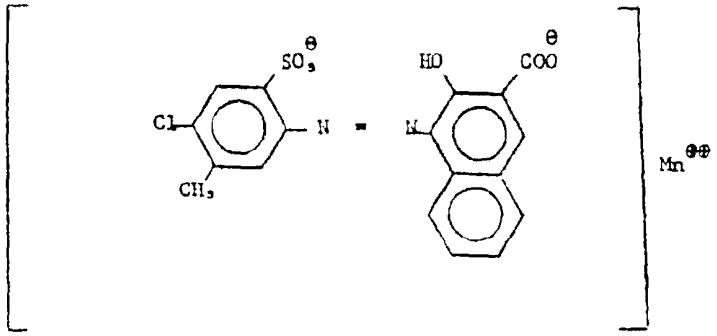


iii. Yellow BON Maroon

The manganese salt of the coupling product from diazotized 4-chloroanthranilic acid with beta-hydroxynaphthoic acid gives a lightfast yellow-shade maroon with superior solvent-bleed-resistance suitable for automotive use or other outdoor finishes. It shows a tendency to change color on baking.



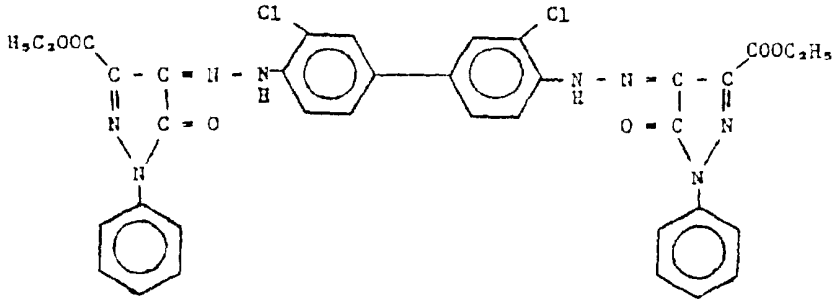
iv. Lithol Red 2G is prepared from the coupling of diazotized 2-chloro-5-aminotoluene-4-sulfonic acid with beta-hydroxynaphthoic acid as the second component.



It is a color of considerable brightness, and is used principally in blending with the inorganic molybdate orange to produce durable red pigments. In this application, it shows fair lightfastness, although tint lightfastness generally is poor. Solvent-bleed-resistance is good but chemical resistance, as would be expected of a precipitated azo dye, is poor. The lithol red 2G shows only fair bake resistance even in molybdate orange blends.

f. Pyrazolone Red

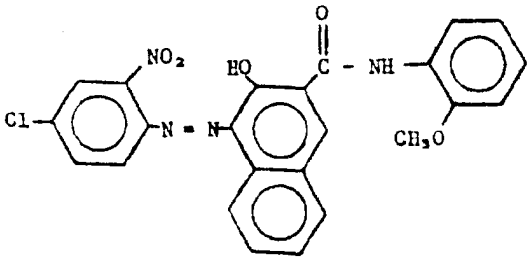
The pyrazolone reds are disazo pigments which offer high color brilliance, excellent masstone lightfastness, high transparency and good bleed, bake, and chemical resistance. They are relatively high in cost, and have poor lightfastness in tint and metallic formulations. A major use is in bicycle and motorcycle finishes.



g. Arylide and Alkali-Resistant Red and Maroon

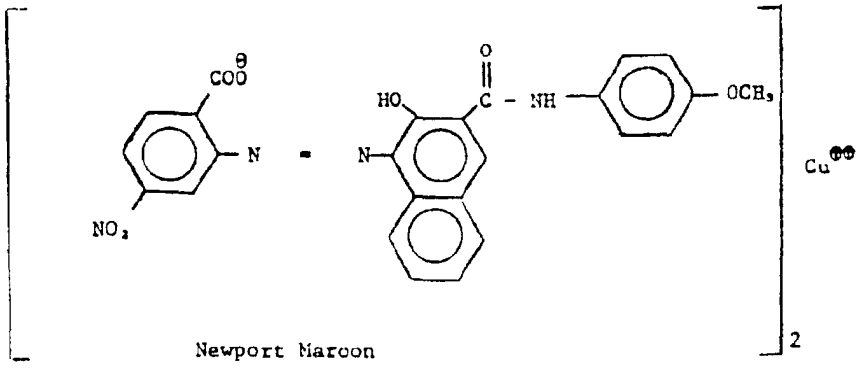
These monoazo pigments which cover a wide range of colors from light reds to dark maroons are characterized by excellent chemical resistance and good bake

resistance. They exhibit low hiding, poor lightfastness especially in tints, and poor bleed resistance. Properties of individual pigments depend on the nature and position of substituents both in the starting amine and amide as well as on particle size of the pigment.



Arylide Maroon

A relatively new maroon product (Newport Maroon) which shows very good masstone outdoor durability is based on the copper salt of the coupling product from diazotized 4-nitroanthranilic acid with Naphthanil RL as the second component.

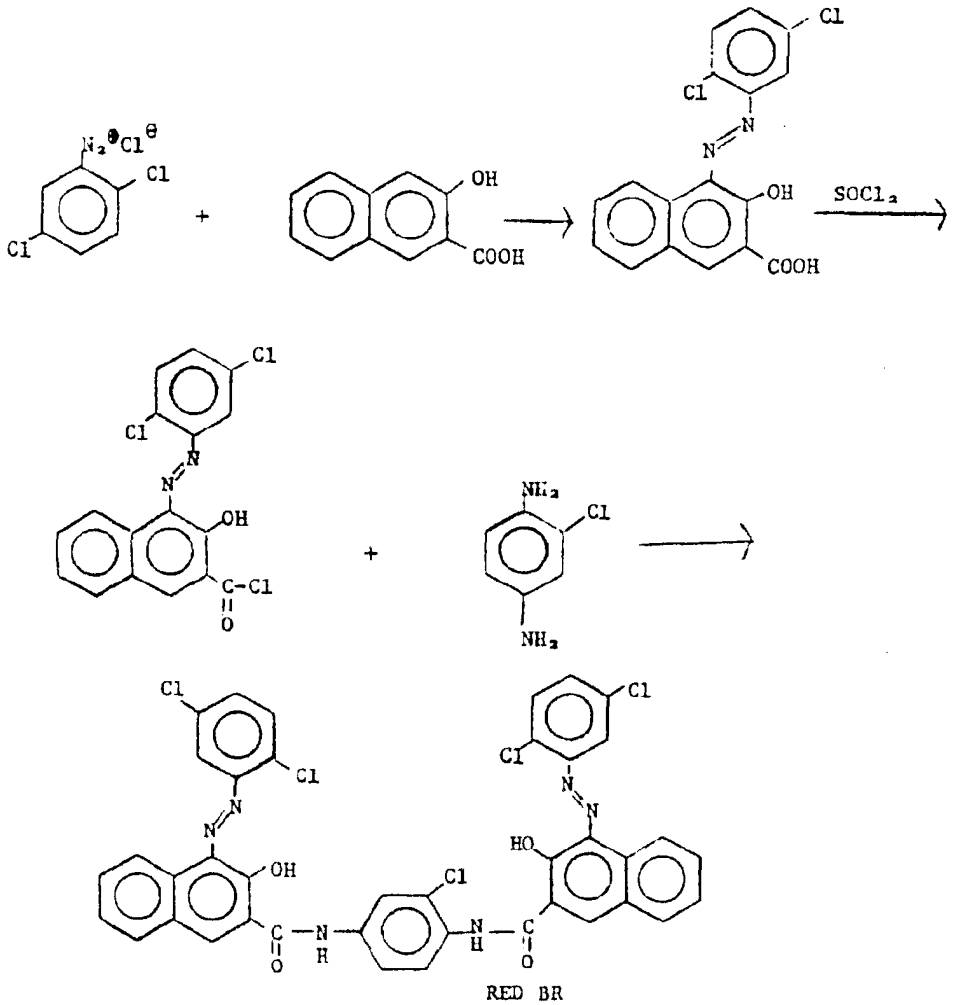


Newport Maroon

It has been used in automotive metallic enamels because of its high transparency, excellent bleed and heat resistance, and very good gloss retention on outdoor exposure.

h. Condensation Azo Reds

Disazo pigments which are not derived from coupling tetrazotized diamines with second components but are obtained by the route outlined below for the preparation of Cromophthal Red BR, are referred to as condensation azo pigments.



RED BR

A typical condensation azo pigment such as Red BR shows excellent bleed resistance, considerable strength and good outdoor durability, particularly in plastic systems.

A series of condensation azo pigments are known both in the red and yellow color range. A typical yellow pigment of similar properties is Cromophthal Yellow 3G.

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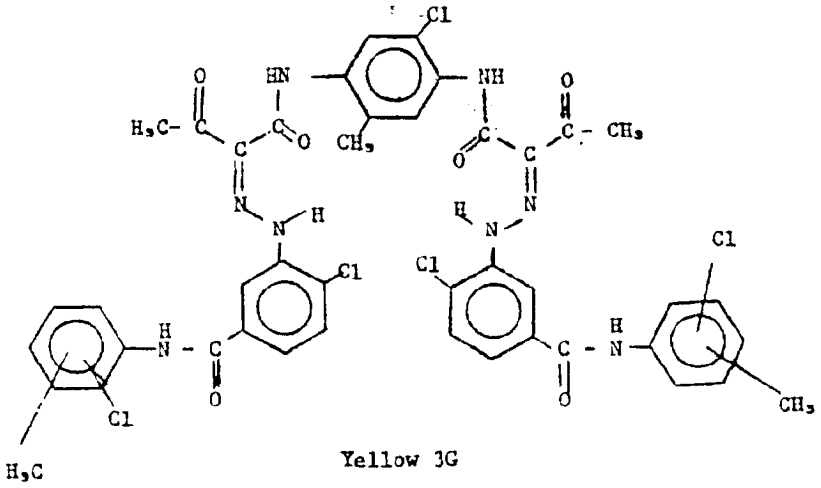


Yellow 3G

NON-AZO ORGANIC PIGMENTS

PIGMENT LAKES

In addition to the use of the term ''lake'' to describe a dry toner pigment extended or reduced with a solid diluent, the term is also used in a more restricted sense to describe an organic pigment which is prepared by the precipitation of a water-soluble dye on an adsorptive surface, usually an inorganic compound such as alumina hydrate. There is uncertainty in some instances as to whether the soluble dye is precipitated on the surface of the inorganic compound to give a ''dyed inorganic pigment'' or whether it is merely precipitated in its presence, the substrate serving no function in the insolubilization. A ''lake'' can also be formed by the precipitation of an insoluble salt from an acid or basic dyestuff. Lakes from acid dyes are usually precipitated using the soluble salts of the alkaline earth metals such as barium or calcium, whereas the basic dyes are ''laked'' by precipitation with the soluble salts of organic acids such as tannic, or with an inorganic acid such as phosphotungstic. Mordant dyes such as alizarin are ''laked'' by precipitation with the soluble salts of metals such as aluminum.

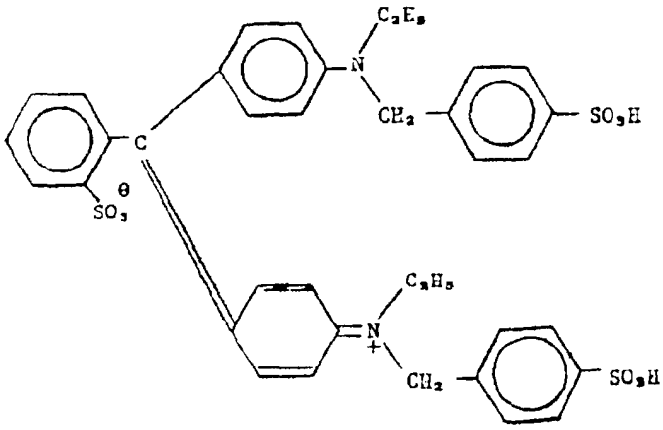
1. Acid Dye Pigment Lakes

Acid dye pigments are based on sulfonic acid derivatives of the basic dyes. The most common adsorbing substrate is aluminum hydrate, by which they are rendered insoluble.

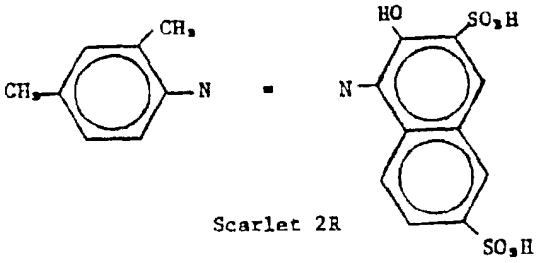
The acid dye pigment lakes are used principally in ink and paper applications and generally show the following properties:

1. High strength, intensity
2. Poor light stability
3. Comparatively poor texture
4. Tendency to react with vehicles
5. Poor bleed resistance

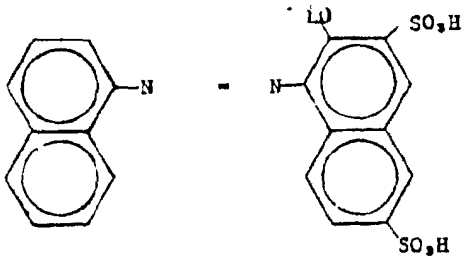
Typical dyes which can be rendered adequately insoluble with alumina hydrate to give a pigment are given below:



Peacock Blue



Scarlet 2R



Azo Bordeaux

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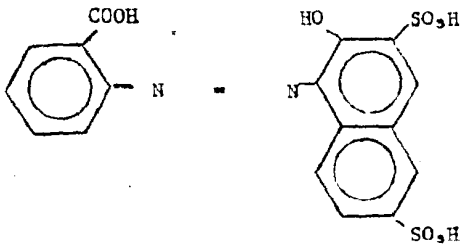
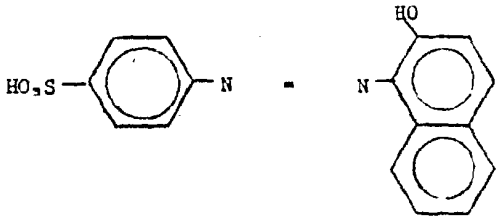
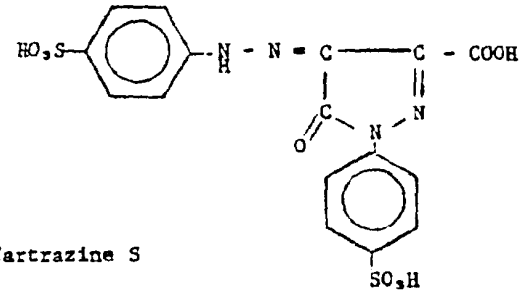


Pigment Scarlet



Orange 2



Tartrazine S

The lakes are generally prepared by adding a solution of the dissolved dye to a suspension of alumina hydrate, followed by precipitation with a metal salt solution such as barium chloride.

Peacock blue is the principal blue lake for printing ink use where light-fastness and bleed resistance are unimportant.

LPH 0072496

2. Basic Dye Pigments

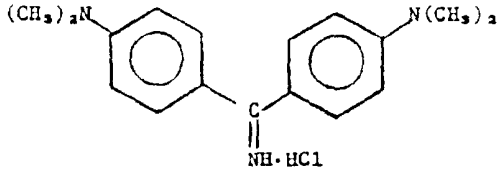
Basic dyes are characterized chemically by the presence of free or substituted amino groups in the molecule. A basic dye pigment is the precipitated product of the reaction between a basic dye and complex inorganic heteropoly acids to give the ''permanent'' type of basic dye pigment on the one hand, and with precipitants such as tannic acid, tartar emetic, clay, and fatty acid or rosin soaps to give the non-permanent or fugitive type, on the other.

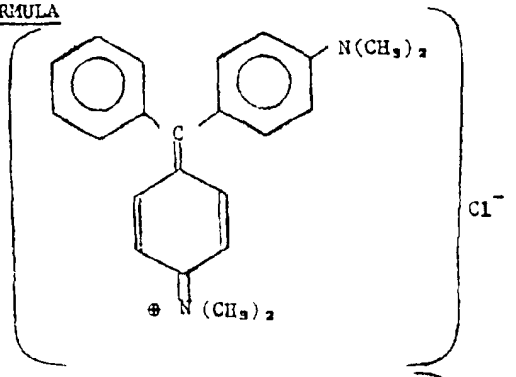
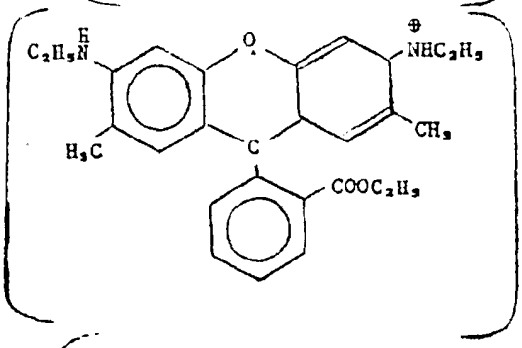
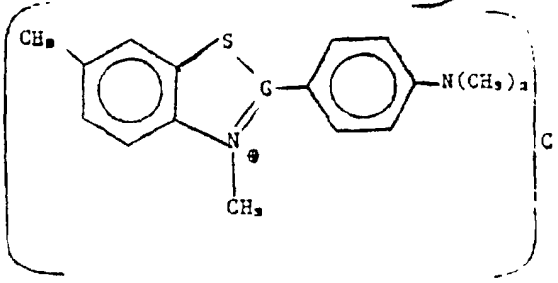
The basic dyes generally are characterized by brilliance of shade, high tinctorial strength and a relatively low level of lightfastness. The latter is materially improved by precipitation with complex phosphorous-metal acids to give pigments of interest primarily for printing inks. Acids such as phosphotungstic (PTA), phosphomolybdic (PMA), and phosphotungstomolybdic (PTMA) are used as precipitants whereby much of the inherent brilliance and strength of the basic dye is retained while imparting insolubility and good lightfastness. Generally, the PTA pigments are superior in lightfastness to the PMA's, although the latter show greater strength.

The basic dye pigment lakes are used principally in ink, paper, paint, and plastics applications and generally show the following properties:

1. High strength, intensity, transparency.
2. High cost.
3. Comparatively poor light stability, except Rhodamine Y and B, which are good in masstone but poor in tint.
4. Tendency to bleed in water and solvents.
5. Alkali-sensitivity.
6. Subject to reduction in certain vehicles such as nitrocellulose.
7. Comparatively poor texture.

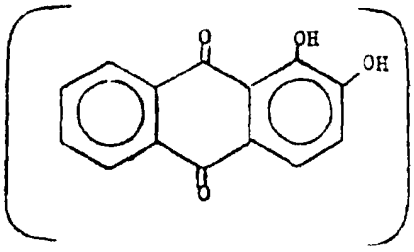
Representative basic dyes used in the pigment industry are given below:

CHEMICAL CLASS	DYE	FORMULA
Ketonimine	Auramine O	

CHEMICAL CLASS	DYE	FORMULA
Triarylmethane	Malachite Green Brilliant Green Rhoduline Blue 6G (Setoglaucine) Methyl Violet B Victoria Blue B Victoria Pure Blue BO Crystal Violet	
Xanthene	Rhodamine 6G	
Thiazine	Thioflavine T	

3. Alizarine Lakes

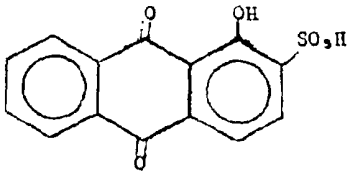
a. Alizarine Red B or madder lake is a coordination complex of alizarin with alumina and calcium plus a sulfonated castor oil and a phosphate. It is a bright, deep, bluish-red of fair lightfastness.



Al Ca Lake

LPH 0072498

b. Helio Fast Rubine 4BL, a sulfonated quinizarin derivative, finds use in the shading of pigments for organic coatings. It is a bright, transparent color with good bleed and chemical resistance but with poor tint lightfastness and bake resistance at high temperatures. The lake is formed by the reaction of the dye with alumina hydrate, probably giving rise to chelate formation. The base material has the following structure:



Helio Fast Rubine 4BL

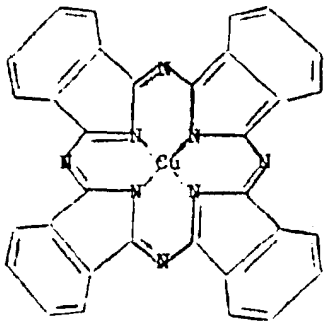
PHTHALOCYANINES

The introduction of the phthalocyanine pigments in 1935 set new standards of excellence in the pigment-consuming industries. They come close to the ideal pigment, being distinguished by their excellent lightfastness, brilliance, bleed and chemical resistance, extreme stability to heat, and exceptionally high tinting strength. The phthalocyanine pigments are restricted to the blue and green regions of the spectrum.

Phthalocyanine pigments are prepared as metal complexes (usually copper) or as metal-free varieties. The metal-free blue is much greener, and the metal-free green is much yellower than their copper-complexed counterparts; the copper phthalocyanines are significantly more lightfast than the metal-free counterparts.

Complexing of the phthalocyanine with metals other than copper (e.g., nickel, iron, aluminum, etc.) also influences the hue, color intensity, and strength of the pigment. The copper complex appears to offer an optimum combination of these properties.

The structure of copper phthalocyanine blue (CPC blue) is shown below:



Mol. Wt. = 576.082

The outstanding fastness and chemical stability of this pigment is attributed to the symmetry of the molecule, the aromatic character of the macro ring system and the ability of the copper atom to promote electrons into the 4p orbitals.

The blue pimgnet was shown to exist in two major crystal modifications: the alpha phase, a red-shade blue, and the beta phase, a green-shade blue, the more stable of the two. An unstabilized alpha crystal can be converted to the beta form simply by heating to about 400°F or by exposure to an aromatic solvent. Furthermore, the unstabilized alpha phase blue is subject to crystal growth in solvents (particularly aromatic solvents). Small size beta can also grow in solvents.

One method of stabilizing the alpha phase blue to crystal growth is by replacing one or less than one (statistically) of the nuclear hydrogens with chlorine whereby some change in hue is obtained.

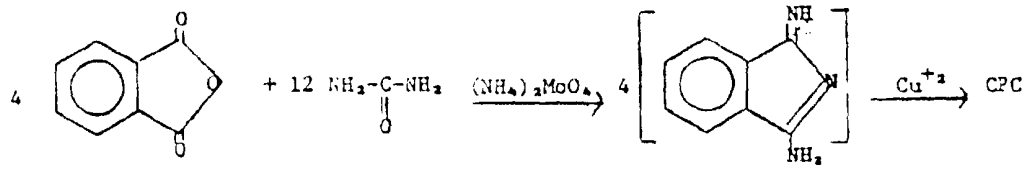
More complete chlorination (i.e., fourteen to sixteen atoms per molecule) results in the conventional polychloro copper phthalocyanine green pigment. Other halogens (e.g., bromine) can be partially substituted to obtain much yellower copper polybromo-chloro-phthalocyanine greens. The degree of bromination of some commercial types varies from four to twelve bromine atoms, the shade becoming yellower with increasing bromine content. The products show performance characteristics similar to those of the polychloro green except for lower tinting strength.

Licensed by Imperial Chemical Industries Ltd., DuPont pioneered the commercial development of the phthalocyanine pigments in this country. Permission for DuPont to use the name ''Monastral'' (in the U.S.A. only) was included in the license agreement.

The name ''Monastral'' is the trademark of a lightfast pigment, not necessarily based on phthalocyanine. For its export markets, however, DuPont uses the name ''Cinquasia'' for its quinacridone line of lightfast pigments.

The specific phthalocyanine pigment types manufactured at Newport are as follows: (1) chlorine-free CPC in two crystal phase forms, viz., alpha-phase (red-shade blue) and beta-phase (green-shade blue), (2) a so-called, semi-chlor with an average chlorine content (ring-substituted) of about four percent by weight, and (3) a modified semi-chlor containing ring-substituted sulfonic acid groups to the extent of about 0.4 weight percent as sulfur.

CPC is synthesized from phthalic anhydride, urea, and a source of copper ions in the presence of ammonium molybdate catalyst and a diluent such as kerosene.



LPH 0072501

''Monastral'' Green is polychloro CPC wherein almost complete (approx. 14.5-15.5 Cl) substitution of chlorine has been realized on the sixteen available ring positions.

''Monastral'' Green Y is a polybromo-polychloro CPC which is a very yellow shade of green as compared to polychloro CPC.

Some of the basic pigments described above receive various finishing treatments at Newark to achieve their full pigmentary potential and to improve their utility in the various end-use systems.

The phthalocyanines must be ''tailor-made'' to meet the various end-use applications and this accounts for the proliferation of chemical types and pigment codes.

PHTHALOCYANINE NOMENCLATURE KEY
(as used in the Pigments Dept.)

First 2 or 3 letters - the first letter indicates whether a blue (B) or a green (G).

New

Blue BR - Chlorine-free α CPC.
Blue BB - Semichloro CPC
Blue BG - Chlorine-free β CPC
Blue BBF- Semichloro, partially sulfonated CPC
CPC AF - Antiflocculant

Green G - PolychloroCPC from sulfur dichloride halogenation
Green GE- PolychloroCPC from eutectic halogenation
Green GY- PolybromochloroCPC from eutectic halogenation

Third letter* - indicates size reduction method, or crude, except for the N designation.

U - crude
S - solvent-milled
X - solvent-breached
A - acid-swelled
D - dispersion-milled
Z - pre-milled crude
N - crystal-phase unstable
NF- non-flocculating

* 4th letter in the case of BBF

LPH 0072502

BASIC PHTHALOCYANINE PROCESSES

1. Basic Product: CPC Blue B (BBS)

Description: A crystal-stable alpha-phase CPC

A crystal-stable alpha-phase CPC containing about 4% chlorine and particle-size-reduced by solvent milling or HT drowning.

Process (Solvent Milling)

Phthalic anhydride, water and caustic soda are reacted to form disodium phthalate. Chlorine is sparged in to give the 4-chloro derivative, mineral acid is added to give the sodium hydrogen 4-chlorophtholate (4-CPA) which is salted out with sodium chloride, and filtered to remove much of the water. The 4-CPA presscake is then reacted in kerosene at 200°C along with phthalic anhydride, urea, copper chloride and ammonium molybdate catalyst. After synthesis, 98% sulfuric acid is added to the reaction mass to form CPC sulfate which settles quickly and allows the removal of most of the kerosene by decantation. The CPC sulfate is hydrolyzed to CPC in the desired alpha-phase by adding water and caustic soda. Filtration and tray drying complete the isolation of the CPC crude from the kerosene. The dry crude is premilled and acetone milled and the acetone is then removed by distillation. The pigment receives a dilute sulfuric acid extraction, filtration and press wash before being converted to the finished products.

Process (HT Drowning)

Pigment is synthesized exactly as described above using kerosene as a diluent. The Blue B pigment in the kerosene slurry is ''acid flushed'' into concentrated sulfuric acid containing 0.4% stearic acid (based on weight of pigment) for foam control and ease of kerosene separation. The sulfuric acid solution of CPC is HT drowned in two stages, first in a ''bullet'' mixer to about 75% sulfuric acid concentration and then in a second stage mixer to about 35% concentration. For manufacture of pigment for paint applications the material is developed by heating with Perclene in the presence of the cationic surfactant Arquad 16-50 (cetyl trimethylammonium chloride). Subsequently an anionic surfactant Emcol P-10-59 (isopropyl amine salt of p-dodecyl benzenesulfonic acid) is added to flocculate the pigment. After filtration and washing the pigment is converted to a finished product.

2. Basic Product: CPC Blue BX (BBX)

Description:

A crystal-stable alpha-phase CPC containing about 4% chlorine and particle-size reduced by solvent breaching.

Process:

Same as for Blue B, except that the acetone milling step is replaced by solvent breaching.

LPH 0072503

3. Basic Product: CPC Blue BBF (BBF)

Description:

A crystal-stable alpha-phase CPC containing about 4% chlorine and flocculation resistant due to the presence of sulfonic acid groups to the extent of about 0.4% sulfur. The crude is particle-size reduced by solvent milling. The shade is similar to that of Blue B but somewhat greener.

Process:

Phthalic anhydride, water, and caustic soda are reacted to form disodium phthalate. Chlorine is sparged in to give the 4-chloro derivative, mineral acid is added to give the sodium hydrogen 4-chlorophthalate (4-CPA) which is salted out with sodium chloride and filtered to remove much of the water. The 4-CPA press-cake is reacted in kerosene at 200°C. together with 4-sulfophthalic acid, phthalic anhydride, urea, copper chloride and ammonium molybdate catalyst. After synthesis, 98% sulfuric acid is added to the reaction mass to form CPC sulfate which settles quickly and allows the removal of most of the kerosene by decantation. The CPC sulfate is hydrolyzed to CPC in the desired alpha-phase by adding water and caustic soda. Filtration and tray drying complete the isolation of the CPC crude from the kerosene. The dry crude is pre-milled and acetone-milled, and the acetone is then removed by distillation. The pigment receives a dilute sulfuric acid extraction, filtration and press wash before being converted to the finished products.

4. Basic Product: CPC Blue BGS (BGS)

Description:

A beta-phase, chlorine-free, green-shade CPC similar to Blue BGD but less intense. The crude is particle-size reduced by solvent milling. Blue BGS is beta-phase stable.

Process:

Phthalic anhydride, urea, copper chloride and ammonium molybdate catalyst are reacted in kerosene medium at 200°C. The crude CPC is isolated by emulsification of the kerosene, filtration, and tray drying. (See chlorine-free crude for details). The dry crude is size-reduced by premilling followed by acetone milling. The acetone is removed by distillation and the pigment then receives a dilute sulfuric acid extraction, filtration and press wash, before being converted to the finished products.

5. Basic Product: CPC Blue R (BR)

Description:

An alpha-phase, chlorine-free CPC. This product is the most red-shade blue CPC in our product line. Blue R is sold in both crystal stable (BRNF) and unstable (BRN) forms. Crystal stability in BRNF is obtained by the use of CPC-AF. Particle size reduction is accomplished by premilling or HT drowning.

Process: (Premilling)

Phthalic anhydride, urea, copper chloride and ammonium molybdate catalyst are reacted in kerosene medium at 200°C. The crude CPC is isolated by emulsification of the kerosene, filtration, and tray drying. The dry crude is size-reduced by premilling (dry ball milling) and acid swelling. The pigment is extracted, filtered, and washed before being converted to the finished products.

6. Basic Product: CPC Blue BGD (BGD)

Description:

A beta-phase, chlorine-free CPC, this product is the most green-shade blue CPC in our product line. Blue BGD is crystal stable. The crude is particle-size reduced by dispersion milling.

Process:

Phthalic anhydride, urea, copper chloride and ammonium molybdate catalyst are reacted in kerosene medium at 200°C. The crude CPC is isolated by emulsification of the kerosene, filtration, and tray drying. The starting crude made in this way is the same as that used for BGS. The dry crude is size-reduced by milling in a ball mill in a substantially dry mixture(dispersion milled)with alum, a surface active agent and a small amount of ''Perclene'' (a beta-phase directing solvent) and iron rods (Cylpebs). The alum is removed from the pigment by acid extraction and filtration and the CPC is converted to the finished products.

7. Basic Product: CPC Green G (G)

Description:

A yellow-shade green polychloro CPC containing about 48% chlorine in the molecule. Green G is crystal stable.

Process:

Phthalic anhydride, urea, copper chloride and ammonium molybdate catalyst

are reacted in kerosene at 200°C. The blue crude is isolated from the kerosene by filtration and tray drying. The dry blue crude is chlorinated by reacting with sulfur dichloride under pressure in the presence of aluminum chloride. The sulfur chloride is removed in a rotating dryer and the green crude is water-extracted and filtered. The presscake is repulped in water and treated with sodium Staybelite® (hydrogenated rosin) and ODCB (o-dichlorobenzene). The ODCB is removed by steam distillation and the pigment is filtered and washed before converting to the finished products.

8. Basic Product: CPC Green GE (GE)

Description:

A yellow-shade green polychloro CPC containing about 48-49% chlorine. Green GE is crystal stable.

Process:

CPC Blue crude (kerosene free) is chlorinated in a eutectic melt of aluminum chloride, sodium chloride, cuprous chloride and ferric chloride at 165-170°C. The end-point of the chlorination is determined by titrating the filtrate of a melt sample hydrolyzed in dilute sulfuric acid, with a potassium permanganate solution. After completion of chlorination, the reaction mixture is drowned into an emulsion of ODCB, dilute sulfuric acid and Emcol P-10-59 (isopropyl amine salt of p-dodecyl benzene sulfonic acid). The resulting crude pigment is breached by reslurrying in dilute aqueous alkali, additional ODCB and Emcol P-10-59, followed by heating to reflux (~100°C). The ODCB is distilled out and the pigment filtered and washed before conversion to finished product.

9. Basic Product: CPC Green Y (GY)

Description:

A very yellow-shade CPC which contains about 12.0-13.5 atoms of bromine and about 1-2.5 atoms of chlorine, Crystal stable.

Process:

CPC Blue crude (kerosene-free) is halogenated at 145°C in a eutectic melt of aluminum chloride, sodium chloride, and cuprous chloride with bromine and chlorine. The halogenation end-point is determined by running a "spectral test", in which a hydrolyzed and isolated dry sample is dissolved in concentrated sulfuric acid and the wavelength of maximum absorption measured. The melt is drowned in water and the crude pigment isolated in presscake form. The pigment is breached by reslurrying the presscake in dilute aqueous alkali with ODCB and sodium Staybelite® and heating to 150°C under pressure for one hour. The pressure is released, the ODCB distilled out and the pigment filtered and washed before conversion to finished product.

PHTHALOCYANINE PIGMENT PROPERTIES

The phthalocyanines possess the following combination of pigment properties:

a. Excellent lightfastness in tint (bronze in deep colors)
b. Excellent bleed resistance
c. High tinting strength
d. High tinctorial purity
e. High resistance to acids and alkalies
f. High chemical inertness.

1. Lightfastness

Copper phthalocyanine pigments exhibit excellent lightfastness in conventional surface coatings wherein the pigmented surface is simultaneously exposed to light and air. In laminated constructions where the inner laminate is pigmented (i.e., air is excluded), phthalocyanine green may exhibit severe color change on exposure to light. It is suggested that the phthalocyanine green is sensitive to photoreduction, but, when exposed to air, is reoxidized to its original color.

As stated earlier, the metal-free phthalocyanines and most of the metal complexes other than copper are inferior in lightfastness to the copper phthalocyanines.

2. Bleed Resistance

Copper phthalocyanines are non-bleeding in water and organic resins and solvents normally encountered in pigmented compositions (i.e., paint, inks, plastics, etc.).

Some copper phthalocyanine blue products bleed in solvents as a result of the chemical modifications made to obtain flocculation resistance and/or crystal stability. Inasmuch as the ultimate particle size of these pigments is in the range of 0.05 µm, the passage of such particles through a filter should not be interpreted as solubility (bleed).

3. Tinting Strength

The tinting strength of unmodified copper phthalocyanine toners is relatively high. The degree of apparent strength one realizes, however, depends upon dispersion as well as the crystal and dispersion stability (i.e.,flocculation resistance) of the pigment.

Unmodified chlorine-free alpha-phase CPC blue is the strongest blue toner. It is slightly stronger than the semi-chlor pigment and stronger than the beta-phase blue and the metal-free blue. In many solvent systems, however, the full potential strength of the unmodified alpha pigment is not realized because of

crystal growth and/or severe flocculation. Accordingly, although inherently weaker and, in some cases, higher in price, the crystal stable and flocculation resistant pigments provide higher apparent strength in such uses.

4. Tinctorial Purity

Phthalocyanine pigments are said to be dichroic. That is, in the aggregate, they reflect highly in the red region of the spectrum and transmit highly in the green region. The amount of scattering of incident light, however, is dependent upon particle size. The hiding power increases as the particle size decreases to about the wavelength of the light being considered. If dispersed to their ultimate particle size (0.04 to 0.06 µm), the phthalocyanines would appear transparent. Normally, however, we cannot disperse these dry pigments to their ultimate particle size nor can we obtain a mono-dispersed system. In a practical dispersion, we obtain particles ranging in size from near ultimate to those approaching forty microns in diameter. The larger particles (i.e., those greater than 0.3 µm) will scatter proportionately more red light than will those which are smaller. The relatively greener light transmitted by the smaller particles, however, is scattered by the TiO_2 in the tint. The combination of green and red light entering the eye appears brown (dull, i.e., low in saturation or intensity). The apparent intensity or tinctorial purity of the phthalocyanines, therefore, is greatly dependent upon the particle size distribution obtained in a dispersion. They will appear dull when poorly dispersed and intense when well dispersed. This is also important in the formulation of metallized finishes. Incidentally, it makes little difference if the large particles are aggregates, flocculates of large crystals, all will produce dullness.

Another factor is that phthalocyanine greens (more so than blues) are capable of being chemically reduced. Accordingly, one occasionally finds that steel ball milling some greens in high acid vehicles results in very dull blue tints. On the other hand, blues are more susceptible to chemical destruction by strong oxidizing agents resulting in the loss of strength and tinctorial purity.

Semi-chloro alpha blue is more crystal stable but less intense in color than chlorine-free alpha blue.

5. Resistance to Acids and Alkalies

With the exception of their solubility in concentrated acids, the phthalocyanine toners are highly resistant to acids and alkalies. The resistance of modified phthalocyanines (such as "Ramapo" and calcium carbonate lakes) is, of course, governed by the nature of the modifier. Resinated pigments, for example, are very reactive with some acids.

6. Chemical Inertness

Except in unusual compositions, the unmodified phthalocyanines are considered highly inert. Copper phthalocyanines do not accelerate the oxidation of rubber nor do they react chemically with conventional vehicles and solvents. The blue, however, can be destroyed by strong oxidizing agents (e.g., peroxides and strong bleaches).

The blue can also be reduced and caused to fade in wet storage in some metallized (aluminum flake) baked alkyd systems. The green can be reduced by both photoreduction and chemical attack. For example, phthalocyanine green discolors badly in laminated construction based on phenol-formaldehyde resins.

The chemical inertness of modified phthalocyanines (i.e., substituted phthalocyanines, resinated and extended lakes) is, of course, influenced by the modifying material.

7. Heat Stability

Although they have their limitations, the phthalocyanines are among the most heat stable of all organic colorants. The most heat stable blue is the beta-phase toner treated with about 15% CPC-AF (BT-465-D). The unsubstituted alpha-phase blue converts to the greener beta-phase at high temperatures (400°F. or higher). The heat resistance of resinated products is lowered by the resinate present. Similarly, the green toners are more heat stable than the resinated (''Ramapo'') toners. The apparent heat stability of the phthalocyanine (or any pigment) may, of course, be influenced by reaction of the pigment with the binder at elevated temperatures or by the presence or absence of air. Accordingly, the heat stability of a pigment may appear quite different in different systems.

8. Durability

The phthalocyanines are usually used in medium to light tints. In this service, their resistance to chemical fade (as opposed to chalk fade) is considered excellent. The phthalocyanines, however, show a pronounced tendency to bronze in deep tints and deep metallics. The blue pigments develop a very red bronze while the greens develop a reddish to golden yellow bronze. At these depths, therefore, the apparent color retention appears rather poor. The beta-phase blues tend to bronze slightly less than the alpha types.

In light tints, chalk fading (TiO_2 chalk) of green tints is significantly superior to blue tints at equivalent depths.

In all other respects (checking, blistering, gloss retention, etc.), the phthalocyanines exhibit excellent durability characteristics within the framework of good formulation and vehicle selection.

9. Viscosity Stability

Unmodified phthalocyanines are generally considered as non-reactive pigments. That is, they do not form soaps or promote polymerization of vehicles. Nevertheless, phthalocyanine dispersions in fluid organic vehicles are characterized by a high order of thixotropy, particularly in aromatic systems. This is probably related to their very small particle size aggravated by the flocculating tendency of the unmodified forms. The degree of thixotropy and yield value obtained in any particular vehicle system may vary greatly with the particular pigment used.

10. Dispersibility

There are two major parameters of dispersion quality for high strength organic pigments such as the phthalocyanines; these are: tinting strength and transparency. As the dispersion of the pigment (i.e., particle size reduction) is improved, the tinting strength increases until ultimate strength is reached. At the same time, the transparency decreases (i.e., opacity increases) until the particle size reaches the range of 0.4 to 0.5 microns after which transparency increases. Accordingly, a grind fineness fully adequate for tinting purposes is far from adequate for applications requiring transparency (e.g., metallic finishes, foil coatings, and transparent plastics).

SOME ABBREVIATIONS USED IN PHTHALOCYANINE TECHNOLOGY

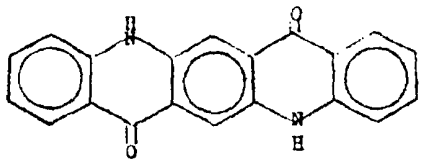
AF	acid-flushing (also used to desgnate anti-flocculant eg. CPC-AF)
AP	acid-pasting
AS	acid-swelling (also called "permutoid swelling")
CF	chlorine-free
CPA	chlorphthalic acid
CPC	copper phthalocyanine
DM	dispersion-milled
HT	high turbulence
EF	emulsion filtration
FR	flocculation-resistant
HF	milling with high-speed revolving disc (Hochberg Finishing)
KF	Kerosene flotation
LC	low copper (in the synthesis) chlorine-free crude
MC	mono-chlor
MF	metal-free
NF	non-flocculating
PA	phthalic anhydride
PC	phthalocyanine
PN	phthalonitrile
SC	semi-chlor
SM	solvent-milled
SPA	sulfo-phthalic acid

Revised by EEJ - 1975

QUINACRIDONES

A major development in the pigment industry in the last two decades has been the commercial introduction of the quinacridone (QA) family of pigments which offer generally outstanding fastness properties in the gold, orange, maroon, scarlet, red, magenta, and violet color ranges. Because of their excellent pigmentary properties, they supplement the phthalocyanine blues and greens in extending the commercial availability of high-grade pigments for applications where a high degree of lightfastness is required. They resemble the phthalocyanines in their structural symmetry, and aromatic character. Similarly, they resemble the phthalocyanines in their excellent pigment properties. The presence of vinologous amide groups in the structure suggest a resemblance to vat dyes such as Indanthrone.

Although discovered in 1935, they were first commercialized by DuPont in 1958 with the release of a yellow-shade red, a blue-shade red, and a violet. All three products are of the same molecular structure, viz., a linear unsubstituted quinacridone, and differ either in crystalline form (polymorphism) or in particle

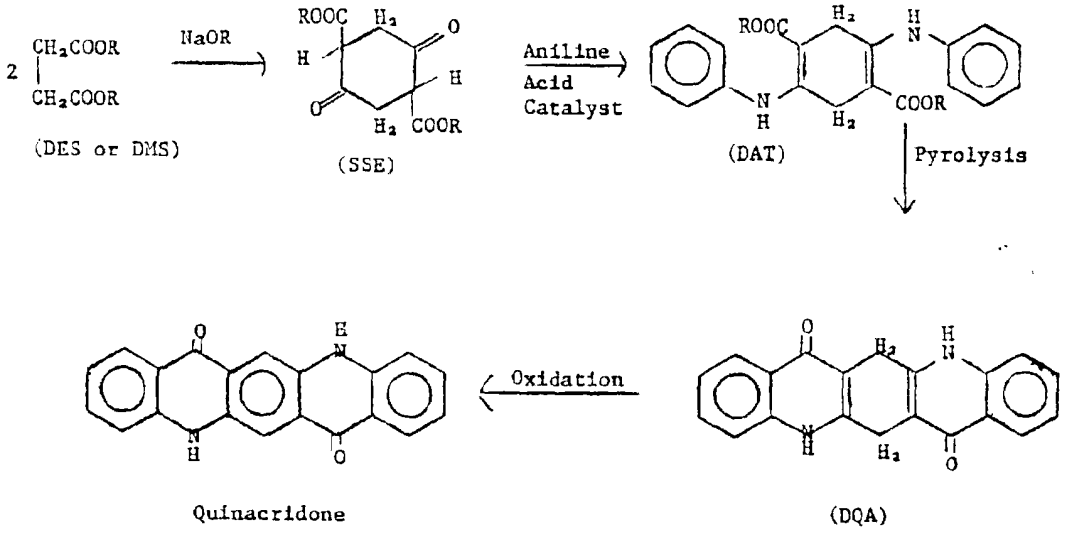


Linear Quinacridone

size. The two red pigments are in the gamma crystalline form and differ in particle size, the blue (Red B) shade being smaller than the yellow shade (Red Y), whereas the violet (Violet R) pigment is in beta crystalline form. The red, alpha crystalline form of quinacridone, not commercialized by DuPont at this time, is the least stable phase of the three polymorphic forms.

The outstanding stability and insolubility of the quinacridone pigments are attributed to the high degree of intermolecular hydrogen bonding between the carbonyl (-C=O) and imino (-NH) groups in the crystal lattice.

The basic synthetic route for quinacridone manufacture at Newport is given below:



Quinacridone (DQA)

Two moles of diethyl(DES) or dimethyl succinate (DMS) react in alcohol in the presence of sodium methylate (NaOMe) and Dowtherm, (DT) which serves as a diluent, to give sodium succinyl succinate (Na_2SSE) as a solid suspension. The Na_2SSE is acidified with acetic acid (45%) giving succinyl succinic ester (SSE) which dissolves in the Dowtherm layer, and the formed sodium acetate dissolves in the aqueous layer. The lower aqueous layer is more dense due to the dissolved salts. The SSE-Dowtherm solution is washed with aqueous salt (NaCl) solution to remove by-products. The SSE yield is about 30%. The SSE-Dowtherm solution is filtered to remove insoluble impurities, and transferred to another vessel where it is reacted with an excess of aniline at 110°C in the presence of trifluoroacetic acid (TFA) catalyst. The product dialkyl 2,5-dianiline-3,6-dihydroterephthalate (DAT) which is formed in about 97% yield, remains in Dowtherm solution provided the temperature is sufficiently high. Water formed during the condensation, excess aniline, and the TFA are distilled out. The aniline and TFA are recycled. The DAT solution is transferred from the reactor to a hold tank and added at a controlled rate (8 hrs.) to boiling Dowtherm to form the insoluble 6,13-dihydroquinacridone (DQA) in about 96% yield and by-product alcohol. The long time devoted to the pyrolysis is designed to minimize the concentration of DAT in order to favor the monomolecular reactions leading to DQA, and minimize undesirable bimolecular reactions. The overall yield of DQA from DES is about 75%.

The DQA is transferred to a hold tank for cooling and subsequent filtration on nylon cloth in a Nutsche filter. Dowtherm and Dowtherm-soluble by-products are removed by applying nitrogen pressure. The residual Dowtherm and by-products in the Nutsche filter cake are washed out using dry methanol. A methanol slurry of DQA is transferred to a DQA hold tank.

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A measured amount of DQA/methanol slurry is transferred to an oxidation tank. The slurry is made up to an exact methanol, sodium hydroxide, water, ''Sitol'' (sodium m-nitrobenzenesulfonate) to DQA ratio for oxidation to quinacridone (QA). The crystal phase of the QA (violet beta or red gamma) is determined by the ratio of the ingredients used which determines which polymorph of DQA is caused to undergo oxidation. The QA is filtered, washed, and dried. The oxidation yield is essentially quantitative. The filtration presscake is spray-dried to give the crude red or violet. The methanol from the oxidation is recovered by distillation (with 10-20% water) for reuse in oxidation.

To make 4,11-dichloroquinacridone, o-chloraniline is used instead of aniline in the above process. p-Toluidine is used in place of aniline to make 2,9-dimethylquinacridone, and p-chloroaniline for the manufacture of 2,9-dichloroquinacridone.

One quinacridone product, Red Y, a crude, relatively large particle size gamma-phase material, is sold as an opaque red pigment.

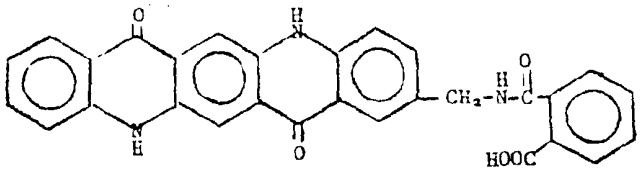
The other quinacridone products are particle-size reduced either by HF milling, dispersion milling, or HT drowning (for description of these techniques, see section on Particle-Size Reduction Methods). Solid solution formation can be accomplished either by co-dispersion-milling or co-HT-drowning the component quinacridones.

1. Flocculation Resistance

The intermolecular hydrogen bonding in QA which is responsible for its relative insolubility and durability is a fairly polar region of the crystal. On the other hand, the large faces of the crystal are fairly non-polar and, therefore, tend to cause flocculation and create rheological problems. In 2,9-diMeQA the polarity of the large faces of the crystal are further reduced causing an increase in flocculation, while 2,9-diclQA which is more polar due to the clorine atoms, shows much improved rheological properties. The improvement is a function of the paint system in which the pigment is used. In thermosetting acrylic enamel the rheology of 2,9-dichlQA is good; this is not however, the case in the more polar solvent system used in thermoplastic acrylic lacquer. In order to enhance the surface polarity of 2,9-dichlQA and that of many solid solutions, the pigments have been treated with quinacridone-2,9-disulfonic or quinacridone-2-monosulfonic acid. Due to similarity of structure, various QA's show an affinity for the treating agents. To fix the treating agents on the surface they are precipitated as their aluminum salts (AQD, aluminum quinacridone disulfonate or AQM, aluminum quinacridone monosulfonate).

Pigments treated in this manner show very good rheological and reflow properties in acrylic lacquer systems.

For less polar media such as alkyd paint systems, an excellent surface treatment is QA-AF of the following structure:



QA-AF

This surface treating agent is not sufficiently polar to be effective in thermoplastic lacquer but functions effectively in alkyd systems.

2. Crystal Stability

Although QA is a very insoluble pigment, the solubility being only 84mg/L in boiling 2-chloronaphthalene, nevertheless QA will undergo Ostwald ripening or crystal growth when exposed to solvents for long periods of time under shearing conditions. The degree of crystal growth is a function of the solvent, more polar solvents, such as those encountered in acrylic lacquers, being more effective than those employed in alkyd systems.

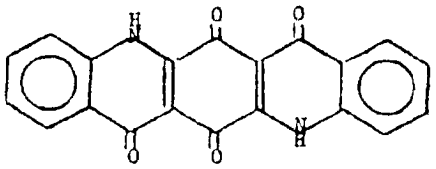
This type of crystal growth is not particularly consequential in tints, but in metallics it leads to serious loss of two-tone character. To avoid this growth phenomenon the surface treatments with AQD, and particularly AQM, are very effective. Once these molecules are fixed on the growing surfaces of a crystal, further orderly growth is effectively inhibited.

Crystal instability is also a problem in high temperature plastics in which solubility is sufficiently high to cause crystal growth or phase conversion, where applicable. QA's treated with QA-AF show definite improvement in heat stability in certain plastic systems. However, for plastics such as polystyrene, ABS, and particularly nylon, processed at temperatures as high as 600°F, the QA's have to be much more insoluble. 2,9-DiClQA magenta is sufficiently insoluble to be a real contender for some high temperature plastic systems. The least soluble of all QA's is the red 2,9-dicarboxyQA which has not yet been commercialized.

The desirable pigmentary characteristics of the unsubstituted quinacridones are also shown by some substituted quinacridones and many binary and ternary solid solution pigments currently on the market. QA, many substituted QA's, DQA, and quinacridonequinone (QAQ) form a series of solid solutions. While the x-ray diffraction pattern, color and durability of a mixture of, for example, 4,11-DiClQA and QA is predictable, a solid solution of these two components shows both a non-additive diffraction pattern and an unpredictable color effect, and greatly improved durability. A variety of solid solutions and solid compounds have been prepared, including a maroon solid solution of QA and QAQ in which the minor component, the quinone, is the solvent and QA is the solute. Similarly, gold and deep gold solid solutions which are available commercially consist of QAQ, QA and DQA.

The major component in the latter two pigments, QAQ, is prepared by the oxidation of QA or DQA with sodium dichromate in aqueous acid medium.

QA ⟶



QAQ

The solid solutions are prepared by co-dispersion milling the components followed by dilute acid extraction. During the latter operation crystal growth and solid solution formation occurs. Alternately, solid solutions are prepared by dissolving the components in concentrated sulfuric acid followed by HT drowning and subsequent particle size development under the influence of dilute acid and heat.

The following solid solutions have been introduced to the trade:

60% QA + 40% 2,9-diMeQA	Maroon B
80% QA + 20% 2,9-diMeQA	Trans Red B
80% QA + 20% 4,11-diClQA	Trans Red Y
60% QA + 40% 4,11-diClQA	Scarlet
44% QA + 30% 4,11-diClQA+16% QAQ+10% DQA	Orange
23% QA + 67% QAQ+10% DQA	Gold
4.5%QA + 85.5%QAQ+10%DQA	Deep Gold

The wide hue range of the quinacridone pigments is finding extensive use in automotive finishes where the excellent durability, including gloss retention, can justify the relatively high cost. The violet quinacridone is finding extensive use for toning white pigments and in blends with the inorganic molybdate orange to formulate high quality, bright, durable, and relatively low cost reds.

Uses of the quinacridones closely parallel those of the phthalocyanines. The relatively few applications for which they are not recommended, include strong, oxidizing atmospheres (chemical decomposition), and highly alkaline compositions (concrete, cement).

LPH 0072515

ABBREVIATIONS USED IN QUINACRIDONE TECHNOLOGY

DES	Diethyl succinate
DMS	Dimethyl succinate
NaOMe	Sodium Methylate
DT	Dowtherm
Na_2SSE	Sodium salt, succinyl succinic ester
SSE	Succinyl succinic ester
DAT	Dialkyl 2,5-dianilino-3,6-dihydroterephthalate
TFA	Trifluoroacetic acid
PTSA	p-Toluenesulfonic acid
DQA	6,13-Dihydroquinacridone
Na_2DQA	Sodium salt, 6 13-dihydroquinacridone
Sitol	Sodium salt, m-nitrobenzene sulfonic acid (sodium m-nitrobenzene sulfonate)
QA	Quinacridone
$2,9\text{-}Me_2QA$	2,9-Dimethylquinacridone
$2,9\text{-}Cl_2QA$	2,9-Dichloroquinacridone
$4,11\text{-}Cl_2QA$	4,11-Dichloroquinacridone
QAQ	Quinacridonequinone
QAAF	Quinacridone antiflocculating agent
	2-(o-carboxyphenylcarboxamidomethyl)QA
AQD	Aluminum quinacridone disulfonate
AQM	Aluminum quinacridone monosulfonate
DM	Dispersion milling
HT	High turbulence
HF	Milling with high speed revolving disc (Hochberg finishing)

Revised by EEJ - 1975

LPH 0072516

QA - N-CODE SYSTEM

CONFIDENTIAL

The following is a summary of the N-code system used for QA Pigments:

° Use of a four digit number -
1st digit - 7 indicates QA
2nd digit - indicates Newport process
3rd & 4th digits - type of pigment.

° 2nd digit designation -
0 - Crude (Wet)
1 - Dispersion milled (wet)
2 - Dispersion milled, Newport laked (wet)
3 -
4 - Dispersion milled crude (dry) - Newport internal code
5 - Spray dried
6 - HT drowned (wet)
7 - Thin film dried semifinished
8 -
9 - Premilled Breached (wet)

° 3rd and 4th digits designation

These digits are used to specify QA types such as:

00 - Gamma
__ 01 - Beta
__ 09 - Maroon
__ 10 - Scarlet, etc.

Within types these digits allow for further specifics:

__ 46 - Magenta (AQM) treated
__ 47 - Magenta
__ 49 - Magenta (AQD) treated, etc.

and thirdly these digit allow for special N-codes being assigned for selected quality code:

_ _ 02 - Gamma for RT-790-D
_ _ 04 - Gamma for RT-796-D
_ _ 03 - Beta for RT-795-D
_ _ 05 - Beta for RT-791-D

This summary should give you a working knowledge of the QA N-code system. Recently several new codes were assigned to conform to this system:

N-7045-A became N-7545-A
N-7000-A became N-7500-A
N-7001-A became N-7501-A
N-7057-A became N-7557-A

The "5" in the 2nd digit denotes that the material is spray dried not wet as the "0" denoted.

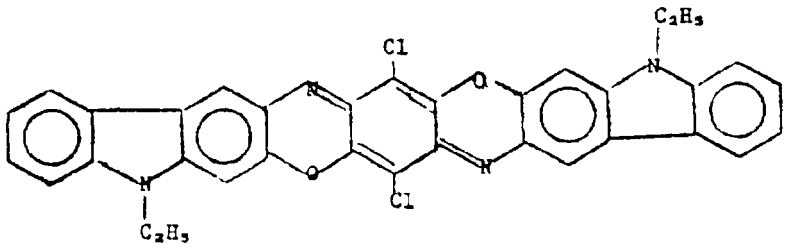
When any new N-codes are assigned they will conform to this system.

LPH 0072517

DIOXAZINE

1. Dioxazine Violet

Carbazole dioxazine violet, a blue-shade violet derived from amino N-ethyl carbazole shows exceptional strength and brilliance, together with excellent heat and bleed-resistance, although some solvent-bleed keeps it from meeting maximum requirements. Lightfastness is acceptable even in light tints. Carbazole dioxazine violet is particularly suitable for shading the phthalocyanine blues to



Carbazole Dioxazine Violet

redder shades, and for the toning of whites where a high degree of permancence is required.

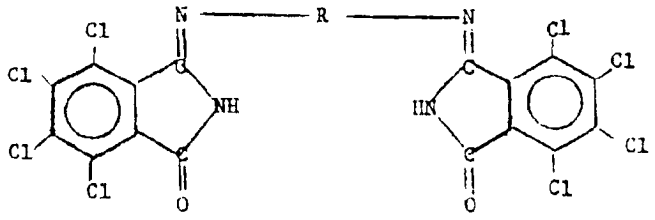
Revised by EEJ - 1975

LPH00072518

DUP110049642

TETRACHLOROISOINDOLINONES

These pigments (''Irgazins'') introduced by Geigy are condensation products of primary diamines with two molecules of 3,3,4,5,6,7-hexachloroisoindolin-1-one, and have the general formula



where R is one of several aromatic groups. The latter determine the shade of the pigment and its fastness properties to a major degree, so that a rather wide spectrum of colors are obtained including yellows, oranges, and reds, by the appropriate variation in the diamine used.

Claims are made for relative insolubility in most organic solvents, excellent fastness to migration in plastics, and to excellent fastness to light and weathering, particularly in light tints. Only a few members of this class, however, may meet all these general standards, particularly in regard to lightfastness.

Revised by EEJ - 1975

VAT DYE PIGMENTS

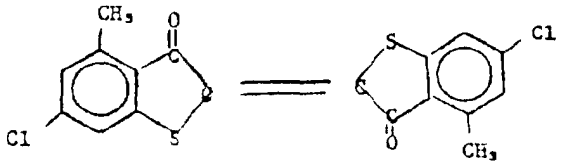
The term ''vat dye'' generally refers to a group of insoluble dyes which can undergo reduction to a water-soluble form and subsequent oxidation whereby the ''vat dye'' is regenerated without loss of color. They are applied to textile fibers by first being solubilized to the ''leuco'' form by a chemical reduction process, in which form the dye has an affinity for the cellulosic fiber. The ''vat dye'' color is then regenerated on the fiber by an oxidation process. In most cases, the colored organic compound contains two or more carbonyl ($\rangle C{=}O$) groups which are susceptible to reduction with sodium hydrosulfite in an alkaline medium to give the ''leuco'' form $\rangle C{-}ONa$.

For adaptation to pigment use, the vat dyes generally require both chemical and physical modification to develop pigmentary strength and brilliance of color. The vat dyes cannot be defined in terms of color or properties inasmuch as they exist in a wide range of hues, and exhibit pigmentary properties ranging from fair to excellent. Generally, however, they are relatively high in price.

1. Thioindigo Pigments

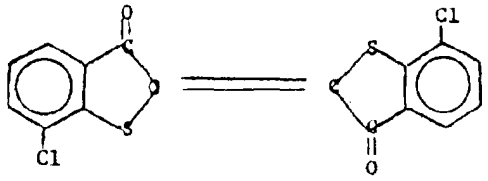
The thioindigo vat dye pigments cover a broad hue range from a yellow shade of red to violet, and although tinctorially bright, vary considerably in lightfastness, bleed resistance, and heat stability. All are symmetrical and contain chlorine, or clorine and methyl groups in the molecule.

Pink



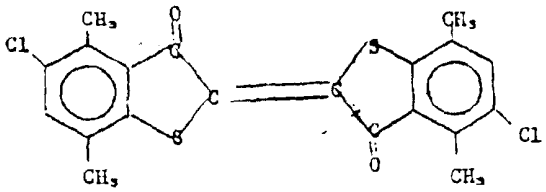
6,6'-dichloro-4,4'-dimethylthioindigo

Red



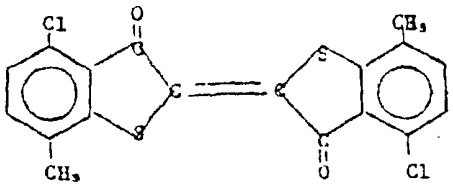
7,7'-dichlorothioindigo

Magenta



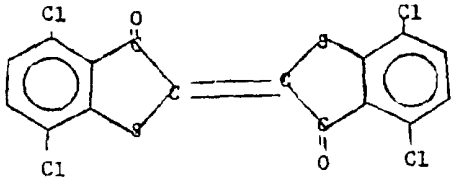
4,4',7,7'-tetramethyl-5,5'-dichlorothioindigo

Red Violet Y



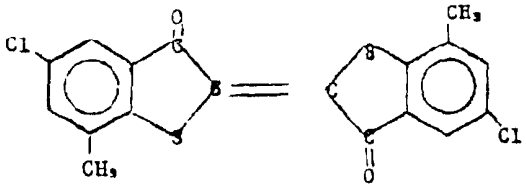
4,4'-dichloro-7,7'dimethylthioindigo

Bordeaux



4,4',7,7'-tetrachlorothioindigo

Red Violet RH



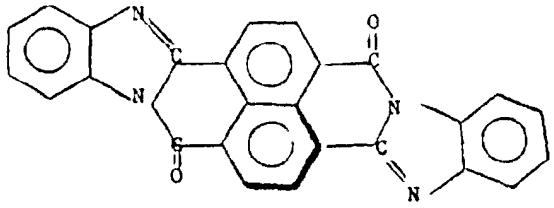
5,5'-dichloro-7,7'-dimethylthioindigo

LPH 0072521

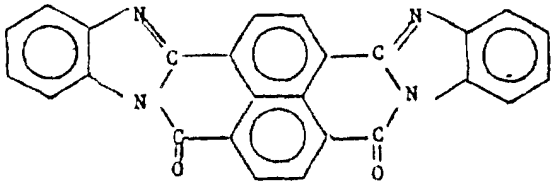
The bordeaux, a dark maroon, is the most lightfast of the thioindigos, even in light tints, and shows excellent resistance to bleed. The red violet Y, also a maroon, shows good lightfastness, and in this respect exceeds the pink, red, magenta, and red-violet RH which show only moderate lightfastness and bleed-resistance. The more lightfast thioindigo pigments are used in automotive finishes.

2. Perinone Pigments

The perinone pigments are benzimidazo derivatives of naphthalene-1,4,5,8-tetracarboxylic acid. These pigments are formed by condensing aromatic o-diamines with the acid or acid anhydride to give what is usually a mixture of the cis- and trans- isomers. Separation of the isomers involves treatment with ethanolic potassium hydroxide in which only the cis isomer is soluble.



Perinone Orange
trans-isomer



Perinone Red
cis-isomer

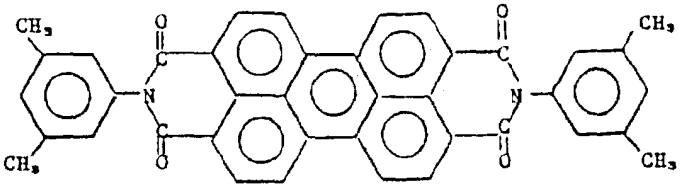
Perinone Orange (Orange GR) exhibits good bleed, bake and chemical resistance, and desirable transparency, but moderate color brightness in metallized automotive paints. Although lightfastness is good in dark shades, it is poor in tint. Perinone orange is used for shading automotive finishes.

The use of perinone red is limited by its relatively high solvent bleed.

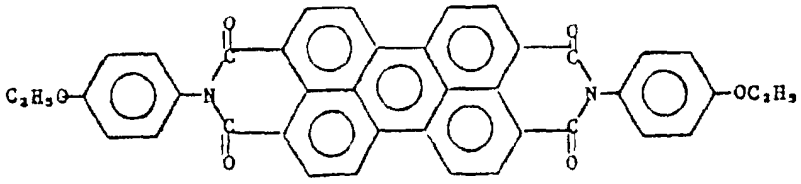
3. Perylene Pigments

The perylene pigments are di-imides of perylene-3,4,9,10-tetracarboxylic acid and although not as bright as the thioindigo pigments, they are generally stronger, and more resistant to chemicals, heat, and solvent bleed.

The perylene scarlet and vermilion are high in tinting strength and show moderate or high color brightness. Lightfastness in dark shades is good, although the vermilion shows moderate lightfastness in tint. Resistance to bleed, bake, and chemicals is excellent. The scarlet and vermilion find use in plastics applications.

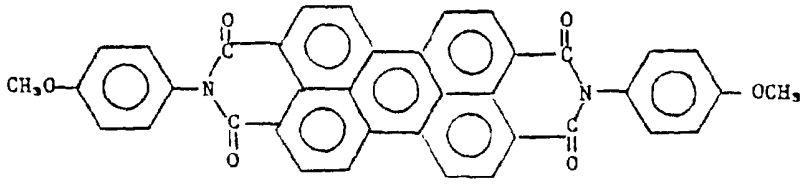


Perylene Scarlet

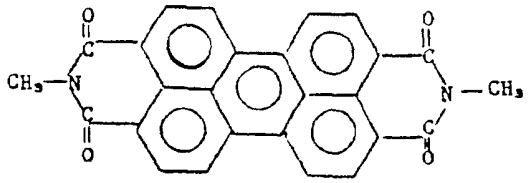


Perylene Vermilion

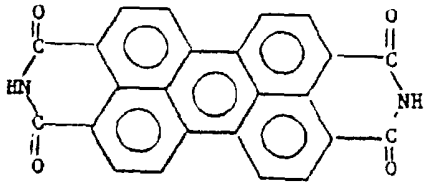
The perylene red, maroon, and bordeaux show excellent lightfastness in contrast with the scarlet and vermilion and also excellent bake resistance, and resistance to reducing agents.



Perylene Red



Perylene Maroon



Perylene Bordeaux

The more lightfast perylenes find use in automotive finishes and in high grade industrial coatings.

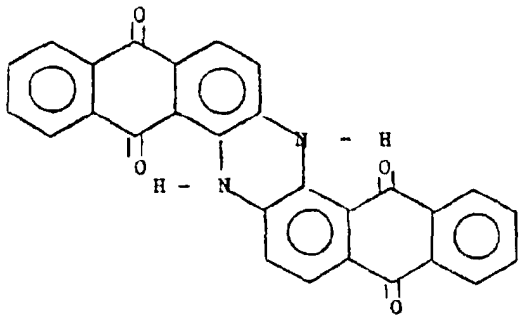
LPH 0072524

4. Anthraquinone Pigments

Representative anthraquinone pigments which have gained wide acceptance are described below.

a. Indanthrone Blue

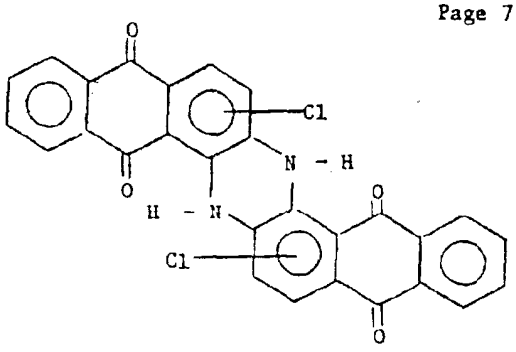
Indanthrone blue is redder in hue although less intense than the phthalocyanine blue pigments and shows good resistance to bleed, bake, and chemicals. It exhibits excellent durability, even in light tints, in virtually all applications. In this respect, it is essentially equivalent to copper phthalocyanine blue, although it bronzes to a lesser degree in full shades in automotive paint systems, and poses no flocculation problems.



Indanthrone Blue

Indanthrone exists in four polymorphic forms of which only one, the alpha modification, finds use as a pigment. The other forms are not suitable, either in stability or tinctorially.

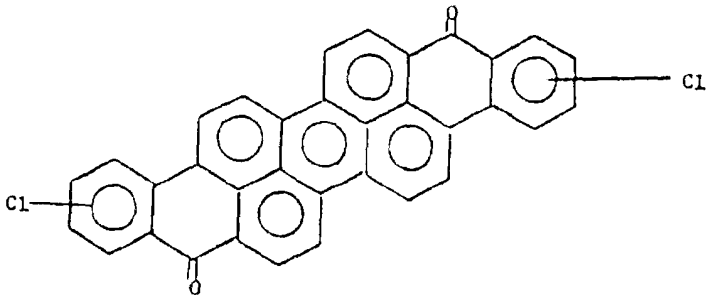
The partially chlorinated indanthrone blues also find use as pigments. Although greener in hue than the unchlorinated, they do not show equivalent stability in bake resistance.



Although somewhat stronger than the phthalocyanine blues, indanthrone blue is approximately three to four times more costly and finds application in automotive and other high quality finishes where redder shade blues are required or where better bronzing characteristics in full shade are desired.

b. Isodibenzanthrone Violet

The lightfastness and durability characteristics of dichloro-isodibenzanthrone, also referred to as dichloroisoviolanthrone, are somewhat comparable to those of the copper phthalocyanine pigments. It is a brilliant, blue-shade violet of high tinting strength, and with excellent chemical resistance. It is somewhat sensitive to solvent-bleed and this has limited its use in some applications. It has found some use for toning high quality blue and gray enamels and for developing durable, bright automotive finishes.

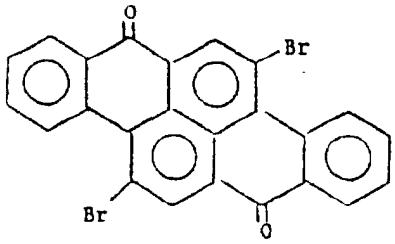


Isodibenzanthrone Violet
Isoviolanthrone

LPH 0072526

c. Anthanthrone Orange

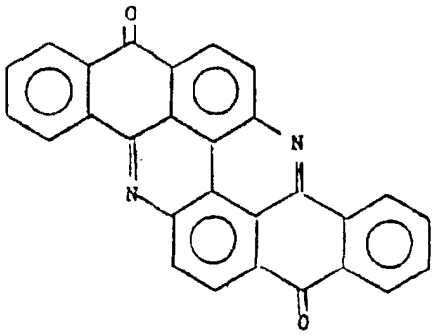
Dibromoanthanthrone (Orange RK) offers good lightfastness at all tint levels and in metallic finishes. It has good bake and chemical resistance, but it is somewhat sensitive to solvent bleed. Its usage is limited by its relatively high cost and moderate color intensity.



Dibromoanthanthrone Orange

d. Flavanthrone Yellow

Flavanthrone yellow is a red-shade yellow of moderate brightness which shows good lightfastness in tint and metallic use and good resistance to bleed, bake, and chemicals. It is relatively high in cost.

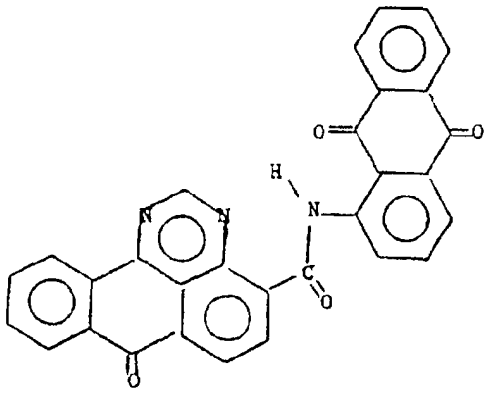


Flavanthrone Yellow

LPH 0072527

e. Anthrapyrimidine Yellow

Anthrapyrimidine Yellow is a transparent, green-shade yellow with excellent lightfastness in tint and metallic finishes and good resistance to bleed, bake, and chemicals. It is relatively high in cost, and shows relatively low color, strength, and intensity in automotive metallic finishes.

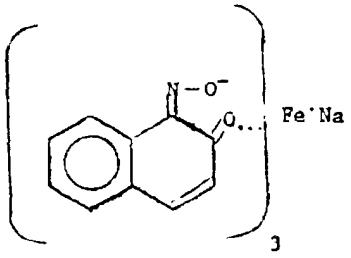


Anthrapyrimidine Yellow

MISCELLANEOUS PIGMENTS

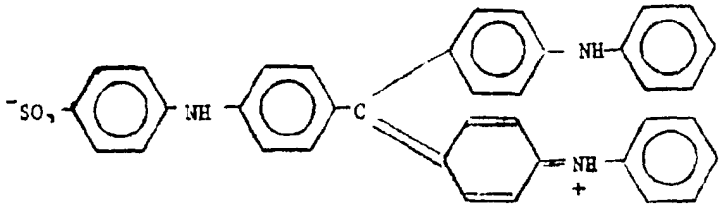
1. Pigment Green B

Pigment Green B, a complex iron salt of 1-nitroso-2-naphthol, is a strong, low cost olive-green, stronger than the inorganic chrome greens, which shows high hiding together with good alkali, bake, and bleed resistance. It is low in color brightness and exhibits poor tint lightfastness. It is used in emulsion paints, rubber, and paper coatings.



2. Alkali Blue (also called Reflex Blue)

Alkali blue is the monosulfonic acid derivative of phenylated rosaniline. Because of its high tinctorial strength, good working properties, and low cost, it is used principally for the ''toning'' of carbon black for printing inks. Alkali blue is moderately fast to light and is characterized by a high degree of intense bronze (''reflex'').



EXTENDER PIGMENTS

The colorless extender pigments used in pigment manufacture are incorporated principally to improve the working and end-use properties of the pigment, and to facilitiate standardization with respect to strength. These results are accomplished by the role of the extender pigment in preventing aggregation during manufacture, and in modifying the surface properties of the pigment. The latter affects wettability by the vehicle, texture, ease of dispersion, gloss, hiding power, rheology, and the overall pigment performance.

The extender pigments used are generally low in refractivity and low in opacity in contrast with the high opacity, high refractivity pigments used as whites such as the white leads, zinc oxides, titanium oxides, lithopones, and antimony oxides. Commonly used extender pigments for organic pigments include barium sulfate (blanc fixe, barytes), alumina hydrate, china clay, calcium carbonate, calcium sulfate, and the metal resinates such as calcium or barium rosinates. Nickel carbonate is used to a considerable extent with the quinacridones. The index of refraction of the extender pigments are in the approximate range 1.48 - 1.66 in contrast with the white pigments above which range from 1.84 - 2.76.

Although technically not an extender pigment in the sense of those described above, aluminum metal flake is used extensively to achieve decorative effects in automotive finishes. Generally, but not necessarily, it is used together with the more transparent colored pigments in automotive paint formulations to give the metallized finishes currently prominent in automotive styling.

Revised by EEJ - 1975

PIGMENT CODES

MARKETED TYPES

Colors of any particular chemical type are frequently marketed in a number of physical forms, namely,

		Examples
1.	Full strength colors	BT-284-D
2.	Resinated colors	BP-173-D
3.	Extended colors or lakes	BL-220-D
4.	Press cakes	BT-295-P
5.	Aqueous dispersions	BW-372-P
6.	Flushed colors	-

Full strength organic colors are known as ''toners.''

Resinated colors are organic toners to which metallic resinates have been added to improve certain properties, chiefly texture. In some cases (lithol reds), metallic resinates can be added without losing strength (''Duol'' effect).

Extended colors are those in which a large fraction (usually 50% to 90%) is an organic base such as alumina hydrate, blanc fixe, whiting, clay, etc. Very few extended inorganic colors are marketed at the present time. Most of the extended colors are organic and, in this case, are frequently termed ''lakes.'' Classically, the term ''laking'' involved chemical interaction or sorption of dyes on inorganic substrates. Today the trade refers to most extended organic colors as ''lakes'' regardless of whether the substrate is present in physical admixture or in chemical combination. Terminology is not always consistent. Thus, the phosphotungstic acid precipitations of basic dyes are called PTA ''toners''; when physically extended with alumina hydrate, etc., they are called ''lakes.''

''Laking'' or the extending of a color may be carried out for a variety of reasons:

1. To convert a soluble dye to a pigment.
2. To improve properties such as dispersion and flocculation resistance.
3. To reduce price per pound.

Press cakes are simply the ''cakes'' of water wet pigment as they come from the filter presses. They are used in the manufacture of flushed colors, aqueous dispersions, and certain special dry dispersions.

Aqueous dispersions are smooth, fluid dispersions of pigments in water prepared from press cakes by the addition of suitable surface active agents (surfactants). Anti-settling agents and mold inhibitors are frequently added. The aqueous dispersions are sold on a commodity basis at a standardized strength. Press cakes are sold on a dry content basis with standardized dry strength.

Flushed colors are colors that have been transferred from the water-wet state (press cake) to a vehicle, without first going through the pigment drying operation, to form a dispersion of the pigment in that vehicle. Flushed colors usually carry a premium and accordingly are attractive only when a user is not equipped to do his own grinding or, because of small volume usage, contamination problems, dusting, etc., he prefers to buy the color already dispersed. Some very hard colors like alkali blue are sold almost exclusively in flushed form. In making flushed colors, the drying and dry grinding steps ordinarily used in the manufacture of pigments are eliminated. The economies resulting are usually offset by the extra inventory costs in carrying a variety of vehicles in stock, etc., and the cost of roller milling flushed colors to eliminate grit particles.

COLOR CODE DESIGNATIONS

The Active Code List records the official names and codes of Du Pont colors. The code number consists of prefix letter or letters, a serial number, and a suffix letter or letters.

1. First Prefix Letters - Designate the color.

   B - Blues, violets, purples

   G - Greens

   R - Reds, maroons

   Y - Yellows, oranges

   F - Browns, tans

   A - Neutral or colorless products, e.g., grays and transparent extenders.

   NF - Nacreous flakes

   K - KROLOR® pigments

2. Second Prefix Letter - These are designations to further characterize the type of product.

   O - Used with "K" to designate KROLOR® Orange, e.g., KO-786-D

   Y - Used with "K" to designate KROLOR® Yellow, e.g., KY-787-D

   E[1] - Used with "Y" to designate Molybdate Orange, e.g., YE-637-D

   T - Used with all organic pigments (toners) with 90-100% color content. Color content comprises the basic coloring material plus normal moisture and excludes all treating agents, substrate, etc., e.g., GT-754-D.

   P - Used with all organic pigments containing 50-89% color content[2], e.g., GP-755-D.

[1] Some years ago, the letters E and L were used as second prefix letters to indicate lake colors. This practice is no longer followed; however, some codes still exist (RE-325-D, RL-417-D, etc.) that were coded on this basis.

[2] For historical reasons, there are certain pigments now coded with "P" such as BP-250-D and GP-511-D, etc., that should carry the "L" designation.

LPH 0072532

L - Used with all organic pigments containing 49% or less color, e.g., GL-761-D.

W - Used for aqueous dispersions sold and standardized on a commodity basis, e.g., GW-749-P.

V - Used for aqueous dispersions for the viscose industry, e.g., RV-741-P.

No second prefix letter is used with some codes: chrome yellows
F-113-D
A-133-D

3. Serial Number - Separate serial numbers are applied to each individual color group, e.g., blues, greens, yellows, etc.

4. Suffix Letters- Are used to designate the physical state of the finished product.

D - Dry powder pigment

P - Pulp or aqueous dispersion

R - Used as a second suffix letter indicates standardization for rubber, e.g., RT-663-DR.

5. Process Letters

These letters are used to designate the process used for producing the pigment. When used as a prefix letter, they classify the process as "Experimental." When used as a suffix letter they designate a "Standard" process. With established codes, it is important to know precisely the process letter applying to the particular formula or material referred to.

For example, AYE-698-D is an experimental molybdate orange made on the "A" process. BYE-698-D is a similar experimental product made on the"B" process. Should the BYE-698-D product be reduced to commercial practice, it would be sold as YE-698-D. Internally, the records would show YE-298-D (B) to indicate that the "B" process was used.

6. Standards

PS (followed by a number) is a product standard representing pigment approved by both Marketing and Manufacturing.

TS (followed by a number) is a temporary standard which may be fairly representative of what is being made but may have undesirable qualities which it is hoped to correct.

SL (followed by a number) is a shipping lot, usually a single lot,which has not been established as representative of the material the Plant can make and has not necessarily been approved by Production or Marketing. This designation is used for experimental material which has been made in limited quantity or for emergency use when the standard has unexpectedly been exhausted.

Revised by B.H.Perkins, Oct. 1975

LPH 0072533

IDENTIFICATION OF PIGMENT COLORS

The identification of a pigment is usually undertaken for the purposes of characterizing an experimental or a competitive pigment, in some cases only after the pigment is first isolated from a colored composition.

Reliable and well established wet chemical methods for the systematic analysis of pigments are available. These procedures usually are long and tedious and have been replaced by more rapid instrumental methods which provide results that are reasonably accurate but not absolute. Knowing only the chemical composition of a pigment is not always sufficient for many identification problems inasmuch as the pigment may be polymorphic, i.e., it may have two or more crystal structures that may differ greatly in color and in other properties.

The identification of a competitive pigment is usually based on information which is supplied with the sample (trade name, manufacturer, uses, selling price, properties, etc.), information which is available from standard references, plus spectrophotometric examination, and appropriate spot tests.

The following reference books are especially useful in developing supplementary information:

Colour Index

This five volume work is the joint effort of the British ''Society of Dyers and Colorists'' and ''The American Association of Textile Chemists and Colorists.'' Volumes 1, 2 and 3 list colorants classified according to their usage. Volume 4 lists colorants according to their chemical constitution, and gives lists of intermediate compounds and of formulas. Volume 5 gives code letters for colorant manufacturers, an index of generic names with colorants listed under each, and an index of commercial names of colorants.

Competitive Index

This index lists varnish drier rubout ratings of our best counteroffer-ings versus competitive pigments. The pigments offered by each major competitor are listed by trade name, code, chemical type (when known), degree of match, and comments versus our nearest standard. This condensed summary is based on several thousand comparisons in our files. It is brought up to date as new competitive evaluations are made so that it is a current and useful reference.

Raw Material Index

Pigments Section - published by the National Paint and Coatings Association, Inc. This index lists pigments according to color and chemical type and provides trade names, codes, manufacturers, specific gravity, particle size, etc.

Competitive Price Schedules

These individual manufacturer's lists identify the pigment by code, chemical type, including selling price, and, in some instances, list end-uses and outstanding properties.

CHEMICAL SPOT TESTING

''Spot tests'' are widely used because they are simple, rapid, and require small pigment samples. To run the test, a very small amount of the unknown pigment is added to concentrated sulfuric acid in a depression on a white porcelain spot plate. A portion of this solution is diluted first with water, and then with concentrated ammonium hydroxide until alkaline. Finally, a separate portion of the sample is spotted with alcoholic potassium hydroxide. Characteristic interactions and color changes result. These are compared to the reactions of known standards treated similarly. Additional information may be obtained by observing the sulfuric acid ''spot'' under ultraviolet light since some pigments fluoresce (e.g., quinacridones and basic dyes). Frequently, a pigment can be positively identified by spot testing. In most cases, it can be determined whether the unknown is an individual chemical or a mixture, and establish the types of pigment present.

Principal objections to spot testing are that it is qualitative, considerable experience is needed, a file of reference standards is necessary, it is difficult to discriminate between closely related pigments, it does not distinguish between polymorphs, and mixtures of pigments may be difficult to handle. Furthermore, with a ''sample'' such as a paint panel, the paint vehicle and the primer may interfere with the test.

PHYSICAL METHODS OF IDENTIFICATION

Reflectance Spectrophotometry

Reflectance spectra in the visible portion of the spectrum provide a convenient means for determining the chemical type of a colored pigment. The analysis is non-destructive and may be applied to pigment dispersions such as a paint film, an ink, or a pigmented plastic. A satisfactory identification can frequently be made by a visual examination of the spectrophotometric curve of an unknown and the curves of standard pigments. For complex systems, a properly programmed computer may be used.

Although reflectance spectrophotometry can be used to differentiate between a green and a blue phthalocyanine pigment, there may not be significant differences between the curves of two phthalocyanine blues.

Infrared Spectrophotometry

This is probably the most extensively used instrumental method for the identification of pigment colors, and is based on the fact that every chemical

compound has a characteristic infrared absorption curve. The pigment is identified by a comparison of its I.R. with reference spectra of known colorants. The method is rapid, applicable to pigment mixtures, permits identification of both specific compounds and polymorphic forms, and works well with most organic pigments. It requires the separation of the pigment from the vehicle in which it is dispersed. Difficulty may be encountered in the identification of pigments present in small proportions. An additional problem is that carbon black and some inorganic oxides and sulfides do not give infrared spectra with much identifying detail.

Elemental Analysis

Metallic elements of significant interest in pigment color identification are readily detected by x-ray fluorescence spectrography. The x-ray procedure is rapid, reliable, non-destructive, and does not require isolation of the pigment from the dispersion medium. Emission spectrography is also convenient and extensively used. Equipment for these analyses is located at the Experimental Lab. The results of elemental analysis will indicate the presence of any inorganic pigments which may have escaped detection in spot testing and infrared examination.

X-ray Diffractometry

X-ray diffraction may be used to identify both a specific compound and also its crystallographic modifications. The method is applicable to both organic and inorganic compounds and is of particular value in the identification of inorganic extender pigments. The method is rapid and non-destructive but has the following disadvantages: the weak diffraction patterns characteristic of pigments of low crystallinity may be obscured, some substances may escape detection because of overlapping peaks, and components present in small amounts may go unnoticed.

UV and Visible Absorption Spectrophotometry

Identification of a pigment by the ultraviolet or visible absorption spectrum of the pigment solution has been used widely. A very small quantity is sufficient for identification. The method does not distinguish between polymorphs.

NMR

Nuclear magnetic resonance spectroscopy is of great value in determination of the structure of new pigments. Its judicious use has played a critical role and greatly expedited identification in otherwise very difficult cases.

Mass Spectrometry

This is a very valuable tool in pigment identification. Most pigments are too non-volatile for the usual techniques but modified procedures have yielded much valuable information, such as the chlorine distribution in ''semi-chlor'' CPC. This work is done for us, on a service basis, by the Central Research and Development Laboratory, since the necessary instrumentation is not available within the Pigments Department.

Revised by B.H.Perkins and O/J.C.Klein 1975

LPH 0072536

[redacted]

PIGMENT USES

GENERAL

Pigments are consumed in a variety of applications to obtain decorative or functional effects, or both. In an automotive finish, for example, the pigment provides not only color but contributes significantly to the exposure durability of the paint film itself. Other functional effects achieved by pigments include anti-corrosion, hiding, primer action, and high visibility such as is obtained with daylight fluorescent pigments. The latter are becoming more prominent because of their functional and decorative properties. They are essentially rigid solutions of fluorescent dyes in suitable synthetic resins, which have been reduced to pigmentary particle size. They are used in various printing processes, in textiles, plastics, and safety markings for vehicles and aircraft.

The more important and established uses for pigment products include the coloration of the following materials and compositions:

Surface coating compositions for interior, exterior, trade and automotive applications, including oleoresinous (oil) paints, water emulsion paints, water borne enamels and lacquers. Also, leather and artificial leather finishes, distempers and lime colors.

Printing inks for rotogravure, lithographic and flexographic systems, including inks for metal plate (food, oil cans, etc.), and foil printing, wallpaper, food wrappers, and packaging materials. Also, textile printing inks for clothing, awnings, book cloth, etc.

Paper coloration by coating or beater dyeing, rubber, carbon paper, shoe polish, roofing granules, concrete and cement, ceramics, fertilizer, seeds, cosmetics, laundry bluing, soaps and detergents, asphalt, molding powder, synthetic resins, and wax compositions.

Coloration of textile fibers by mass pigmentation including nylon, viscose, and cellulose acetate, etc.

Plastics including polyvinyl chloride sheet and plastisol top coatings, polyethylene, polypropylene, polystyrene, acrylonitrile-butadiene-styrene, etc.

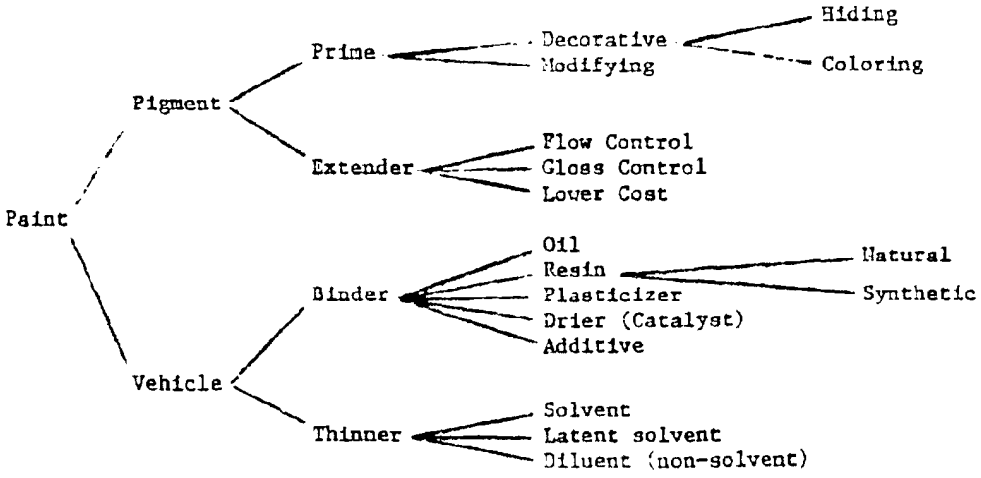
Artists' materials including oils, crayons, chalk, colored pencils, modeling clay, etc.

MAJOR PIGMENT END-USE SYSTEMS

PAINT

More than eight hundred million gallons of paint, worth over two billion dollars at the wholesale level, are sold annually in this country. More than half of all the white pigments made, and half of the pigment colors, are sold to the paint industry.

The composition of a paint is outline below:



DEFINITIONS

1. Paint

A mixture of pigment with a suitable vehicle, which forms a solid adherent covering or film when spread on a surface in a thin coat.

2. Pigment

A finely-divided solid material which, when dispersed in paint, imparts a desirable property such as color, opacity, consistency, or mold control.

3. Prime Pigments

White and colored pigments which are used in paints primarily for their decorative effect and their ability to hide a surface. They operate by the scattering and absorption of light. Some pigments also protect the substrate as, for example, red lead and zinc chromate on iron and steel.

Other pigments have special functional effects, e.g., (a) antimony oxide used in fire retardant paints, (b) cuprous oxide and mercuric oxide for antifouling effects in boat bottom paints (cuprous oxide also controls mold), and (c) zinc oxide which gives greater film hardness, decreases erosion, and inhibits mold growth.

4. Modifying Pigments

For mold control, UV absorption, and film hardening, etc.

5. Extender Pigments

Transparent and colorless pigments or extenders which serve the following purposes:

a. Increase body or consistency.
b. Reduce gloss to a semi-gloss or flat level.
c. Lower cost.
d. Control flooding and floating of prime pigments.
e. Control settling.
f. Provide ''tooth'' for succeeding coats.
g. Improve ease of sanding of primers.

The most commonly used extenders are:

a. Whiting (calcium carbonate)
b. Talc (hydrous magnesium silicate)
c. Calcium sulfate in titanium'calcium pigment
d. Clay (hydrous aluminum silicate)

e. Silica, amorphous and diatomaceous
f. Mica (hydrous potassium aluminum silicate)
g. Barytes (natural ground barium sulfate)
h. Blanc fixe (precipitated barium sulfate)

6. Vehicle

The vehicle (liquid that carries the pigment is usually composed of two parts:

The binder or non-volatile portion, and

The thinner or volatile portion.

Vehicles that are 100% non-volatile are also possible as, for example, "boiled" linseed oil.

7. Binder

The non-volatile portion of the vehicle. This group consists of oils (linseed, soya, tung, castor, etc.), natural resins (rosin, shellac, etc.), synthetic resins (phenolic, maleic, alkyds, polyester, acrylic, styrene-butadiene, epoxy, etc.), plasticizers (dioctyl phthalate, tricresyl phosphate, etc.), driers (metal naphthenates), and other additives.

8. Plasticizers

Plasticizers make a film more plastic or flexible. Many oils and resins form sufficiently flexible films without the need for extra plasticizers.

9. Driers

Driers are required to promote the polymerization, and speed the drying of, oils and alkyds. They are usually added to the paint as the metal naphthenates, although other soluble compounds such as the linoleates, octoates, and tallates are also used.

10. Thinner

Thinners may be solvents for the binder or merely dilute or disperse it. It is a volatile liquid, which reduces the consistency of the paint to a useful level.

11. Diluent

A non-solvent which the vehicle will tolerate, at least up to a certain point, without ''kicking out'' the binder.

12. Latent Solvent

Although ethyl and butyl alcohols will not dissolve nitrocellulose by themselves, they enhance the solvent power of the true solvents.

13. Emulsion Paint

Water-thinable paints. The types of latex emulsions used most extensively in the coatings industry are styrene/butadiene, polyvinyl acetate and acrylic.

ORGANIC FINISHES TERMINOLOGY

1. Alkyd

A term which characterizes generally a wide range of synthetic resins. An alkyd is a condensation product involving a polybasic organic acid such as phthalic or maleic acid and a polyhydric alcohol such as glycerine and glycols, usually with the addition of a modifying and plasticizing agent such as linseed, soya, or tung oil. Examples include Syntex 26, Syntex 62,* Syntex 3145, Aroplaz 2502, etc. Melamine formaldehyde resins are added to alkyds to improve curing speed, wrinkling resistance, and hardness without interfering with adhesion and durability.

2. Lacquers

A solution of polymer in a suitable solvent to which plasticizers and resins may or may not have been added. There are many kinds of lacquers, viz., nitrocellulose, cellulose acetate, methyl cellulose, acrylic, among others. Lacquers contain a relatively high amount of solvent and dry primarily by evaporation.

3. 30J Type Alkyd

Baking vehicle consisting of non-drying oil alkyd blended with 15% or more of melamine resin is referred to also as ''Super Alkyd'' or as the F and F product, ''Dulux 100.'' The 30J formulation used by Newark R & D consists of Syntex 3145/Cymel 248-8, 70/30 on the vehicle solids basis.

4. 32J Acrylic Enamel

Thermosetting acrylic vehicles crosslinked with melamine are important exterior finishes because of their combination of appearance, hardness, chemical resistance, and durability characteristics. 32J is seldom used anymore in R&D evaluations.

Commercially used automotive thermosetting acrylic vehicles are proprietary products although similar materials are available from suppliers such as Rohm and Haas, Union Carbide, and Archer-Daniels-Midland (ADM).

The formulation used by Newark is Aroset 777 (ADM), an alkyd modified hydroxyl-type thermosetting acrylic polymer crosslinked with Cymel 243-3, a melamine formaldehyde. Aroset 777/Cymel 243-3, 70/30 on the vehicle solids basis.

* Aroplaz 1082 M-50 has replaced Syntex 62.

5. TAE-4

This terminology is used by Newark Research and Development for a thermosetting acrylic enamel consisting of an unmodified hydroxyl type thermosetting acrylic polymer crosslinked with a melamine formaldehyde.

Newark's current formulation is: D-4221-A_2/D-4214M, 70/30 on the vehicle solids basis. These are Chrysler vehicles obtained through Chestnut Run. Ford's thermosetting acrylic enamel is based on the resins A-8599/A-35106:70/30 on vehicle solids. These vehicles are obtained from Ford.

Note: Thermosetting acrylic enamels combine the attractive properties of thermoplastic acrylic lacquer (durability, chemical resistance, good aging and weathering properties, color retention) with increased hardness, stain resistance, washability.

6. Thermoplastic Acrylic Lacquers - ''Reflow'' Lacquers

Currently used by General Motors for automotive finishes. They consist of acrylic co-polymers with cellulose acetate butyrate and plasticizers. These finishes can be ''reflowed,'' i.e., an item can be spot repaired and simply rebaked to obtain good gloss without repainting.

The system used by Newark and Chestnut Run is designated 926 - 927 lacquer and ' is representative of the type supplied by F and F to General Motors.

Note: CAB chipping is necessary to obtain maximum transparency and/or intensity with some pigments. Sand milling is less costly and preferred whenever adequate color properties can be developed.

A more detailed general discussion on paints including a bibliography appears in Section 15 of the Sales Training Manual. Other specific types of paints and finishes including trade sales finishes, emulsion paints, industrial and automotive finishes, trim enamels, metal protective finishes, etc., are described elsewhere in the Sales Manual.

Edited by B.H.Perkins, 1975

PLASTICS

Plastics have developed rapidly into a large and diverse industry. Although vinyl, polystyrene and the polyolefins are still the major resins of the industry, others are finding increasing use because of particular properties and advantages which they offer. Each of these systems is characterized by a set of formulating, processing and end-use conditions which determines to a large degree the pigment properties required.

PLASTIC SYSTEMS

Plastics are synthetic materials which are solid in the normal finished state, but which have sufficient fluidity at some stage of manufacture to permit their forming under heat and/or pressure. In addition to molded and extruded forms, plastics can be made into film, sheeting, filaments, coatings, and foams. They are also used as an integral part of many paints, elastomers and adhesives, and as a laminant or impregnant for other materials.

Plastics are classified as either thermoplastic or thermosetting. Thermoplastics become soft and fluid when heated sufficiently, and harden again when cooled, whereas thermosetting materials become permanent in shape when first cured and cannot be re-formed by further heat or pressure. Chemically, both types are highly polymerized materials, the thermoplastic being primarily a linear polymer with little, if any, cross-linking, and the thermoset being a product that cross-links upon curing.

Thermoplastic	Thermosetting
Vinyls	Phenolics
Polystyrene	Amino plastics
Polyethylene	Polyesters
Polypropylene	Epoxies
Polyamide	Silicones
Fluorocarbons	Alkyds
Acrylics	
ABS (acrylonitrile-butadiene-styrene)	
Acetal	
Cellulosics	

PIGMENT PROPERTIES OF IMPORTANCE

Pigments selected for use in any system must satisfy processing as well as end-use requirements. In plastics, the processing requirements can be particularly rigorous and may severely limit the number of pigments available for such use. Pigment properties of importance in each category are as follows:

Processing	End-Use Application
Heat stability	Color, strength, cost
Dispersibility	Lightfastness
Chemical resistance (reactivity)	Crocking and migration
Effect on rheology	Chemical resistance
	Heat stability
	Electrical conductivity
	Toxicity

End-use properties such as color, strength, cost, lightfastness, and crocking might appear to be inherent qualities of a pigment/resin system and independent of the processing conditions. However, dispersion can have a marked effect on the color and strength (hence, cost) obtained. Poor dispersion can also degrade the physical properties and lead to early failure on outdoor exposure as a result of inadequate protection of the resin. A pigment or any other ingredient having borderline heat stability can adversely affect color, lightfastness, and resistance to crocking.

Heat stability is perhaps the most important single property to be considered in the selection of pigments for the coloring of a plastic. Thermoplastics are generally processed at temperatures ranging from 300 to 700°F., and products made from them may be used at temperatures of 200°F. and higher. The period of time that the pigmented plastic is held at these temperatures can be critical. Thermosetting resins are generally processed at moderate temperatures but may be used continuously at high temperatures. "Hot spots" in the processing equipment and processing delays which extend the time which the material is held in the molten condition are common sources of difficulty. The heat stability of a pigment is likely to vary from one resin system to another because of differences in the chemistry of the respective systems and the conditions of processing. Heat instability arises from inherent pigment instability, pigment interaction with the plastic, or pigment solubility in the plastic.

The chemical resistance required in ultimate application usually differs significantly from that required for processing. The oils, solvents, and chemicals, etc., with which a finished product might come in contact can be predicted with fair reliability and the pigments then selected on that basis. However, a large variety of plasticizers, stabilizers, anti-oxidants, catalysts, lubricants, etc., might be encountered during processing, the presence of which might be either unknown or undisclosed. Furthermore, the resins themselves can become strongly active chemically under the processing or curing conditions.

A more extensive description of plastics and their pigmentation including processing equipment and a bibliography will be found in Sections 29 and 30 of the Sales Training Manual.

PRINTING INKS

The modern trend in printing, particularly in the packaging and advertising field, is toward the use of more color, thereby creating a demand for brighter and stronger pigment colors for the manufacture of printing inks. In addition to intensity and strength, demand continues for greater durability, i.e., better light stability, greater resistance to chemicals and heat, and greater resistance to bleed in water, edible fats and greases, solvents, oils, etc. These needs come as a result of the development and use of new vehicles, new applications, particularly for the food packaging field, expanded use of printing in metal decorating, the use of heat-set inks, and the general overall increase in printing production from the various printing processes. In addition to these demands involving the end-use characteristics of the printed material, there are the needs of the ink maker. His demands generally are for colors that are softer in texture and more readily wet with vehicles so that they may be more easily ground and dispersed.

A printing ink is essentially a dispersion of pigments in a vehicle with other materials added to impart specific properties. The vehicles used can be aqueous or non-aqueous and they include a great variety of materials. An ink must possess rheological properties suitable for the specific type of printing press used and suitable to the material being printed. The ink must print sharply and meet the drying time requirements of the printer.

Printing inks are classified basically into three types:

1. Typographic or letterpress inks
2. Planographic or lithographic inks
3. Intaglio or gravure inks.

Typographic printing is done from a raised surface, lithographic printing from a plane surface, and gravure printing from a recessed surface.

Detailed descriptions of the various printing processes and of printing inks are given in Section 28 of the Sales Training Manual.

Colorants consumed by major plastics groups

Market	Resin containing colorants, 1,000 metric tons '74	'75	Compound, % '74	'75	Dry color,[a] % '74	'75	Concentrate % '74	'75	Total colorants consumed, metric tons[b] '74	'75
Low density PE										
Blow molding	26.00	15.60	8	6	12	10	80	84	426	258
Coatings	25.00	20.00	20	15	Nc	N	80	85	963	770
Film	376.00	300.00	8	7	N	N	92	93	12,900	10,320
Sheet and profiles	6.80	5.00	11	10	N	N	89	90	410	300
Injection molding	370.00	260.00	12	10	40	38	48	52	3,170	2,220
Wire and cable	197.00	120.00	23	20	14	13	63	67	2,450	1,470
Others	260.50	208.00	27	25	14	14	59	61	2,400	1,920
Total	1,261.20	928.60							22,719	17,258
High density PE										
Blow molding	480.20	430.00	12	10	8	8	80	82	5,160	4,600
Injection molding	265.50	175.00	24	22	34	34	42	44	2,760	1,730
Pipe and profiles	99.75	85.00	60	58	20	21	20	21	1,440	1,190
Wire and cable	30.00	20.00	56	54	18	18	26	28	244	180
Others	144.30	115.00	36	35	33	33	31	32	1,320	1,120
Total	1,019.75	825.00							10,924	8,820
Polyvinyl chloride										
Calendering	588.20	350.00	N	N	50	48	50	52	12,960	7,750
Coatings	293.50	200.00	9	8	45	44	46	50	6,098	4,288
Extrusion	648.00	486.00	6	4	46	46	48	50	9,540	7,155
Molding	238.00	166.00	15	12	58	58	27	30	2,450	1,710
Others	228.50	158.00	2	2	74	74	24	24	2,520	1,810
Total	1,994.20	1,380.00							33,566	22,701
Polystyrene										
Injection molding	593.00	410.00	16	14	48	47	36	39	7,020	4,910
Sheet extrusion	317.50	228.00	38	36	22	22	40	42	9,840	6,870
Others	408.00	288.00	30	30	50	51	20	19	4,800	3,360
Total	1,318.50	926.00							21,660	15,140
Polypropylene										
Injection molding	497.50	350.00	20	15	33	33	47	52	6,060	4,240
Multi/monofilaments	236.40	165.00	4	2	N	N	96	98	2,520	1,760
Sheet extrusion	8.00	6.00	82	82	N	N	18	18	210	158
Others	75.50	54.00	35	34	10	11	55	55	1,260	980
Total	817.40	575.00							10,050	7,138
ABS										
Injection molding	120.50	72.00	43	40	12	12	45	48	2,340	1,400
Pipe extrusion	70.00	42.00	60	59	5	5	34	36	1,260	890
Sheet extrusion	80.00	45.00	50	48	5	5	45	47	1,445	940
Others	29.00	17.00	49	48	5	5	46	47	1,820	870
Total	299.50	176.00							6,865	4,100
Grand total	6,710.65	4,790.60							105,584	75,157

Source: Modern Plastics and industry estimates.

a—Includes nondusting colors, paste dispersions, liquid systems, etc.
b—Ratio colorant/lb. of resin varies from 0.5 to over 5%. Average is about 1.25%.
c—None or negligible.
d—Accounts for roughly 75% of total colorants in plastics.

offering from this supplier is Permanent Red TG-01, a vat red cited for good weatherability and heat stability to 550° F. Price tag of $3.95/lb. makes it a good replacement for more-expensive high-performance reds for PP fibers and PS molding compounds.

New dyes include American Color & Chemical's recently broadened Amaplast line, consisting of 100% oil soluble azoics and anthraquinones. They're claimed to exhibit good thermal and light stability, to be easily dispersed, and to yield good transparent and opaque shades in styrenics, acrylics, nylons, PC, polysulfone, thermoplastic polyester, and other resins.

Also new, from Dayglo, are three fluorescent yellow dyes priced in the $10.50 to $13.50/lb. range. These colors are said to be compatible with styrenated materials and to offer cost savings over stronger and more expensive dyes.

To date, post-process dyeing of plastics parts has been a specialty of a few custom shops, like Colorite Industrial Dyers of New York, but a new three-step process offered under license by Hooker Chemical (Niagara Falls, N.Y.) may change this situation. The three steps: 1) surface sensitizing of the plastic with solvent, 2) insertion of a reactive chemical into the surface, and 3) reaction of the chemical with a dye. Claimed to offer significant economies in coloring PE, PP, PS, ABS, PVC, nylons, and various other plastics, test parts reportedly have been abraded on a Tabor unit to a depth of 1 mil without exposing the natural matrix.

Pricing: a mixed bag

Compared with this time last year, inorganic colorant prices are relatively stable. Lists remain unchanged since June '74 (see Sept. 1974 MPI, p. 58), with three exceptions: the cost of chrome yellows and AR type blues has declined 3¢ and 10¢ to 63¢ and $1/lb., respectively, while that of TiO_2 advanced $3^1/_2$¢/lb. to $43^1/_2$¢/lb. early in August. This last could mean an increase in concentrate pricing in late '75 or early '76.

For organics, the situation is different, with pigment prices up across the board, but not as drastically as last year. Two exceptions are dianisidine orange and DNA orange, down 25¢ and 30¢ to $4.75 and $3.45/lb., respectively. Increases on Bon reds, diarylide yellows, lithol rubines, 2B reds, phthalos, and others range from 7 to 33%.—*A.S.W.*

[redacted]

[redacted]

PIGMENT STANDARDIZATION

Pigment product standardization, a vital and necessary factor in the pigment industry, takes into consideration the enduse application for which the pigment is intended. Because of the complexity of the product, pigments can be standardized only in terms of performance, color, durability, and working properties, and, often, only for the specific application or vehicle system for which the pigment is intended. A given pigment type may be dispersible in one system but poorly so in another and exhibit different durability and even color from one system to another. It is for such reasons that a given pigment chemical type will often appear on the market in a variety of forms, each designed to suit a specific vehicle system or condition of use.

Because of the inadequacy of existing techniques, the required functional properties of a pigment cannot always be described adequately in terms of the basic chemical structure and physical properties. Standardization of product is most effectively and economically achieved to a major degree by careful control of the manufacturing process insofar as economics permit in a competitive industry. A partial listing of the pigmentary and working properties which may require standardization by the pigment manufacturer in addition to hue is as follows:

1. Tinctorial or tinting strength.
2. Dry fineness.
3. Texture (grit, ease of dispersion, rate of strength development).
4. Specific gravity, dry bulk.
5. Oil absorption.
6. Solvent bleed.
7. Dusting characteristics.
8. Dry appearance.
9. Wetting characteristics.
10. Hiding power (opacity or transparency).
11. Rheological behavior in different vehicles.
12. Thixotropy.
13. Storage stability.
14. Crystal growth or change in solvents.
15. Combustibility.
16. Moisture and volatile matter.
17. Hygroscopic tendencies.
18. Water-soluble salts.
19. Lightfastness.
20. Gloss in paint.
21. Flocculation in paint.

The list for pigment standardization can be expanded for a variety of application systems to meet the specific needs of these systems. Workable pigment product standards which specify properties in terms of acceptable ranges or limits and permissible deviations are established by the pigment manufacturer only insofar as they can be practically achieved in large scale manufacture and are acceptable to the pigment user. The problem is complicated by the fact that the physical differences corresponding to the desired tolerances are not always easy to define nor, as in the case of durability and working properties, are they always subject to quick or accurate measurement.

For discussion of the various types of standards (PS, TS, SL) see Section 23 Page 4.

Revised by B.H.Perkins 1975

PROCESS SCALE-UP

Scale-up of a process furnishes data and experience that will aid in the difficult transition from the research laboratory to a commercial plant. This scale-up is accomplished in a pilot plant or semi-works.

As opposed to a full scale production plant, the pilot plant's primary objectives are to obtain experimentally both operating and equipment data for a new process, produce a new product in experimental quantities for study or for trade sampling, or to do any combination of these functions on any product or process whether new or already in existence.

The necessity for process scale-up in a pilot unit arises for the following reasons. First, the chemical data available cannot always predict with accuracy the effect on a chemical process when the process batch size is increased manifold. The pilot unit which is intermediate in size between the laboratory and the production plant serves to test the theories and data obtained in the laboratory. It is almost impossible to design a large complex plant from laboratory data alone. Second, there is the need to produce larger amounts of the final product under conditions more likely to approximate those that will be encountered in the large scale plant so that its properties and uses may be critically examined. Third, many industrial processes produce considerable quantities of wastes so that disposal problems must be examined. The research chemist's apparatus is not always large enough to discover small amounts of such undesirable by-products. Problems not apparent on a small scale will often reveal themselves under the conditions of scale-up.

It is important to try a new process in a model of the proposed plant before committing large sums of money on a production unit. It has been quoted many times, "Make your mistakes on a small scale and your profits on a large one."

The Newark Semi-Works facilities include experimental units for testing processes in selected equipment. The individual pieces of equipment are available for the development and improvement of processes and procedures. A brief description of the various pieces of equipment now located at the unit process facilities follows. More detailed descriptions of the individual units available at Newark and at Newport appear in Section 28.

1. Reactors

These vessels, either glass-lined or of stainless steel, are used to carry out chemical reactions in liquid media, either organic or aqueous.

2. Vats

These vessels are used for the storage and processing (preparation of solutions, aqueous extractions, etc.) of solids in aqueous media.

3. Filter Press

This equipment is used for the separation of solids from aqueous slurries and is effected by passing the liquid through a porous medium (filter cloth, etc.). The solids are retained on the surface of the filter medium in the form of a cake.

4. Shriver Thickener

This equipment operates on the principles of thickening and filtering. The slurry is drawn through a filtration medium whereby it is dewatered to a large degree and then back to the storage vat. The solid material in all cases is discharged as a thick sludge rather than as a filter cake. If salt removal is desired, the water removed through the filter medium is replaced by water in the storage vat and the slurry recirculated.

5. Pressure Nutsche

Similar to the ceramic nutsche except that it is enclosed and operates by application of a gas pressure (generally nitrogen) above the filter medium. Application is limited to slurries which will not corrode stainless steel.

6. Super-Centrifuge (Now in Physics Lab, #28 Bldg.)

A centrifuge is designed to subject material, held in it or being passed through it, to a centrifugal force. The Sharples ''super-centrifuge'' is capable of obtaining speeds up to 50,000 rpm and is used to make liquid-solid or liquid-liquid separations. The particle size of the fraction separated depends on the speed (rpm) and flow through the equipment.

7. Ball Mill

These mills have a cylindrical shell and rotate on a horizontal axis. They are used to reduce the particle size of solid materials. The mills are charged with a grinding medium such as steel balls, porcelain balls, or steel rods. The mill accomplishes size reduction by impact, shear, and attrition during the rotation of the mill. The mill may be operated dry or wet.

8. Colloid Mill

The mill accomplishes size reduction (dispersion) by gravity feed of the slurry through a narrow opening between two surfaces that move at high speed with respect to each other. The smallest opening is in the order of 0.001 in. The whirling currents set up within the mill subject the product to both hydraulic shear and impact.

9. Homogenizer

The homogenizer is used to put incompatible or immiscible components into a stabilized suspension in a liquid medium. It functions by passing the product under pressure between close but relatively fixed surfaces. The high velocity, hydraulic shear, pressure release, and impact render the dispersed phase into a very fine state of subdivision of the order of one micron in diameter.

10. Tray Dryers

One type of batch circulation dryer, in which heated air circulates over the wet material until the latter reaches the required moisture content. The granular material, pastes, or slurries to be dried are placed in trays which are supported by stationery or movable racks in the dryer.

11. Vacuum Dryer

A type of shelf dryer consisting of a vacuum-tight chamber with heated shelves. Volatile material is removed by applying vacuum to the material being processed. The vacuum dryer is useful either for removing highly volatile material at low temperatures or for removing high boiling material at elevated temperatures but below the boiling point of the volatile material being removed.

12. Abbé-Lanart Mixer

This equipment is used to process slurries too thick to stir, but capable of flow. A high-speed centrifugal impeller at the bottom of the vessel circulates the charge. It is used for breaking down press cakes with minimum dilution, making additions to thick slurries, and incorporating solids into thick slurries.

13. Baker-Perkins Mixer

This equipment uses relatively slowly rotating, intermeshing horizontal blades to agitate very thick slurries or taffy-like masses. Heating or cooling can be achieved by circulating the appropriate heat-transfer liquid through the jacket surrounding the mixer.

14. Mikropulverizer

This is a hammer mill used for the grinding of dry materials. The grinding action results from impact and attrition between lumps or particles of the material being ground and the grinding elements.

15. Flash Distillation Unit

This unit is used for the continuous removal of a volatile solvent from an aqueous slurry, by allowing the superheated slurry (steam) to flash in a cyclone. This removes the volatile portion which is condensed, while the stripped slurry exits through another outlet.

16. Parr Hydrogenation Apparatus

This equipment can be used for hydrogenation up to 60 psi and 100°C. Hydrogenation is carried out in glass bottles of about 400 ml. maximum capacity.

17. Carius Furnace

A furnace for heating sealed glass tubes under autogenous pressure. Maximum temperature approximately 300°C.

18. Autoclaves

Several autoclaves are available for heating materials under pressure and with agitation. Maximum pressure is 5000 psi; maximum temperature is 650°F.

Revised by ROM and BHP in 1975

SEMI-WORKS FACILITIES

NEWARK SEMI-WORKS

1. General

The Newark Semi-Works facilities are located in Buildings #14, #116, #117, and #118. These facilities were established to provide experimental units for operating in appropriate equipment. The individual pieces of equipment are available for studies by all R & D personnel and associated groups engaged in the development and improvement of products, processes, procedures, and equipment.

Arrangement can be made to use these facilities through the R & D Supervisor of the New Inorganic, Services and Physical Chemistry Group or, for conventional uses of the type done routinely, arrangements may be made with the R & D Group Supervisor in immediate charge of the area. For control purposes, a written request for the authorization of studies in these facilities is required.

2. Facilities

The Semi-Works equipment and location are as follows:

Reactors and Tanks

Vat No.	Location	Type	Size	Description or Use
15	14 Bldg.	Glass lined	100 gal.)	Jacketed for Dowtherm,
110	"	" "	100 ")	Steam or
111	"	Stainless steel	100 ")	Water.
29	"	" "	100 "	Jacketed for steam heat.
106	"	" "	370 "	" " " "
9	"	Tile lined	152 "	Sparger steam extract.
11	"	Carbon Brick Lin.	283 "	" " "
97	"	Stainless steel	107 "	Cooling water supply
96	"	" "	54 "	Portable, On dolly.

Filtration Equipment

Type	Location	Size and Use
Bronze Filter Press	14 Bldg.	16 frames at 0.135 cu.ft./frame Total capacity 2.16 cu.ft. For neutral or slightly acid filtration and washing.

Type	Location	Size and Use
FRP Filter Press	14 Bldg.	12 frames at 0.180 cu.ft./frame Total capacity 2.16 cu.ft. For neutral, slightly alkaline, and strongly acid filtrations and washing.
Shriver Thickener Press	''	12 plates. Used for washing or thickening slurries.
Stainless Steel Nutsche	''	100 gal. capacity. For pressure filtering and washing of hot solvent mixtures. Teflon cloth.

Ball Mills - All mills located in 14 Bldg.

Size	Type	Use:
58 gal.	Steel	Charged with 1000 lbs. of 1'' X 5/8'' cylpebs and 100 pounds 20 penny nails for dispersion or dry milling. Mill is jacketed for heating or cooling.
58 gal.	Steel	Charged with 951 lbs. of ''Wheelabrator'' 1/8'' Steel shot. This charge is used for solvent milling. Mill is jacketed for heating or cooling.

Note: The dispersion mill has a Reeves drive to vary rotation speeds from approximately 18 to 98 RPM. Normal speed is 40 RPM. The solvent mill has a fixed speed of 39 RPM.

Dryers

Name	Location	Capacity	Use
Gordon-Davis (Low Velocity)	14 Bldg.	40 Stainless Steel pans 30'' X 30'' X 1-1/2''	For drying water wet press cake.
Vacuum Dryer (Stokes)	14 Bldg.	15 Stainless Steel pans 30'' X 30'' X 1-1/2''	For drying solvent wet cake.

Pulverizer

Size	Type	Conditions
5''	''Mikropul'' hammer mill	Regular (Low) speed normally uses 1/8'' round perforated screen. High speed normally uses 0.066'' round perforated screen. Other size screens are available.

LPH 0072554

Homogenizer

Type

Manton-Gaulin 15M 8TBA SMD 15 gallon per hour rated capacity.
0 to 7,500 PSI operating range.

Colloid Mill

Type

Manton-Gaulin Type 2F, rates vary according to disc opening.

Hydroclone

Type

Baur Bros. Centri-Cleaner with 3/4'' inlet and outlet.

Mixer

Type

Abbe-Lenart, Capacity 22 gallons, Stainless steel construction.

The following pieces of equipment are available for high pressure reactions in our No. 118 Pressure Research Building.

Parr Hydrogenation Apparatus

For hydrogenations up to 60 psi and 100°C. Hydrogenation is carried out in glass bottles of about 400 ml. maximum capacity. These operations are set up and carried out by laboratory personnel.

Carius Furnace

A furnace is available for heating sealed glass tubes for autogenous pressure. Maximum temperature is approximately 300°C. This operation is also carried out by laboratory personnel. Attention is required only to load tubes and assure temperature stability.

''Magnedrive'' Autoclave

A stainless steel autoclave, turbine agitated, maximum usable capacity of 1/2 liter, is available for heating materials under pressure. Maximum pressure of 5000 psi and maximum temperature of 343°C. are the operating limits. This equipment can be set up and run by either Laboratory or Semi-Works personnel. Operation usually requires continuous operator attention.

Magnedash Autoclave

A monel autoclave, dasher agitated, is available for heating materials under pressure. Maximum pressure of 5,000 psi and maximum temperature of 343°C. are the operating limits. Maximum usable volume is 150 ml. Operation by either Laboratory or Semi-Works usually requires constant operator attention.

PROCESS ENGINEERING (MANUFACTURING DIVISION)

The Research and Development Division maintains close liaison with Process Engineering at Newark and its counterpart at Newport. The principal functions of Process Engineering, a division of Product Control, Manufacturing Division, are as follows:

1. Monitor and Control Quality and Yield of All Production

- Issue making/processing instructions for each batch or campaign.
- Develop and apply process variables.
- Determine process goal yields.
- Improve ''OK Straight'' performance.
- Assist Operations on processing problems.
- Provide code to code cleaning requirements for all operating equipment for use in setting up production schedules.
- Provide the plant with safe, reproducible processes.
- Provide finished product blending guides for use by the Color Testing Laboratory in standardizing production.
- Act as a clearing house for all operating equipment changes.
- Participate in operating quality investigations.
- Assist the Color Testing Laboratory in standardizing production.
- Spot check operating areas for adherence to specifications.

2. Control Quality of Raw Materials

- Develop raw material specifications in conjunction with suppliers.
- Develop alternate and/or more economical sources of raw material supply.
- Evaluate raw material pre-shipment samples.

3. Develop and/or Assist in Plant Development of New Products and Processes

- Develop new or improved products as requested by Marketing.
- Maintain close liaison with R + D activities and assist in bringing new processes into the plant.
- Assist in development of scope of work for new projects.

4. Reduce Costs Primarily through Technical Studies

- Participate in plant cost reduction program.
- Reduce process ingredient, utility, and labor cost.
- Develop most economical process batch size.

5. Miscellaneous

- Develop customer finished product specification in conjunction with Marketing and Area Supervisor-Color Control.
- Select components and guide formulation of representative finished product replenishment or replacement standards.
- Train operating supervision on quality control activities and on pigment technology.

Revised by D.C.Gero 1975

RAW MATERIAL ''N'' CODES

The ''N'' code system was designed to facilitate the use, storage, and accounting of approximately one thousand raw materials used on the Newark plant. The system was devised to eliminate the need for the operator or technician to know the chemical identification of the material being used, and thus minimize the possibility of confusion resulting from the misinterpretation of complicated chemical names. This ''N'' number system also fits in well with the concept of a stepwise formula and the IBM accounting system now in use on this plant.

''N'' numbers are assigned in numerical sequence disregarding composition or use of the material. The number is stencilled on each package and, in general, is put on by the supplier. A periodic review of the ''N'' number assignments point out numbers of materials that are no longer required on the plant. When materials are obsoleted, the ''N'' number is returned to the available pool for reassignment. A complete ''N'' code file, including specifications for the material, is maintained in the ''vault'' (2nd floor, #23 Building). Information on Newark N-codes can be obtained from Mary Magyar, Ext. 249. Newport N-code information (as of 4/1/75) is included in Tables I, II, and III.

In addition to the number, the ''N'' code at Newark includes an alphabetical suffix (N-3-A, N-16-B, N-27-D, etc.) designed to classify the raw materials into safety categories by type of hazard involved and the precautions necessary in their handling. The categories are as follows:

A - Minimum Hazard

B - Internal Poison

C - External Poison

D - Corrosive Material

E - Flammable or Explosive Material

A more complete discussion of this safety classification system and the personal protective equipment required for handling materials in different categories may be found in Appendix A of the ''Newark Safety Code.''

Revised by J.F.Maurer

LPH 0072559

TABLE I

NEWPORT QA CODES

TYPE	CODE
Gamma	7402
Beta	7403
Maroon	7409
Scarlet	7410
Pink	7455
Maroon B	7423
Magenta	7447
Trans. Red	7458
Trans. Red B	7427
QAAF	7031
QAQ	7044
QAQ (NNF)	88
QADS	99
QAMS	100

TYPE	CODE
Gamma	7102
Beta	7103
Beta	7105
Maroon	7109
Scarlet	7110
Maroon B	7123
Maroon + AQD	7154
Pink	7155
Gamma Lake	7202
Trans. Red	7058
Maroon B (AQM)	7126
Trans. Red B	7127
QAAF	7031
HTG Untr.	7638
HTG + $NiCO_3$	7161
Violet (KRO)	7042
Violet (Plas.)	7643
Magenta (AQD)	7049
HTG	7137
Orange	7150
Deep Gold	7152
Orange + AQD	7250
Violet (30-J)	7056
Violet	7059

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LPH 0072560

TABLE II

NEWPORT CPC CODES

Blue			Green		
Type	Code	Description	Type	Code	Description
BB	Crude		GB II	Crude	
LC	Crude		GG II	Crude	
BBF	Crude		GE III	Crude	
BBX II	8500	Breached Blue B	GBU II	8000	GB Crude
BBX III	8530	HTD	GGX II	8100/ 8101	Breached GG
BBS II	8510	Solv.Mill.Blue B	GEX III	8103/ 8104	
BB III	8540	HTD			
BB III	8521	HTD	GYX III	8201	Brominated Green
BBFS II	8551	Solv.Milled BBF			Breach
BBFS II	8552	Solv.Milled BBF + "Elvacite"	GGU II	GT-801-D	Dry GG Crude
BBF III	8550	HTD	GGU II	GT-827-P	Press cake GG crude
BGS II	8600	Solv.Milled LC	GYU III	GT-824-P	Press cake GY crude
BRA II	8802	Acid Swelled LC	GEU III	GT-826-P	Press cake GE crude
BRA III	8810	HTD			
AFA II	8900	Complex (Swelled)	GGX III	GT-822-P	Breached GG
BBU II	8520	BB Crude			
LC I	BT-443-D	LC Crude			
BGD II	8700)	Dispersion milled, extracted			
BGD II	8710)				
BGD II	8730)				
BGD II	BT-436-P)				
BGD II	BT-487-P)				
AFA II	BT-474-P	Complex Swelled			
BB III	BT-481-P	HTD			
BRA III	BT-401-P	HTD			
BGD III	BT-282-P	Hi Solids			
BRA III	BT-483-P	Hi Solids			
BGS III	BT-485-P	Hi Solids			
BB III	BT-486-P	Hi Solids			

Revised by J.F.Maurer

LPH 0072561

TABLE III

''AFFLAIR'' CODES

Lot Series	Code	Name	Semi Fin. Code
1000	NF-103-D	Gold	9926-02-080
2000	NF-104-D	Pearl	081
4000	NF-108-D	''	984
	NF-109-D	''	
7000	NF-134-D	Improved Pearl	088
8000	NF-135-D	Satin Pearl	089
9000	NF-137-D	Improved Pearl	091
14000	NF-138-D	Ultra Luster Pearl	092
10000	NF-139-D	Gold	093
11000	NF-140-D	Deep Gold	094
None	NF-141-D	High Luster Pearl Base	095
12000	NF-142-D	Glimmer (Pearl)	096
13000	NF-143-D	Tex. (Pearl)	097
18000	NF-145-D	Green	099
15000	NF-146-D	Autopearl	100
	NF-147-D	High Luster Gold (Ultra Luster Gold)	101
16000	NF-148-D	Humidity Resistant Gold	102
17000	NF-149-D	Blue	103
	NF-150-D	Blue	
	NF-151-D	Green	105
19000	NF-152-D	Flash	
	NF-153-D	(No Std.) Obsolete	
3500	NF-154-D	Pearl	
6000	NF-155-D	New Satin	
	NF-156-D	Glimmer (Ultra High Luster)	
5000	NF-157-D	Deep Gold	
12500	NF-158-D	Ti-100-FK	
1500	NF-144-D	Deep Gold + 30% Mica	
5500	NF-109-D	NF-108 + 1% Ultra Marine Mixture	

Prepared by J.F.Maurer

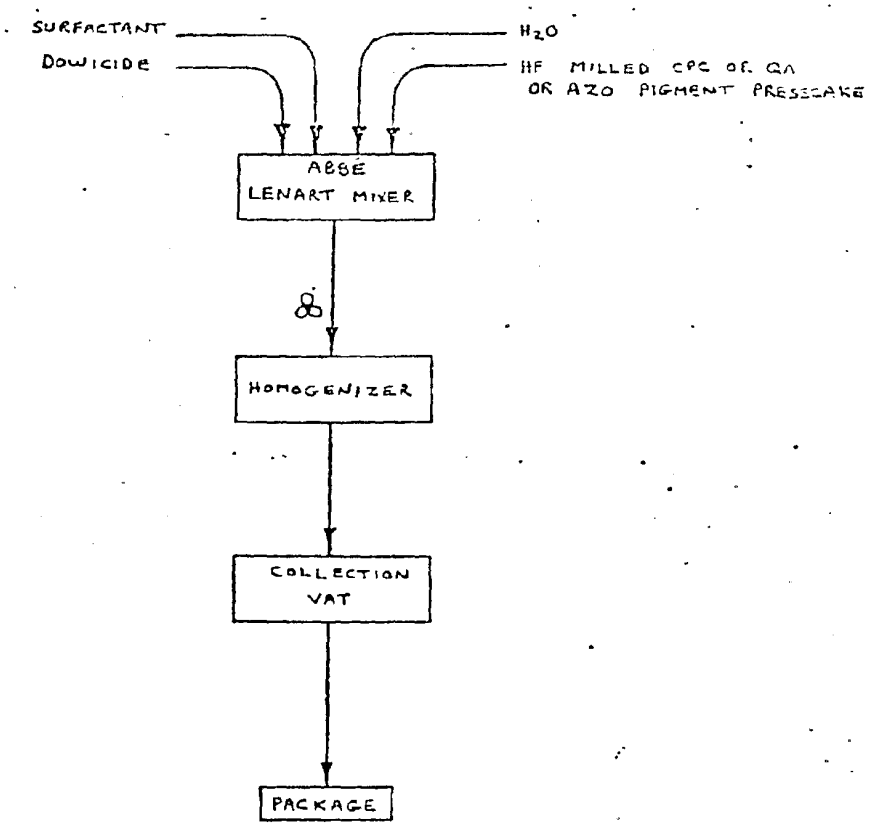
LPH 0072562

NEWARK PLANT

SKETCH #1

DISPERSED PASTE PROCESS

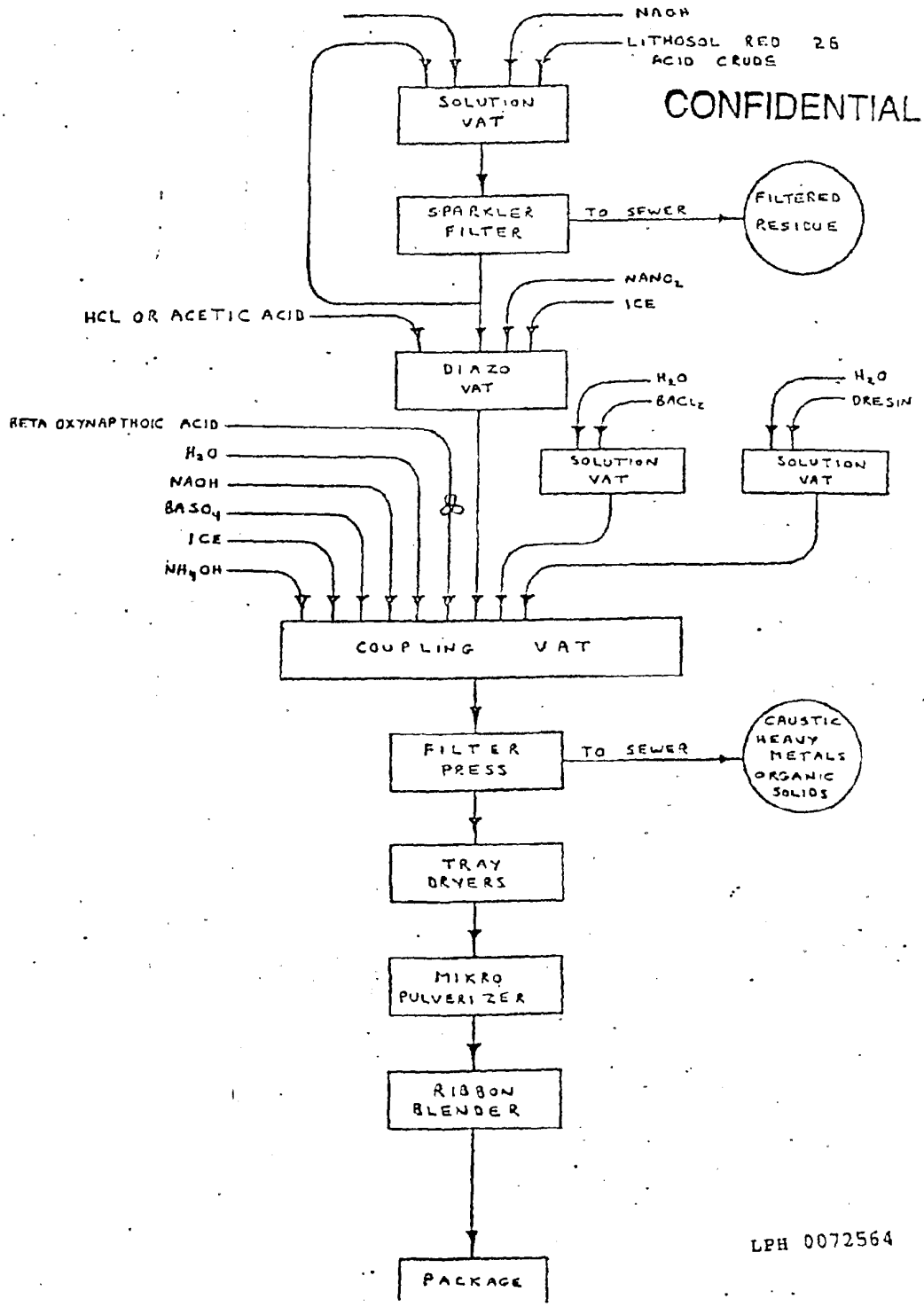
CONFIDENTIAL



LPH 0072563

NEWARK PLANT — SKETCH #2

ORGANIC AND PIGMENT FACILITIES



CONFIDENTIAL

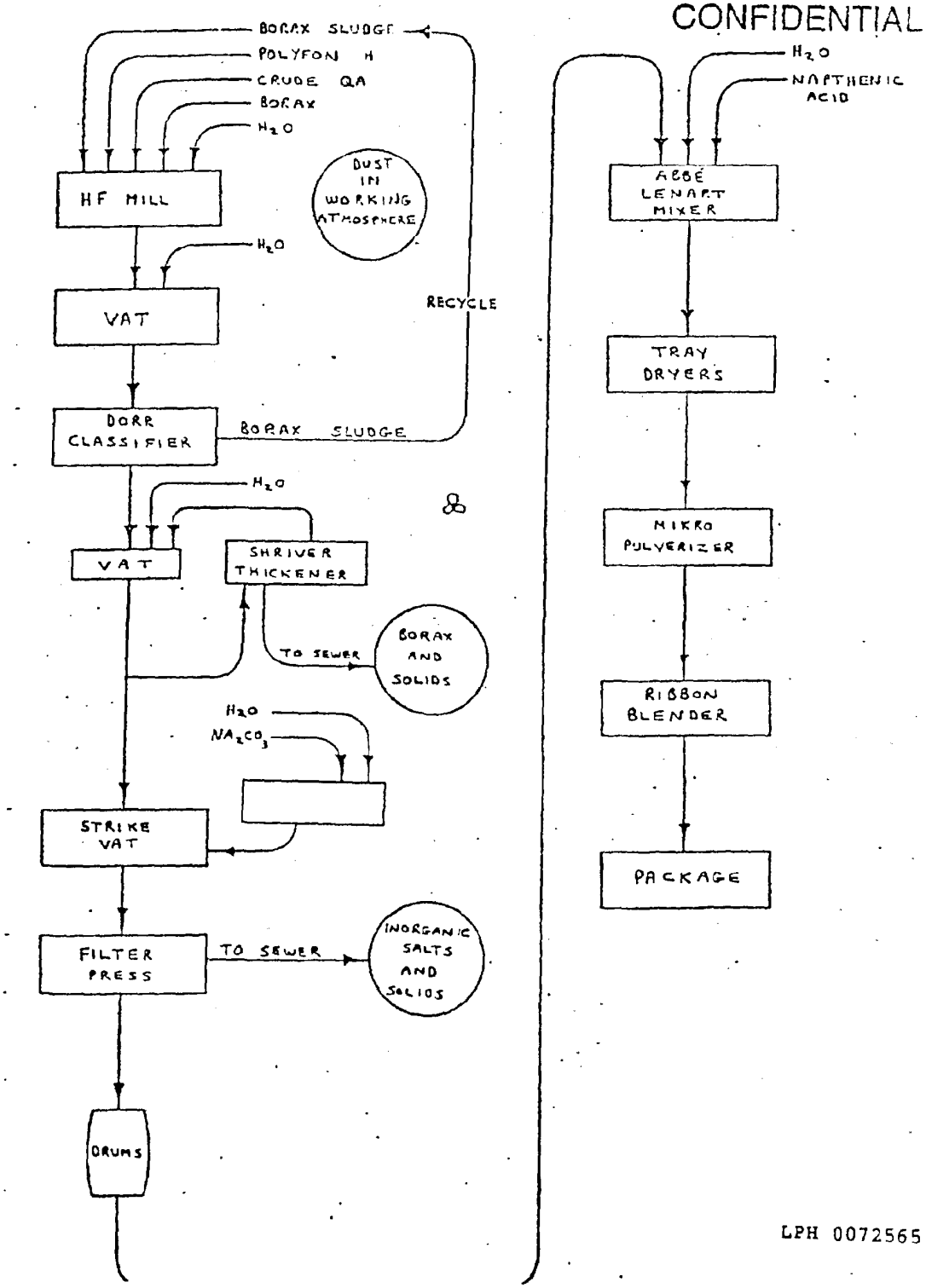
LPH 0072564

NEWARK PLANT

SKETCH #3

QUINACRIDONE MILLING PROCESS

CONFIDENTIAL



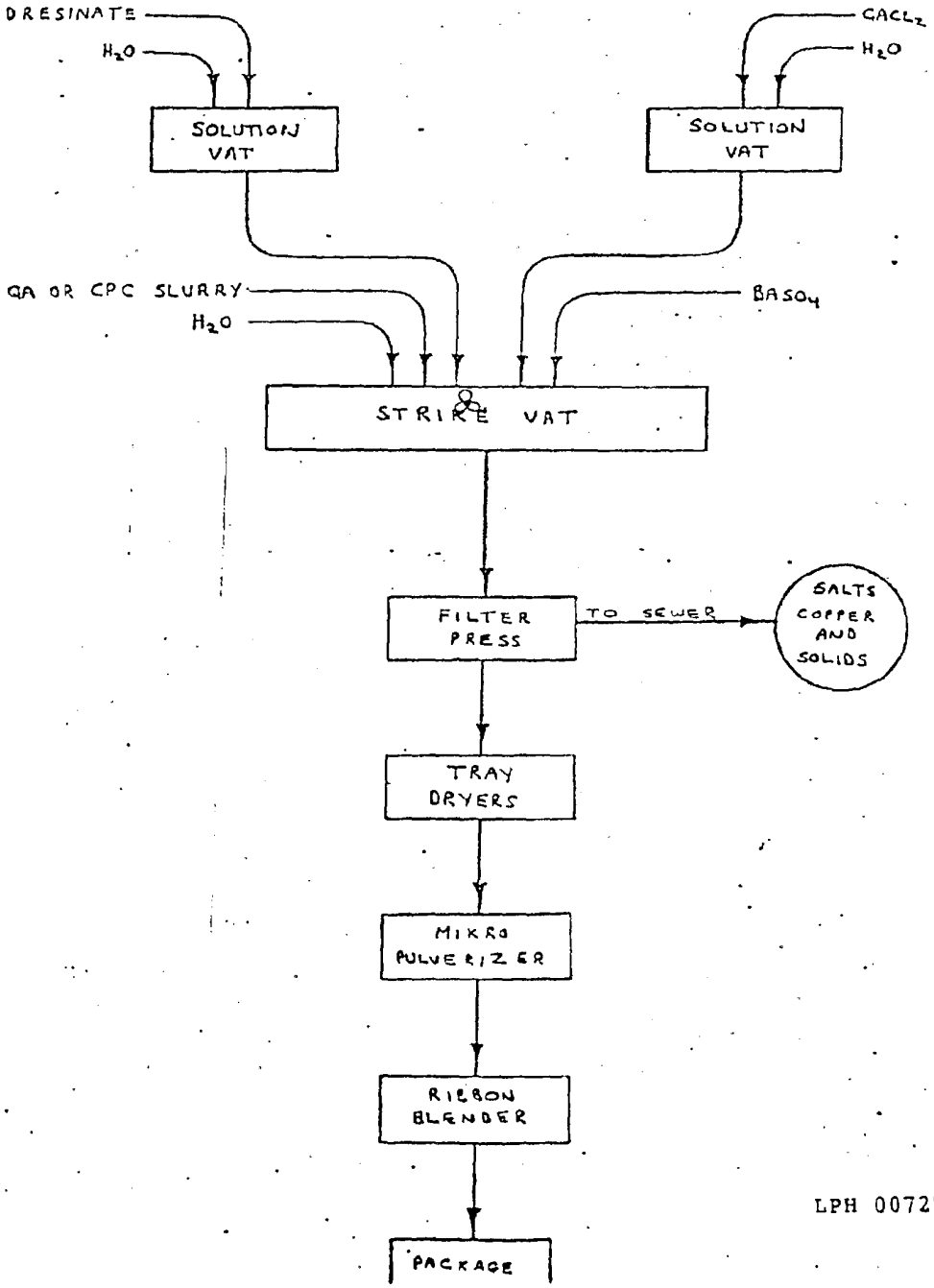
LPH 0072565

NEWARK PLANT

SKETCH #4

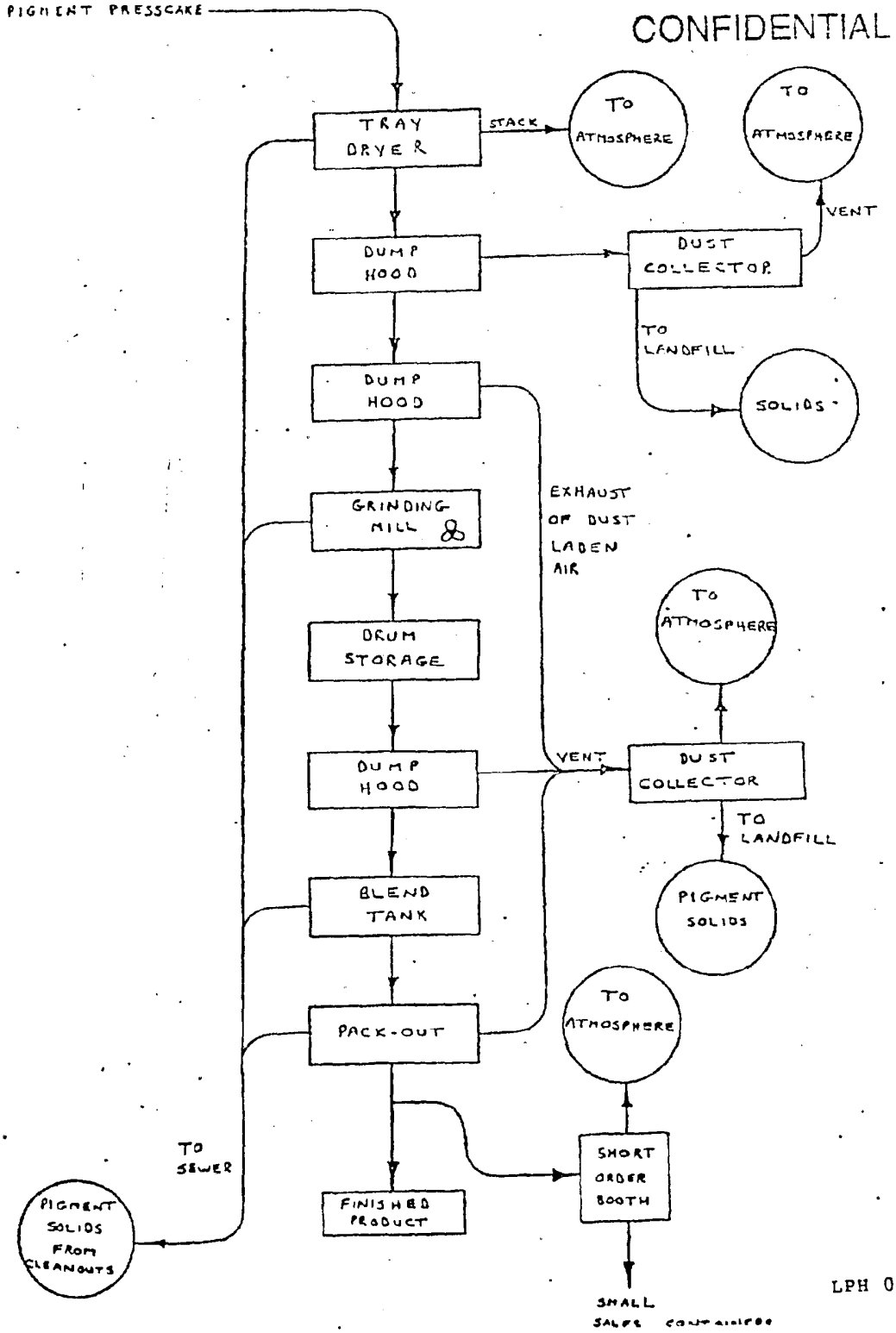
CPC OR QA LAKING PROCESS

CONFIDENTIAL



LPH 0072566

PIGMENT DRYING, GRINDING AND FINISHING



LPH 0072567

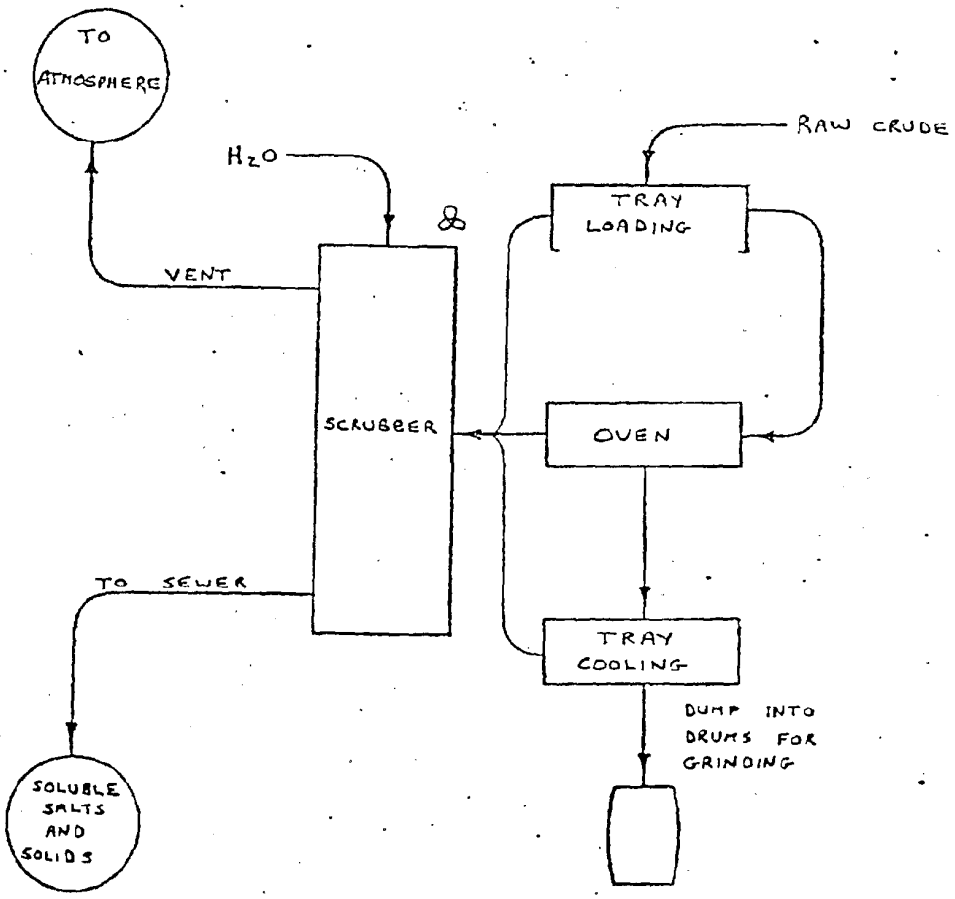
NEWARK PLANT

36 BUILDING

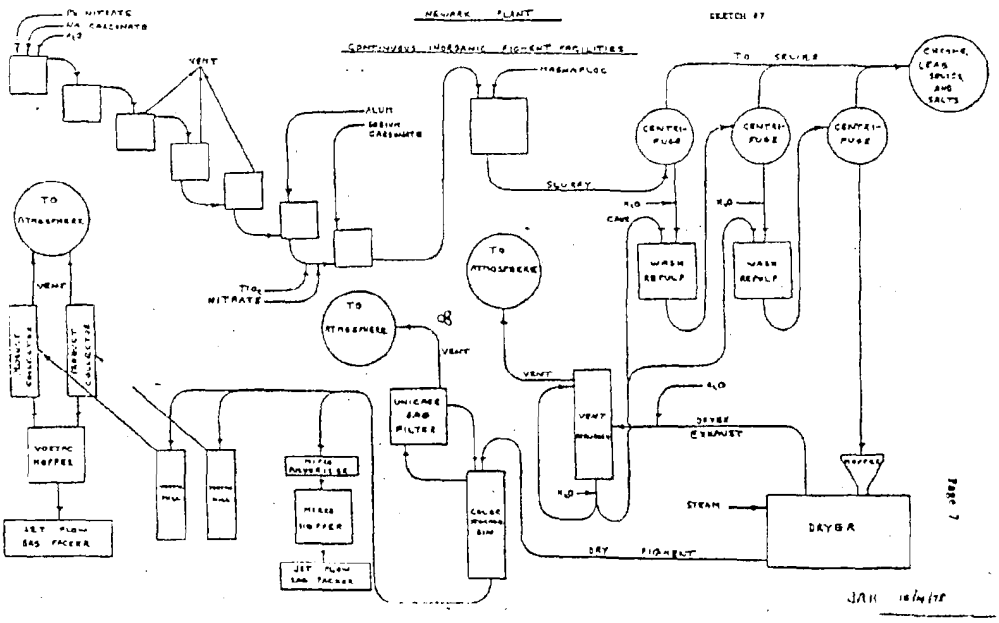
CFC - AF PRODUCTION FACILITIES

CONFIDENTIAL

SKETCH #6



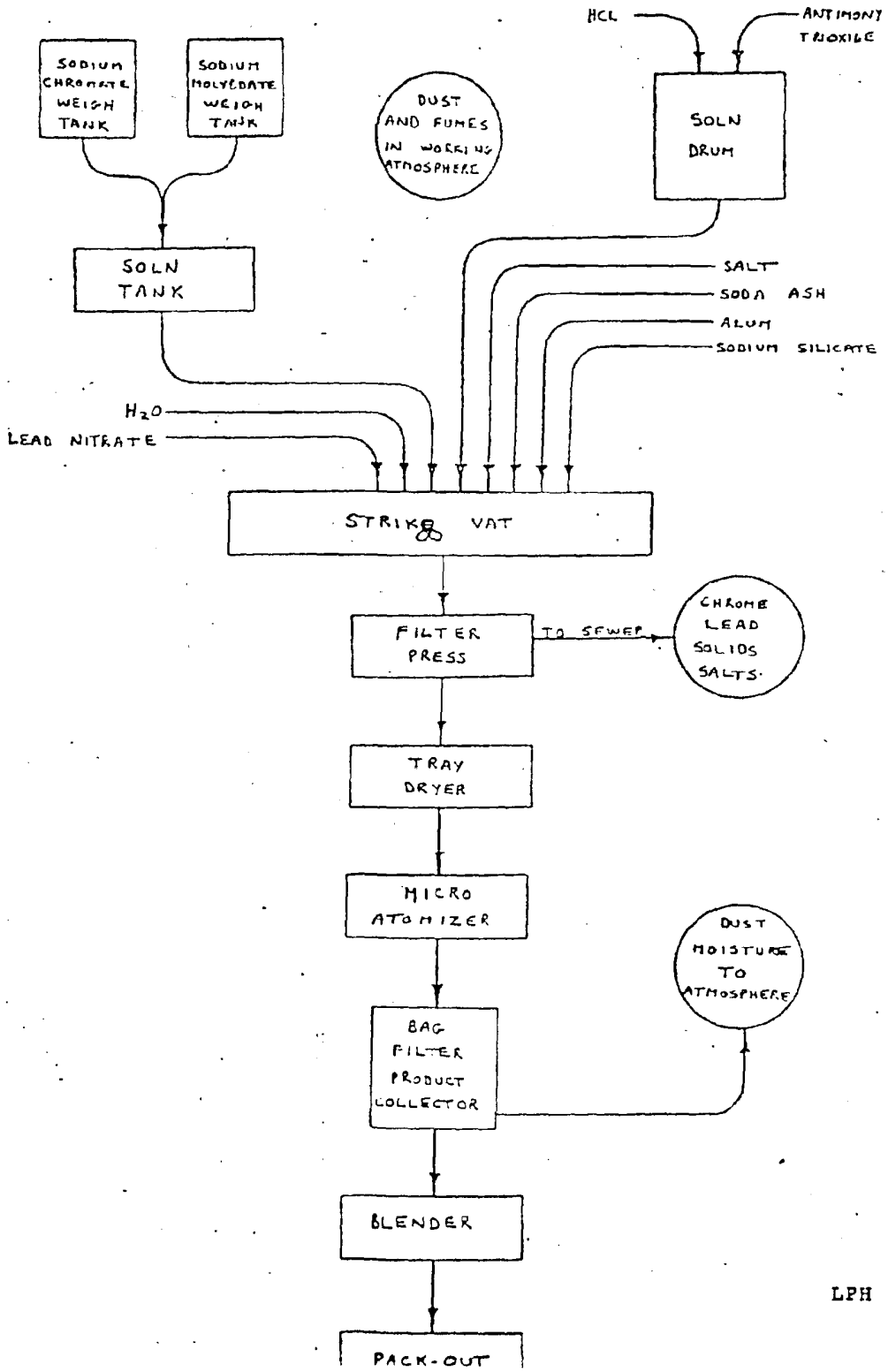
LPH 0072568



NITRIC ACID FROM STORAGE
T-400
LEAD NITRATE RECEIVE TANK
MIST TRAP
ABSORPTION TOWER
NO
T-1410
T-401
LEAD NITRATE RETURN TANK
TO WASTE TREATMENT
NITRIC ACID FROM STORAGE
LEAD NITRATE RECEIVE

LFH 0072570

BATCH MOLYBDATE FACILITIES

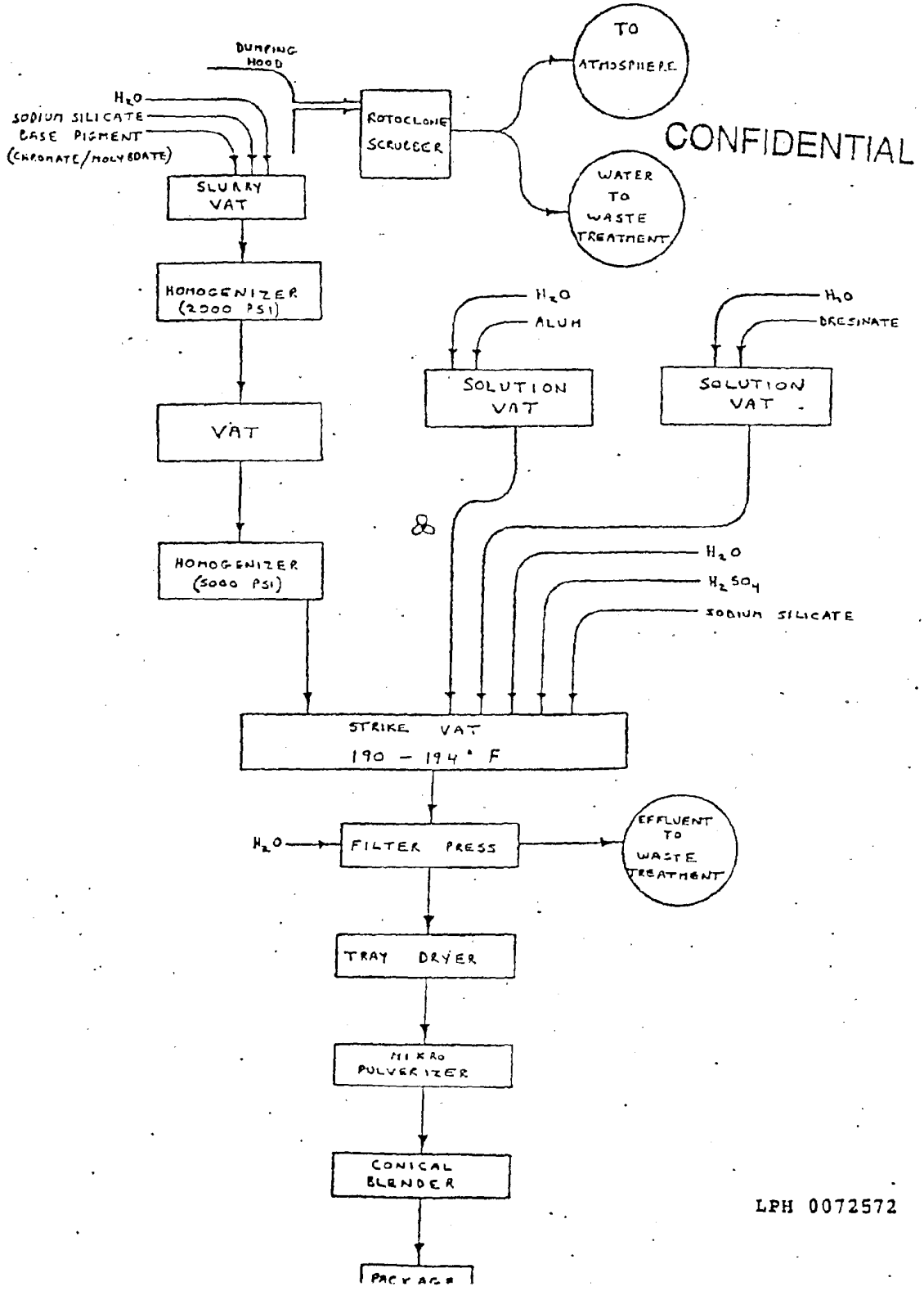


LPH 0072571

NELMAR PLANT

TYPICAL KROLOR® PROCESS

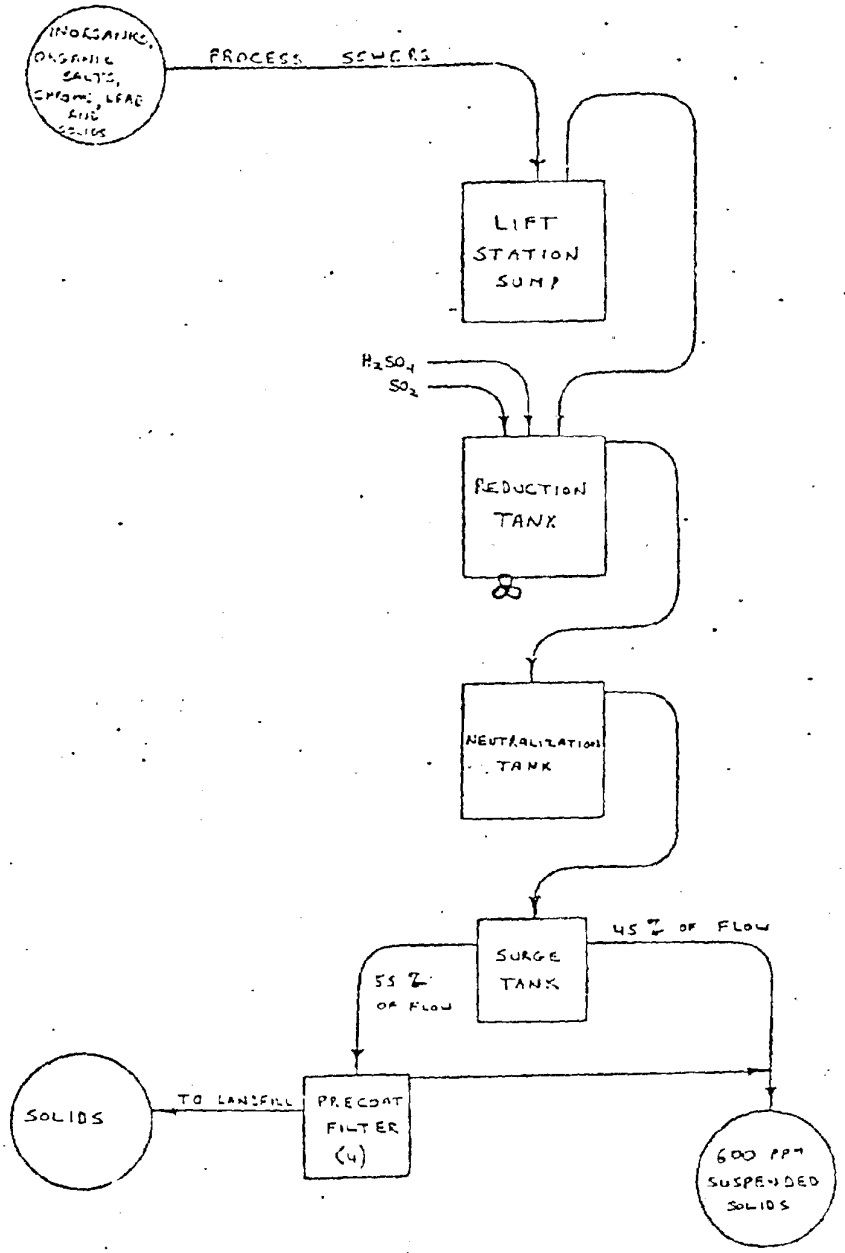
SKETCH #10
Page 10



CONFIDENTIAL

LPH 0072572

NEWARK PLANT — WASTE TREATMENT - CHROMIUM (2/66)



WASTE TREATMENT CHEMISTRY

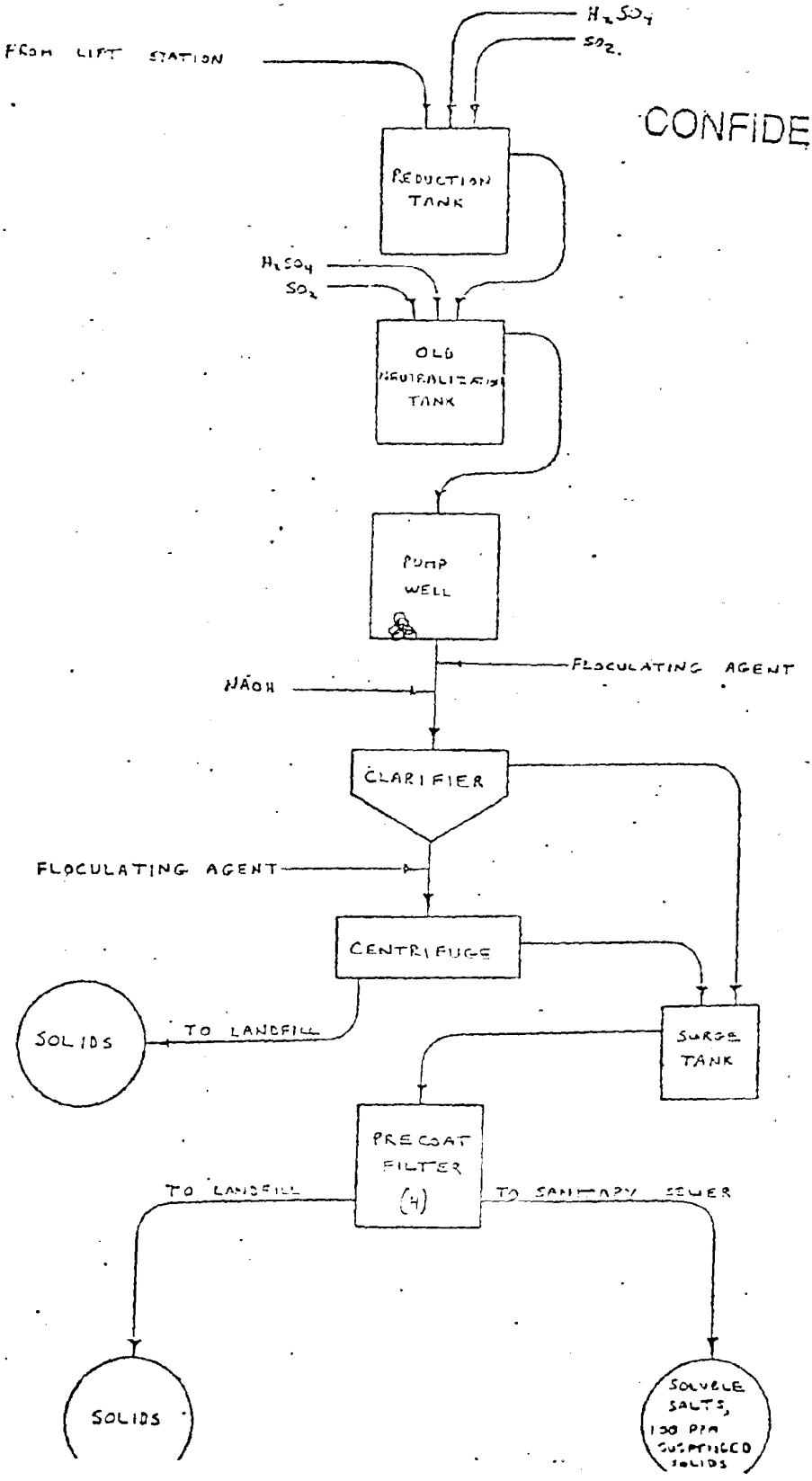
REDUCTION TANK

SOLUBLE CHROMIUM + SO_2 + H_2SO_4 ⟶ REDUCED CHROMIUM + SO_3

LPH 0072573

NEUTRALIZATION

REDUCED CHROMIUM + NAOH ⟶ CHROMIUM HYDROXIDE (INSOLUBLE)

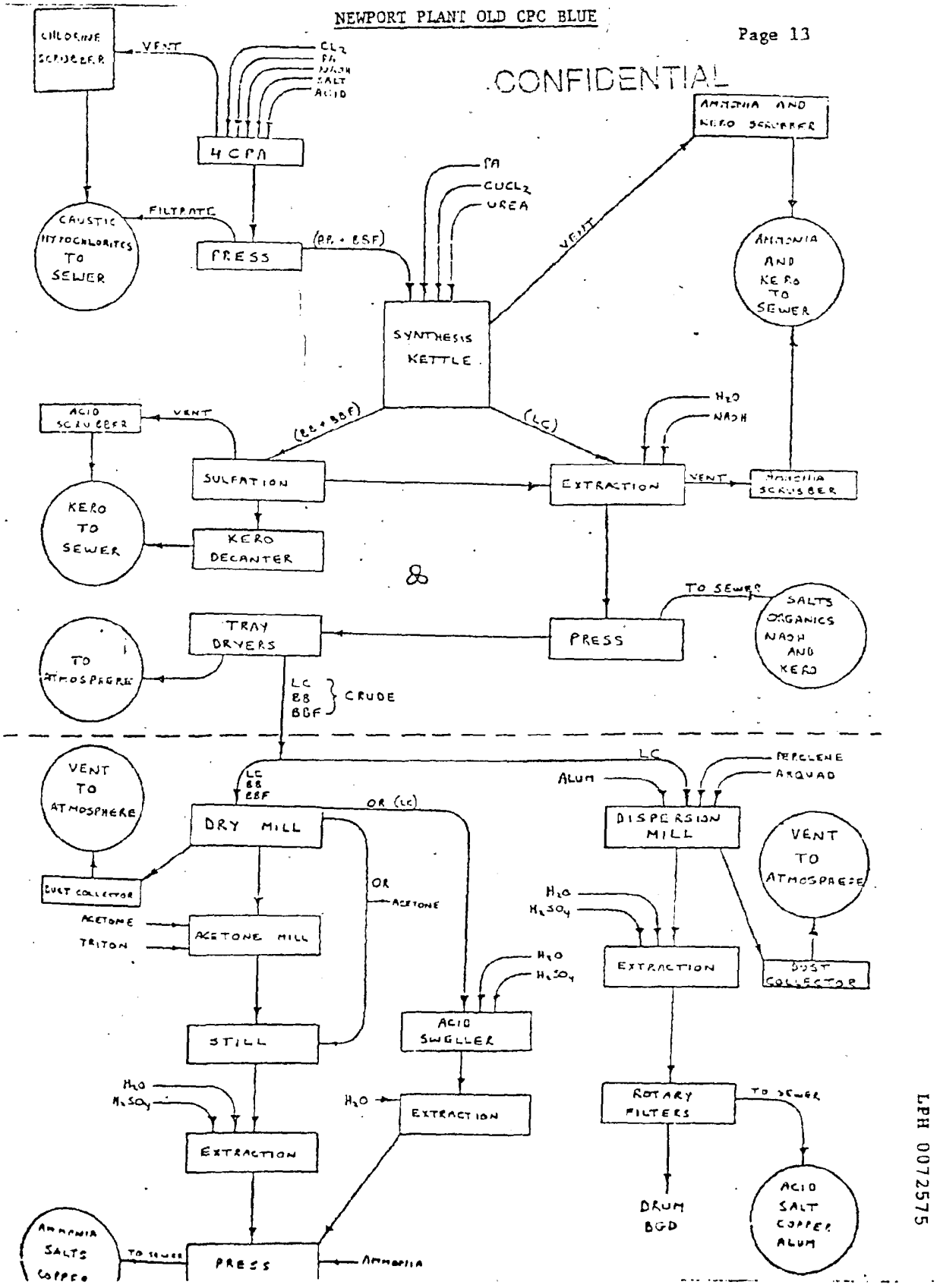


CONFIDENTIAL

LPH 0072574

NEWPORT PLANT OLD CPC BLUE

CONFIDENTIAL



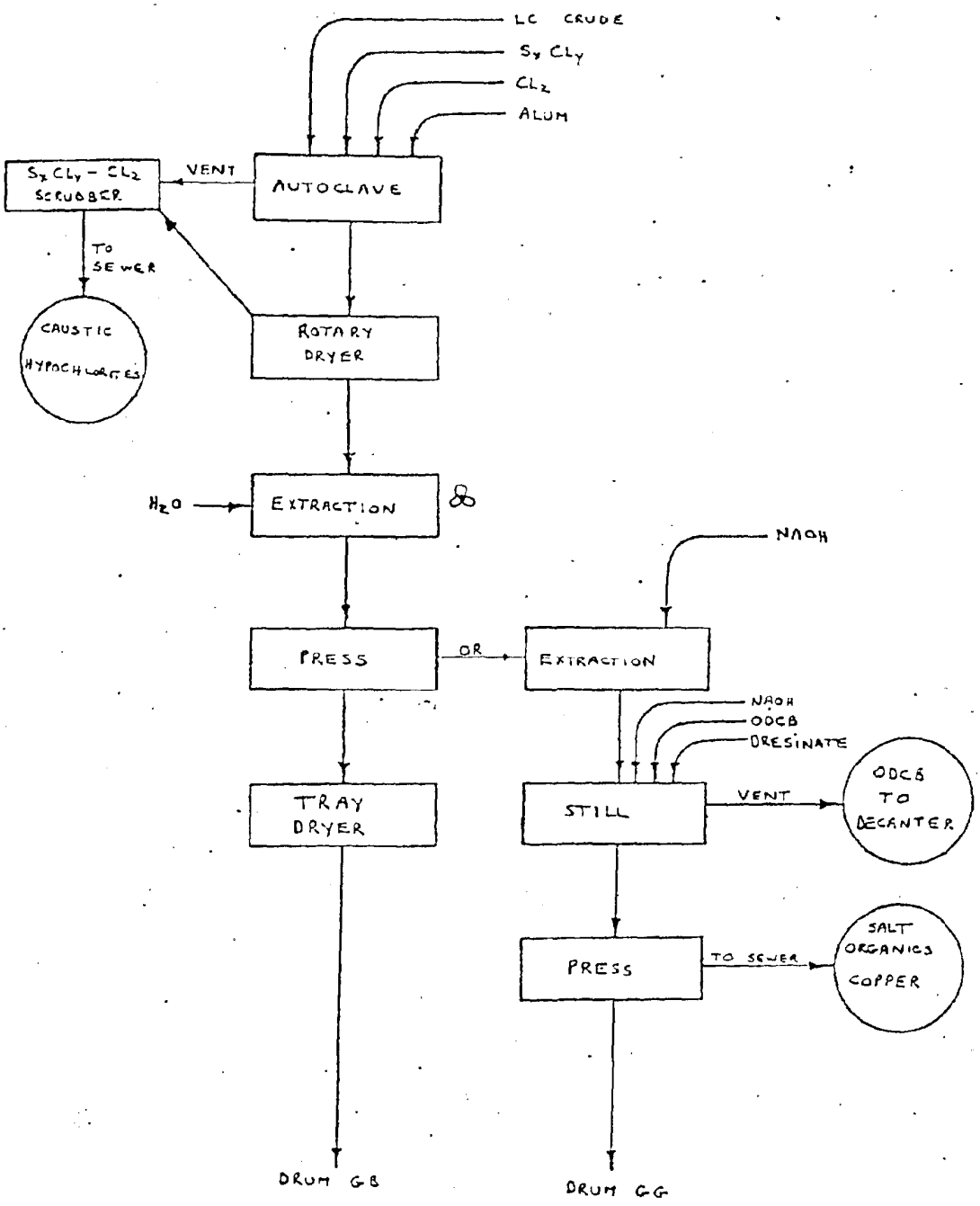
LPH 0072575

NEWPORT PLANT

CONFIDENTIAL

OLD CPC GREEN

SKETCH #2
Page 14

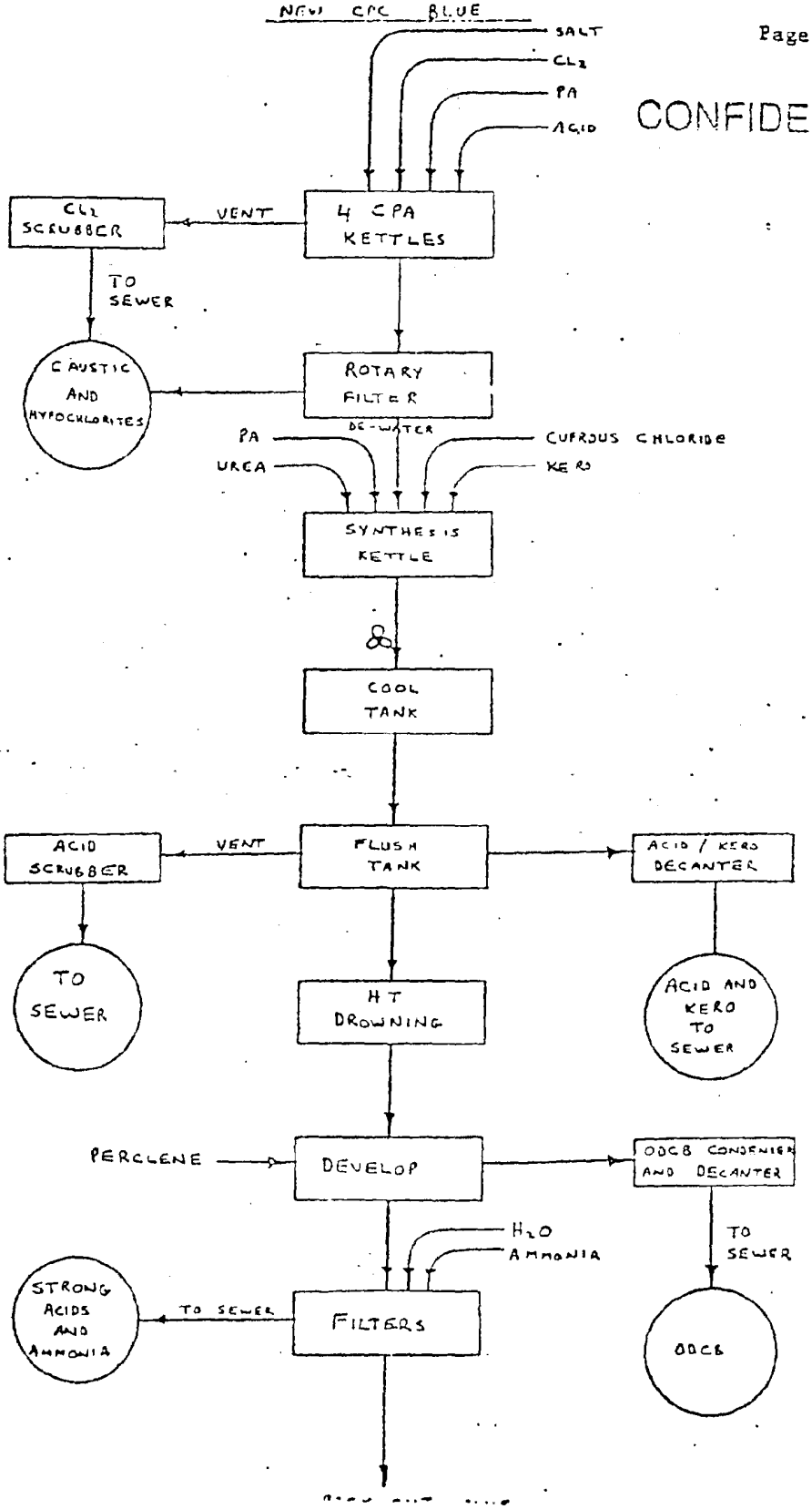


LPH 0072576

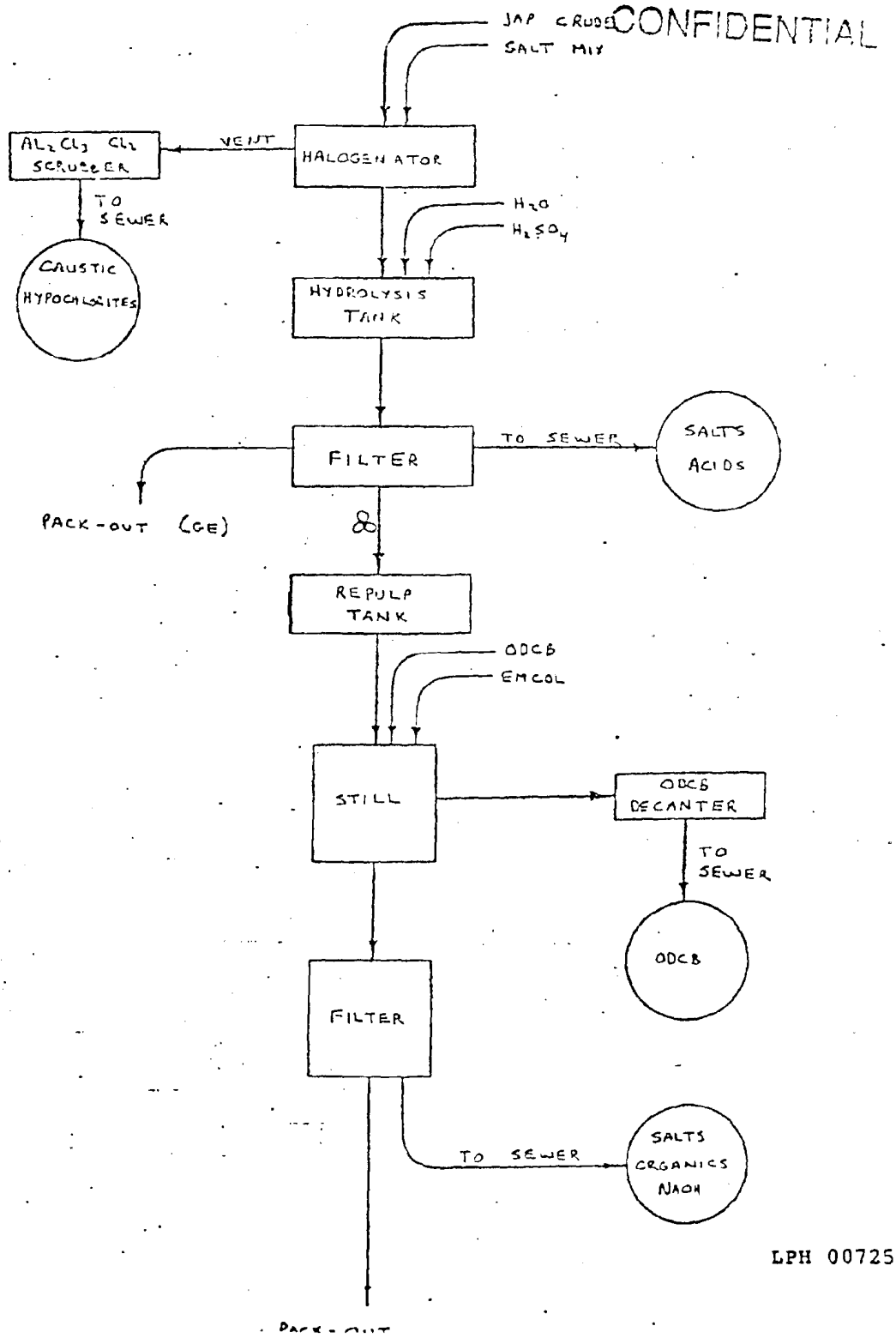
CONFIDENTIAL

NEWPORT PLANT

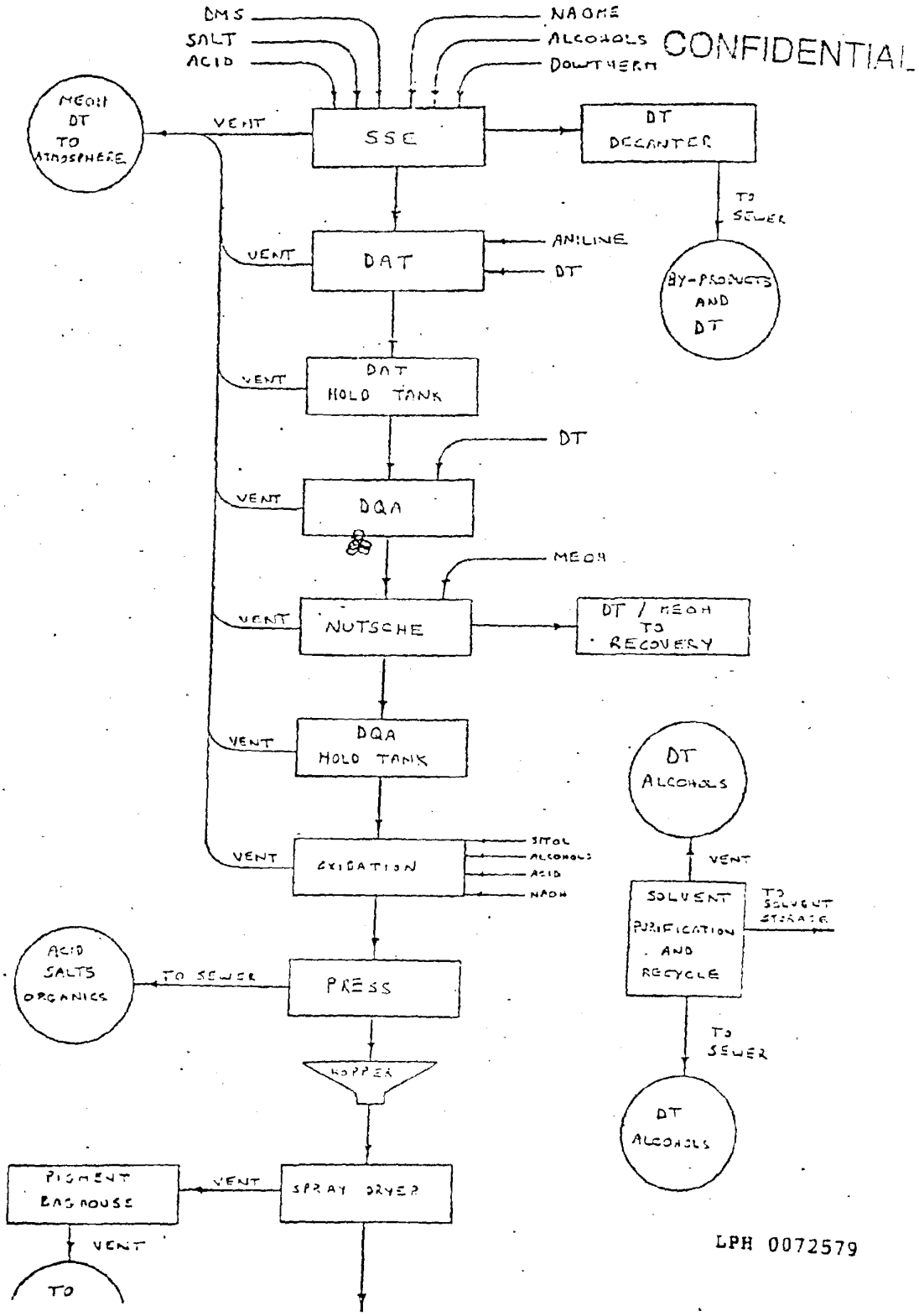
NEW CPC BLUE



LPH 0072577



LPH 0072578



LPH 0072579

NEWPORT PLANT

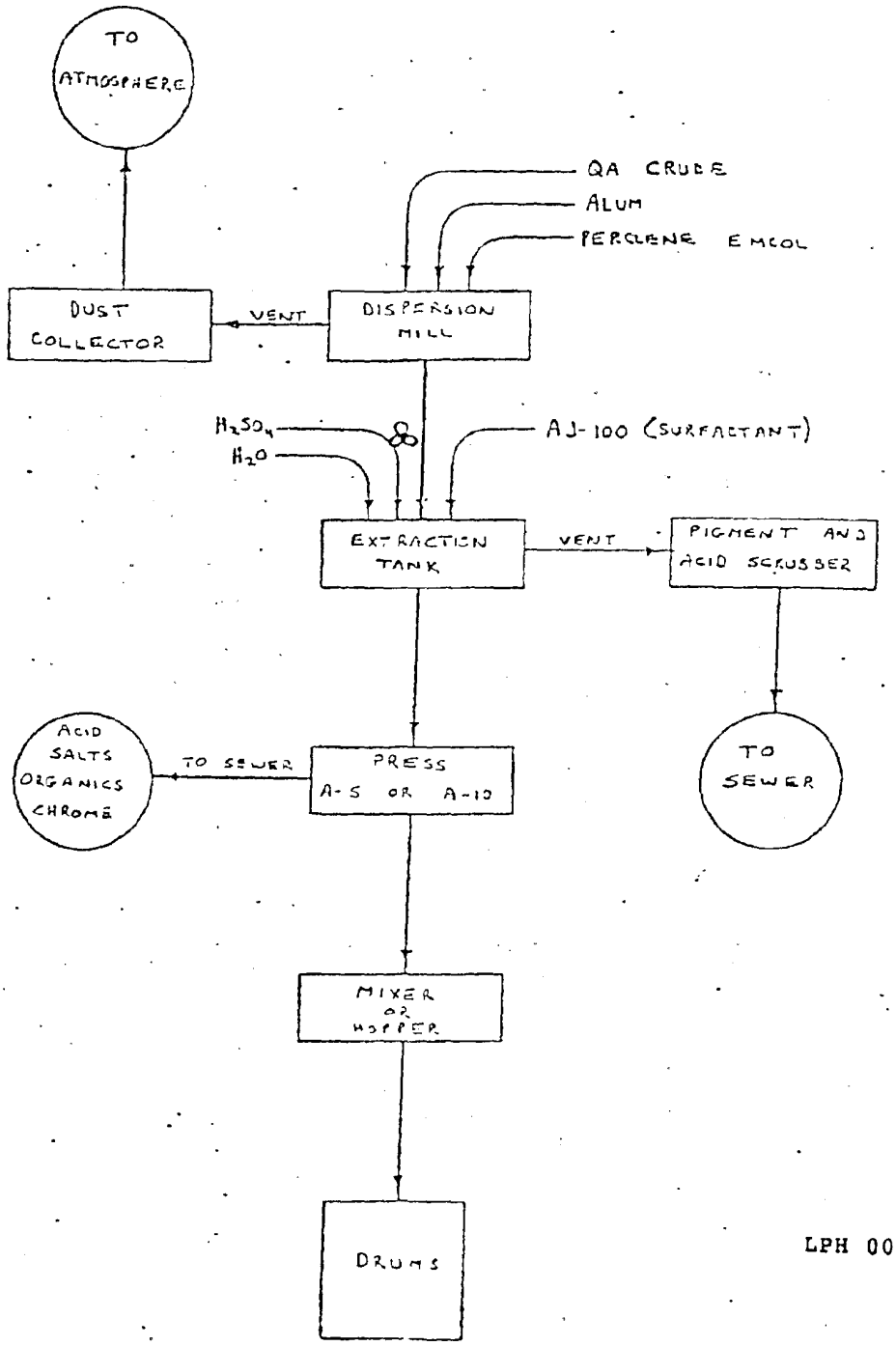
QA FINISHING

SKETCH #6

Page 13

EXTRACTIONS

CONFIDENTIAL



LPH 0072580

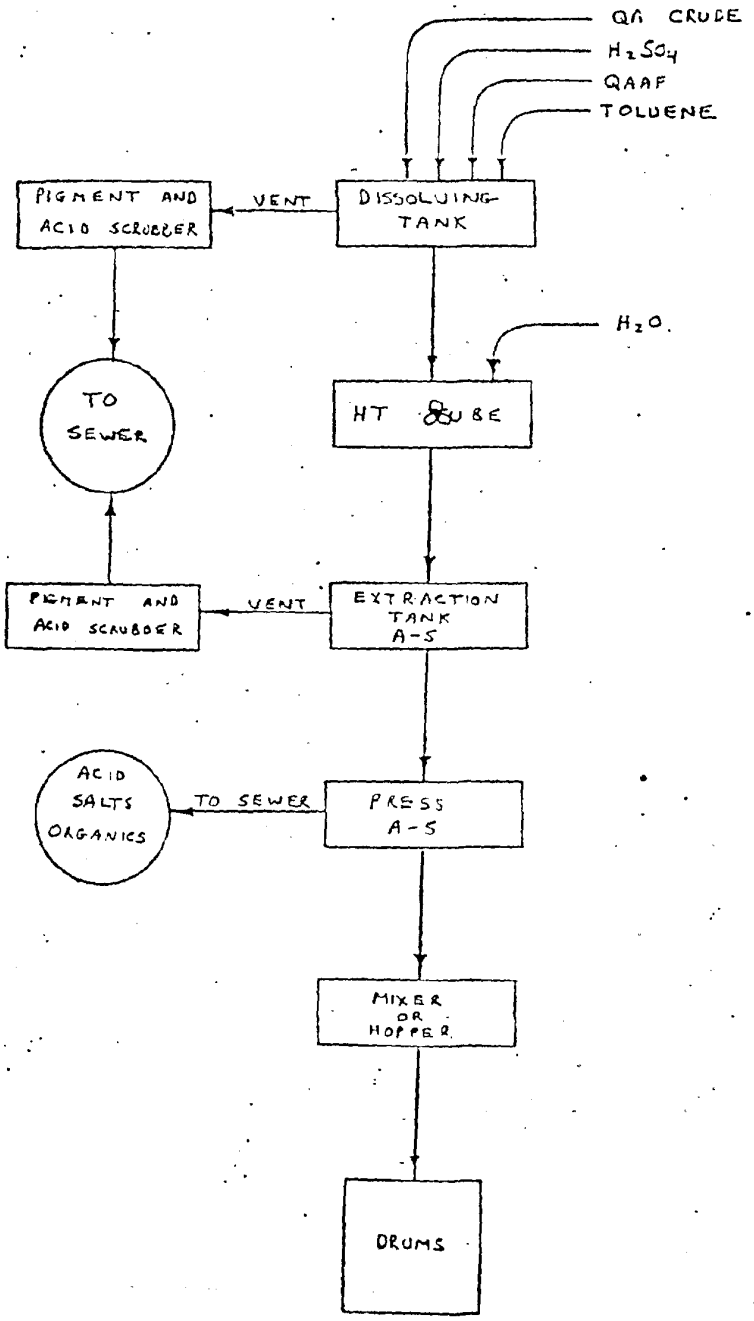
NEWPORT PLANT

QA FINISHING

HT BROWNING

SKETCH #7

CONFIDENTIAL



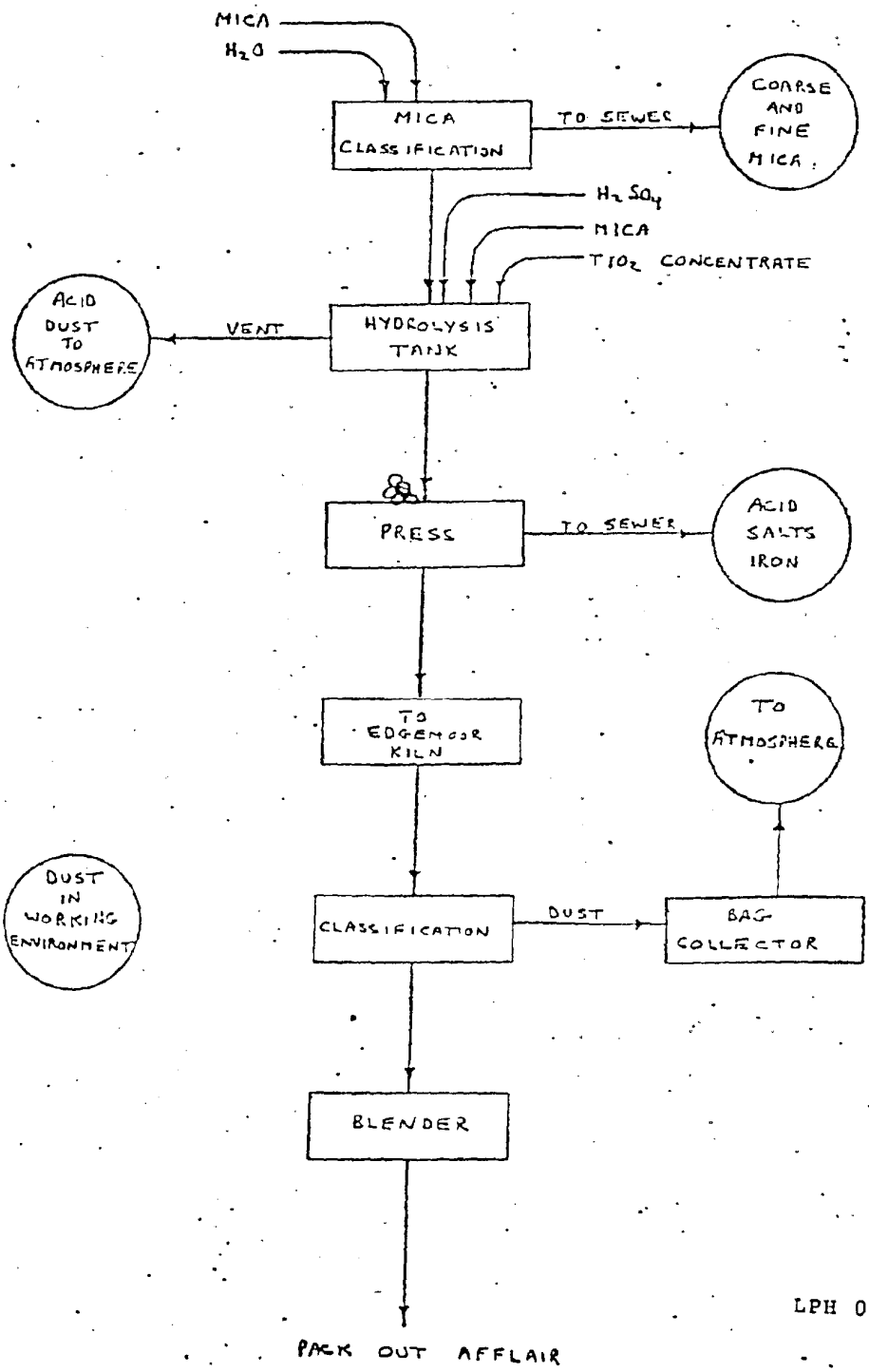
LPH 0072581

NEWPORT PLANT

AFFLAIR®

CONFIDENTIAL

SKETCH #3



LPH 0072582

GENERAL INFORMATION

ABSENCES

The employee should notify his immediate superior as early as possible on the first day of the absence. Insofar as the absence can be anticipated, notice should be given in advance.

If an employee becomes ill while at work, his immediate supervisor should be notified.

PAYMENT OF SALARIES (EXEMPT PERSONNEL)

1. Newark

Salaries are paid by check on the 15th and last working day of each month except in December when the second check of the month is delivered before Christmas. If the 15th falls on a Saturday, Sunday, or holiday, the pay date is moved forward to Friday, or to the day before the holiday. If the last working day of the month falls on the last Friday of the month, the pay date is moved forward to Thursday.

In all cases, checks are usually available for delivery after 3:00 P. M. on the day preceding the pay date.

2. Newport

Salaries are paid by check on the last working day of the month. If the last day falls on a Friday, the pay date is Thursday.

In all cases, checks are usually available for delivery after 3:00 P. M. on the day preceding the pay date.

Arrangements can be made for the automatic deposit of an employee's salary check in a bank designated by the employee. Salaried employees are encouraged to use this service.

VACATIONS

The vacation plan is as follows:

Years of Continuous Service	Weeks of Vacation
1 to 5	2
5 to 10	3
10 to 20	4
20 to 35	5
35 or more	6

After 15 yrears of service, the vacation plan provides for carrying weeks of vacation forward to succeeding years as follows:

Years of Continuous Service	Weeks Carried Forward for Any Year	Maximum Weeks Carried Forward
15 to 20	1	1
20 to 25	2	2
25 to 35	2	3
35 or more	2	4

A new Exempt salary employee placed on the roll between January 1st and June 30th (inclusive) of the current calendar year is eligible for one week's vacation with pay during the current calendar year.

A new salary employee who is placed on the roll on or after July 1 of the current calendar year is not eligible for a vacation during the current calendar year.

Salary employees with less than one year's service, who were on the roll on December 31st of the preceding year are eligible for two weeks vacation with pay during the current calendar year.

Both the wishes of the employee and the efficient operation of the laboratory are considered in scheduling vacations.

ACCIDENTS AT WORK

An injured employee must report to the Plant Hospital for treatment no matter how slight the injury may be. Supervision should be informed of the accident as soon as possible.

HOLIDAYS

The Research and Development Division observes the following ten holidays:

New Year's Day
Floating Holiday
Good Friday
Memorial Day
Independence Day
Labor Day
Thanksgiving Day
Day After Thanksgiving
Day before Christmas
Christmas

When a holiday falls on Saturday, it is observed on the preceding Friday. When the holiday falls on a Sunday, it is observed on the following Monday. When December 24th falls on a Sunday, the following Tuesday is observed as the holiday. When Christmas falls on Saturday and is observed on Friday, the December 24th holiday will be observed on the preceding Thursday.

Revised by BHP - 1975

CC W. S. Struve
Plant Mgr/Asst Plt Mgr-Newark
Plant Manager - Newport
Production Supv of Area
Product Supt., Proc. Eng
Area Supervisors (Involved)
R and D Supervisors - Newark
Technical Superintendent-Newport
Other Involved
File

AREA
XOB No._____(Batch Inorganic Designation)
XOO No._____(Other Organic Designation)
XOI No._____(Continuous Inorganic Designation
XOC No._____(CFC Designation)
XOQ No._____(QA Designation)

TITLE

OBJECTIVE

BACKGROUND (Include reasons for test and potential benefits if new procedure is successful)

STARTING DATE (To be determined by Product Control, Manufacturing, and R and D)

NUMBER OF TEST BATCHES

PRELIMINARY PREPARATIONS/CLEANING REQUIREMENTS

RAW MATERIAL REQUIREMENTS

PROCEDURE (Be specific and attach batch cards)

TEST RESPONSIBILITY (Who will follow run)

SAMPLES REQUIRED

TESTING (Who and what)

DISPOSITION OF TEST MATERIAL AND CODE DESIGNATION

SAFETY ASPECTS

CLOSING REPORT RESPONSIBILITY

APPROVALS

CHEMIST/ENGINEER	PROCESS ENGINEERING
PRODUCTION-AREA SUPERVISOR	PRODUCT CONTROL
PRODUCTION SUPERVISOR	ENVIRONMENTAL CONTROL
R AND D SUPERVISOR	

LPH 0072587

FORMAL PROCEDURE

NEWARK EXPERIMENTAL PLANT TRIALS

A written procedure (see attachment) is being established to formalize experimental plant trials by either Manufacturing or R and D. Essential to the procedure is a review of the test method by all affected agencies and approval by R and D and Manufacturing. When instituted, the system should better inform people involved in the test, improve both test scheduling and coverage, and provide better documentation of methods and results.

This procedure should be used when a new process or product is tested in the plant or when a major change is made in an existing process. Manufacturing, Process Engineering, and R and D should determine at the outset of the proposed change if the formal written procedure is needed.

The attachment details the format. To initiate such a document, contact Process Engineering and they will provide a number for each experimental plant run. Note also that a closing report will be required.

1/6/77 -A. P. Smith

CO-OPERATIVE PROGRAMS

- DU PONT PIGMENTS DEPARTMENT

  - "LUCITE" SOLUTION LACQUER (926/927 LINES)
  - WATERBORNE ENAMEL (358/359 LINES)

- HARMON

  - "LUCITE" SOLUTION LACQUER (867/868 LINES)
  - WATERBORNE ENAMEL (358/359 LINES)

- CIBA-GEIGY

  - "LUCITE" SOLUTION LACQUER (926/927 LINES)

- BASF

  - "LUCITE" SOLUTION LACQUER (926/927 LINES)

- HOECHST (PENDING)

  - "LUCITE" SOLUTION LACQUER (926/927 LINES)
  - WATERBORNE ENAMEL (358/359 LINES)

SAFETY

The primary principle of safety in our laboratories, as in the entire DuPont Company, is that all personal injuries are avoidable.

Safety in laboratory and pilot plant work is based on the premise that each individual technical man must be the major factor in his own safety and that of his fellow workers.

Our responsibility for safety follows the line organization. Each individual up to and including the Laboratory Director is personally responsible for freedom from injuries of ones self and all subordinates. Safety responsibility cannot be delegated.

Colors R and D acts in concert with the primary agency (usually the Manufacturing Division) at each location. The head of the laboratory is a permanent member of the Central Safety Committee, the policy making group. Other members of the technical staff serve on various sub-committees, especially where their technical competence can make substantial contributions.

Laboratory safety programs are the joint responsibility of the Research and Development and Production laboratories.

A three-man Laboratory Safety Policy Committee consists of two Research Supervisors and a Production Area Supervisor. They investigate, evaluate and implement action to see that safety in the laboratory is a dynamic, moving program. New regulations, operating procedures, equipment and supplies are reviewed by this Committee whenever a question of safety is involved. Feedback to this committee is supplied from the following regular safety activities.

Research Supervisors' Meeting

Held monthly at which time the state of laboratory safety performance is critically examined. Matters requiring changes in rules or procedures are usually referred to the Policy Committee.

Monthly Inspection

A three-man team of technical personnel conducts a detailed inspection. A primary topic is usually featured and any unsafe conditions and procedures are noted.

Group Safety Meeting

Each functional group conducts a bi-weekly meeting devoted to safety. Each member of the group has an opportunity to conduct a meeting.

Each individual must take personal responsibility to familiarize himself with the manual: "SAFETY IN LABORATORY AND SEMI-WORKS ACTIVITIES" as well as the general plant safety rules, and the specific rules applying to any area in which he may have to operate.

LPH 0072590

Revised by BHP - 1975

SECURITY

Through its program of research and development, DuPont accumulates a vast amount of valuable technical information. Although patent protection is obtained wherever possible, it is well recognized that a great deal of technical ''know-how'' cannot be covered in this way. It is in this area that the Company recognizes its responsibility to provide proper safeguards and its reliance on all personnel to regard all Company information as confidential.

Company responsibility is to provide proper facilities for safeguarding recorded material and to promulgate rules to govern personnel conduct in the handling and discussion of Company information. Some precautions are:

1. Lock doors when offices are left unoccupied, particularly at lunch time.

2. Guard against unauthorized persons penetrating Company offices.

3. Do not accommodate investigators - government or others - without Management clearance.

4. Do not leave confidential papers where they may be seen by unauthorized persons.

5. Put away papers in desks and files at night. Use locks where appropriate.

6. Shred or tear up all papers before putting them in wastebaskets.

7. Arrange for destruction by burning or shredding of very confidential papers.

8. Adhere to the procedures outlined in the booklet entitled ''Guide for Safeguarding DuPont Company Documents and Information'', particularly those with reference to transmission and marking documents with the standard legends:

    a. DuPont Confidential - Special Control
    b. Personal and Confidential
    c. For DuPont Use Only

9. Do not discuss confidential matters in elevators or other public places, or in business or social gatherings where unauthorized persons may obtain confidential information.

10. Be careful when using telephones where one may be overheard, such as on multi-party residence phones.

11. Be careful in using communications, such as telegrams and teletypes to which persons other than the addressee have access.

12. Report to Management any incidents which appear to involve risks with respect to safeguarding Company information.

Contacts with vendors should be made through local Plant Buyers. They are kept informed by the Energy and Materials Department in Wilmington of special conditions applying to any particular supplier.

Contacts with outsiders should be discussed with your supervisor. In oral or written presentation, care should be exercised to avoid disclosing end-use, specific process or equipment details of significance.

Revised by BHP - 1975

RESEARCH AND DEVELOPMENT NOTEBOOKS

SUGGESTED RULES FOR RECORDING EXPERIMENTAL DATA

1. All experimental data should be recorded in ink in bound notebooks provided for the purpose. All such notebooks should have consecutively numbered pages.

2. It should be the aim to record a complete experiment, including all tests, on consecutive pages. Where sufficient space has not been allowed, suitable cross re references to the continuation of the record should always be made. This is in contrast to the diary type notebook favored in many laboratories, but is believed to be more adaptable for our type of work.

3. Each completed experiment should show the following information:

a. The date on which started.

b. The names of all those concerned in planning and carrying out the experiment and their relation to the work.

c. The reason for the experiment.

d. Complete details of the work done.

e. A record of all tests made including references to the testing methods used.

f. Conclusions drawn from the results are to be recorded in the handwriting of that person whose conclusions they were; ordinarily, also the one who planned the work.

g. Signature of the person drawing the conclusions and the date signed.

h. A point often overlooked is the proper reference to any previous discussion in which the work may have been suggested by another party, such as a director or supervisor of research, or a co-worker.

4. No erasures are to occur in the record. Corrections or changes should be made by cancellation, leaving the original entry legible. Where it may be desired to correct errors in fact or conclusion discovered after the record is complete, or to add information not originally available, this should be done by means of a dated and signed note without cancellation of the original.

5. Each completed experiment should be read, signed, and dated by a witness who is one who understnads the purpose of the experiment and the result obtained, and who is not likely to be an inventor, or co-inventor, of any process or product described therein.

6. If it is desired that the witness be able to testify to a reduction to practice of a new idea, he must do either of the following:

a. Observe the complete experiment including tests and be able to testify of his own knowledge as to all details, including the identity of starting materials and the measure of success; or (probably preferable)

b. Actually reproduce the experiment following the instructions of the inventor.

The extremes represented in this Section 6 are probably justified only in exceptional cases but constitute the only practical methods of conclusive proof of a successful experiment.

7. The bound notebook is to be preserved intact. In no case should any page or part of a page be removed. If it is desired to attach loose sheets recording original data, they may be of value only if they are signed, dated, and witnessed.

8. It is obvious that the elapsed time between the beginning of an experiment and its final conclusion should be kept to the minimum.

Edited by BEP - 1975

PREPARATION OF A PATENT PROPOSAL

In the drafting of any patent application, the primary responsibility for initiation of patent activity lies with the research supervisor. The supervisor will normally assign a chemist to collect the available information and incorporate this information into a patent proposal which is forwarded to the Legal Department.

The attorney or patent agent will review the patent proposal and prepare a patent application. Normally additional consultation with the chemist and supervisor is required to insure that the full scope of protection to which we are entitled is obtained.

The following outline points out the essential parts of a patent proposal together with certain auxiliary information which the attorney requires in determining inventorship. It should be followed closely in organizing the information and preparing the patent proposal.

Perhaps, this outline may also help in recognizing invention and this is an added reason why it should be familiar to each member of the staff and considered carefully in connection with all your problems.

OUTLINE OF PATENT PROPOSAL

1. Summary of the Invention.
2. State of the Art.
3. Advantages over the Existing Technology.
4. Examples (Experimental).
5. Utility and Characterization.
6. Claims.
7. Invention Record.
8. Non-Du Pont Disclosures or Use.

THE PATENT PROPOSAL

1. Summary of the Invention

A statement as to what is new is basic to any patent proposal submitted. It must be consistent with the results of the experimental examples and describe the important features which are critical to operability of the invention.

A good way to arrive at this statement, for instance, is to formulate the broadest statement which will avoid the prior art and then modify it as needed to make it conform to the known facts. This is often an effective way of pointing out gaps in our knowledge.

Revised by G.A.Hapka, Legal Dept.

LPH 0072595

2. State of the Art

This section is primarily to educate the attorney or patent agent in the art and should be a complete statement or description of the known prior art. For the purposes of the patent proposal, it should include the following:

a. A search of the prior published art such as patents, technical journals, and the like, with a listing of pertinent references and some discussion of each together with a record of what art has been searched.

b. A statement of the problems and deficiencies of the art as known.

c. Unpublished information, if any, in our own reports, in complaints from the trade, and the like, which often help in outlining the problem.

3. Advantages over Existing Technology

Discuss the reasons why the discovery is valuable in comparison to known technology. Is it a new way to achieve something that has been done before, do you observe improved results, have you discovered a new compound, do you project cost benefits?

4. Experimental Examples

Examples of the invention should include several detailed, workable recipes for carrying out the invention. Such examples should enable a reader to repeat the procedure and get the same result. Where suitable, a control test showing results obtained without benefit of the invention. This test should parallel the invention recipe but is carried out without employing the critical features of the invention.

In general, all examples should refer to and identify experiments actually carried out from which samples are available for special tests which might be necessary to support statements made in the disclosure or in subsequent arguments before the Patent Office.

In addition to the detailed examples, the disclosures should include statements as to modification and equivalents wherever possible. This is the place to bring out the effects and the limits of variables such as temperature, concentration, pH, times of reactions, impurities, alternative materials, etc.

Revised by G.A.Hapka, Legal Dept.

LPH 0072596

5. Product Utility and Characterization

The patent application should clearly state the field of use for the invention. The specific applications if not discussed relative to the advantage of the invention should be clearly stated in this section.

If the invention is a new product, a description in terms of intrinsic properties should be included. For a pigment these could be particle shape, size distribution, chemical composition, structure, new type of coating or an effective new combination of such characteristics. In-use properties such as improved hiding power, tinting strength, or lightfastness are also useful in characterizing the invention.

6. Claims

The drafting of the claims is not our responsibility. Nevertheless, we can assist very much by pointing out what should be claimed. The summary of the invention may be the basis for the broadest claim, but we should point out preferred species. We can claim a number of separate species providing there is a generic claim which covers all of them.

In process claims, we should point out the broadest range of conditions as well as a preferred range. In some cases, it may be desirable to claim a specific set of conditions.

Our role with respect to claims is to point out the scope of the invention as well as the most important aspects. It is the attorney who expresses these in approved legal phraseology.

7. Invention Record

Provide reference to all notebook pages, reports, and any other written description that relates to the patent proposal. The references should identify the author of the document, the notebook by number and page, the record and a summary of the contents of the page. (Photocopies can be supplied in place of the summary.) It is also helpful to the legal staff to be advised of others within Du Pont whose work may relate to the invention.

Inventorship is determined by the legal staff after the invention has been clearly defined. This determination is primarily made on the basis of documented information. Please note, if the patent proposal is the first written record of the invention, it should be witnessed and dated.

8. Disclosures or Use

The Legal Department should be advised of any disclosures to non-Du Pont personnel or commercial use of the invention either within Du Pont or by third parties. Information relating to customer sampling, actual sale, or the like is important in considering patentability. Present operations and future plans for commercialization are important information and our operations can affect our ability to obtain both U.S. and foreign patent rights.

It is recognized that the information requested above may not always be available. When the proposal is prepared, however, gaps in our knowledge should be recognized and pointed out. If the above outline is kept in mind while the experimental work is underway, the gaps should be found less often.

Revised by G.A.Hapka, Legal Dept.

RESEARCH AND DEVELOPMENT FILES

A new simplified technical filing system to facilitate information retrieval is being instituted at Newark (1975). Filing is to be by the following classifications:

TECHNICAL FILE
AZOS
COMPETITIVES
CONSTRUCTION PROJECTS
COSTS AND FORECASTS
CPC
  Capacity
  Processing
ENVIRONMENTAL (Waste Treatment, OSHA)
ENERGY PROBLEMS
INORGANICS
  Capacity
  Processing
  Afflair©
  Lead Chromates, Krolor©
  Zinc Chromates and Strontium Chromate
  Other Inorganics
INSTRUMENTAL, ANALYTICAL AND PHYSICAL
MISCELLANEOUS PIGMENTS
PLANT ASSISTANCE
  Continuous Unit
  Intermediates, Semi-Finished
  Lead Nitrate
  Batch Making
  Pressing
  Drying
  Grinding
  Packing
QUINACRIDONE
  Capacity
  Synthesis and Processing
  Solid Solutions
GENERAL CORRESPONDENCE
  Color Code List
  Customer Correspondence and Trips
  Literature
  Manuals
  Meetings (Agendas and Notices, Minutes)
  Outside (Non-Customer) Contacts and Correspondence
  Policies and Procedures
  Price Announcements
  Safety and Health
  Work Requests
  Routine Summaries (Mo. Reports, Newsletters)
  (XOR's and XOP's are filed in looseleaf)

The filing classification is to be designated by the originator, for material originating at Newark. Filing classification for Newark incoming mail is to be specified by the addressee.

LPH 0072599

An Author file of outgoing correspondence is maintained, in addition to the subject file.

Incoming file is by subject.

Administrative files (budgets, forecasts, costs, etc.) are maintained separately from the Technical files. The secretary to the Laboratory Director should be consulted on retrieval of material from these files.

Seldom used files on non-technical subjects (union correspondence, clothing reports, etc) which are duplicated in the Newark plant (Non R and D) files, are no longer kept by R and D.

A numerical file is maintained of R and D reports on specific subjects (KN reports). Reports are given a numerical "KN" designation, for example, KN-75-52. The first two digits indicate the year the report was issued, and the second group of digits is the sequence number assigned to reports. The separate subject index of reports has been discontinued at Newark. A Central Report Index is maintained by the Information Systems Department in Wilmington, where KN reports are also filed.

Newport R and D files are kept by the secretary to the Technical Superintendant. R and D reports are kept in the Newport Library. A new filing system for Newport is under development by an R and D Committee.

by BHP 1975

INFORMATION RETRIEVAL

1. Du Pont Company

The Information Systems Department has developed a DuPont Information Network to implement technical information transfer programs. This department, the central Du Pont source, provides a wide variety of information services and also operates the Technical Library, Wilmington.

They issue a ''Guide to Information Sources'' which is updated regularly and furnishes a point of contact for each department in the company that issues reports on technical investigations.

The Central Report Index (CRI) of the Information Systems Department contains records of nearly 150,000 reports. The reports are indexed in depth. CRI will also search, on request, published literature.

A Central Patent Index (CPI) also provides access to patent literature in the many fields of interest to DuPont. CPI will search, on request, U. S. Patents, foreign patents, and/or the non-patent scientific literature. Pigments Department requests for these services are coordinated by R. J. Bruehlman, Newport.

Other compilations are now available or are in process. Among these are the ''Analytical and Test Method Index'', the ''Index to Du Pont Analytical and Physical Test Equipment'', the ''Directory of Company Information Sources and Personnel'', a ''Library of Programmed Instruction Courses'', and a wide variety of others. Contacts should be made through local library personnel who are kept informed of company-wide activities in this field.

2. Pigments Department - Colors

a. Finished products are identified by a code number consisting of a three digit serial number with prefix and suffix letters denoting the color and physical form. (A detailed description is furnished in another section). All processes, costs, production records, sales statistics, etc. originate with coded products.

The approximately 130 finished products are combined, on the basis of chemical or process similarities into twenty (20) Color Cost Groups. Ultimately, these are categorized as the following color products types.

Krolor®
Afflair
Other Inorganics
''Monastral'' Quinacridone
''Monastral'' - CPC
Other Organic

b. Physical assets at all DuPont locations are the responsibility of the local engineering group. Detailed information on facilities and equipment can be obtained through them.

LPH 0072601

3. Colors Research and Development

Data accumulated in pursuit of research and development goals must be recorded in a manner that permits accessibility at any subsequent time.

The following media are used to record experimental work:

a. Notebooks
b. Monthly Summary Reports (covers work of a research group)
c. Progress and Final (KN) Reports on specific subjects
d. Correspondence Files
e. Exposure Series

The key to information retrieval is the formal (KN) report. These reports are to be prepared following the ''Guideline for a Uniform DuPont Technical Report'' which was developed by an Interdepartmental Committee. Copies of the guide are in R and D offices or may be obtained from Central Report Index, Wilmington. The reports are filed numerically at Newark, and, indexed in depth, by the Central Report Index, Wilmington, where the information is computerized for retrieval.

Correspondence is also filed by the system described under ''R and D File Systems'' (Section F, this book).

Obtaining a KN report on a specific study would provide the following information:

a. Period Covered

This is helpful in limiting search of correspondence and other files.

b. Author and Supervisor Approving the Report

This can lead to the proper Monthly Summary Report which oftimes contains additional data.

c. Notebook References

These contain the chemist's record of his experimental work.

Record of development information such as Pilot Unit and Plant batch numbers, end-use tests, patent status and so forth. These reports and card index files are maintained in the Research and Development Library at Newark and Newport and at CRI, Wilmington.

Studies not covered by a KN report may be referred to in Monthly Summary Reports of the appropriate group or in correspondence. Retrieval of information from the correspondence files is more fully covered in the description of the file classification system.

Completed and inactive notebooks are kept in the Newark Library and in the office of the Secretary to the Technical Superintendent at Newport.

Revised by BHP 1975

RESEARCH AND DEVELOPMENT COST AND ACCOUNTING

The cost of performing research and development activities includes:

Direct costs, such as:

Compensation and other employment costs of Research and Development personnel for time spent on the specific project.

Cost of materials used directly on the specific project.

All other direct costs incurred for the specific project, including work done by outside organizations.

Other expenses (assigned or allocated, as appropriate) such as:

Compensation and other employment costs of supervisory, clerical, or other personnel of the technical unit for time devoted to Research and Development work.

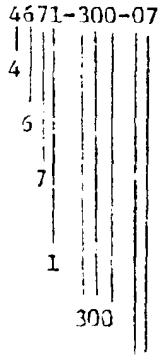
Technical management, including Wilmington Office technical management.

Expense of operating and maintaining facilities used in Research and Development.

Proportionate share of expense of operating and maintaining general plant facilities necessary to supplement Research and Development facilities.

To properly accumulate costs, a system of significant numbers has been set up. This delineates the type of activity, the product line or area of investigation, the agency performing the work and the location.

A list of Pigments Department Research and Development expense accounting codes is issued periodically by the Accounting Section, Wilmington. Requests for new codes or information on existing codes may be obtained from H. E. Clendaniel, extension 6878, Wilmington. The following examples will illustrate the significance of the digits.



Work on Quinacridones performed at Newark

Research and Development Division (Agency doing work)

Colors (Product Line)

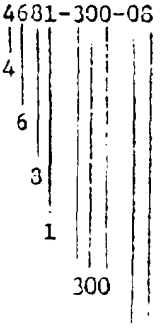
Responsibility code. Work Authorized by - . 7 means Newark (Indicates responsibility for whom work is done).

Improvement of Established Business (I.E.B.)

Quinacridones

Source - where work is done, in this case, Newark. If work done by e.g. Engineering Dept., code may be 12 instead of 7.

4671-400-07 — Change in second group of digits (to 400) indicates CPC instead of QA



Work on Phthalocyanines at Newport

Research and Development Division

Colors

Responsibility code - work authorized by - 8 means Newport

I. E. B.

Quinacridones

Source. Where work is done; in this instance, Newport. These 2 digits are not ordinarily used by the chemist or engineer.

It is essential that cost accumulation be accurate and this necessitates the proper use of cost codes.

The following illustrate typical cost coding for requests for goods and services initiated by technical personnel.

	NEWARK	NEWPORT
Purchase Requisition	4607-04-999	4607-XX-XXX*
Repair Order	4604-04-999 4605-04-999	4604-XX-XXX 4606-XX-XXX

*XX-XXX To be filled in by appropriate Newport R and D expense code. For example, supplies charged to QA: 4607-81-300

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	NEWARK	NEWPORT
Stores Ticket	4607-04-999	4607-XX-XXX
Monthly Salary Distribution	4601-71-200**	4601-XX-XXX
Operating Labor	4603-71-200**	4603-XX-XXX
Service by Outside Vendor	4634-71-300**	4634-XX-XXX

**200 means that the work is charged to Inorganics; For Quinacridones, for example, 300 would be used in place of 200, the remainder of the charge code remaining the same. Note that a final "07" code (Newark Plant) is not used here.

All of the above six codes (e.g. 4607-04-999, etc.) are for internal use at Newark or Newport only. The third and fourth digits are inserted to denote the type of expense and are used only on the plant site. These numbers are not used when supplying cost codes to other DuPont locations.

For all non-technical work or for technical work by groups other than Central Research and Development Department, Engineering Department, and Pigments Technical Service, the proper designation is:

For Newark, 8209 (General Ledger Number)
4671-300

(Note that 8209 is on a separate line.)

For Newport, 8211-
4681-300

8209 and 8211 have universal meaning throughout the Company:

82 is Pigments Department

09 is Newark Plant, 11 is Newport Plant

The 4671-300 is meaningful only to Pigments Department personnel; therefore, the General Ledger number is essential.

For Technical work done for us (either Newark or Newport) by outside groups with which we maintain a budget, Central Research and Development Department, Engineering Department, Pigments Technical Service, Chestnut Run , the proper code, in the case of quinacridone, is

8253
4671-300(Newark)
4681-300(Newport)

Revised by BHPerkins - 1975

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COMPUTER USE

A teletype terminal of the ''RAPIDATA'' Time Sharing Computer System is located in the Physics Lab, First Floor No. 23 Building at Newark. Communication between the user and computer is maintained through a teletype unit by use of keyboard or paper punch tape. Four distinct languages may be employed for programming this system: BASIC Language, ALGOL, COBOL, and FORTRAN. A library of programs commonly used in mathematics, business and technical work is supplied by RAPIDATA and may be used simply by calling their respective codes from computer storage.

The Newport R and D Laboratory has access to two terminals connected, on a time-sharing basis, to the PDP-10 computer at the Experimental Station. A teletype offers 10 cps; the other terminal is a 1030 unit which provides either 10 cps or 30 cps and also has a wide carriage with a width of 130 characters.

Manuals and assistance are available for those who would like to learn BASIC Language and FORTRAN. FORTRAN may also be learned through the use of I.B.M. manuals and ''Computer Programming for Chemists'' by K. Wibery.

TENTATIVE SCHEDULE FOR GROUP STUDY SESSIONS - 1976

Date	Location	Time	Leader	Redbook Sections	Topi
12/5/75	Newport (A-207 Confr. Rm.)	9:00 AM	ARH	7, 8, 9	Light Scatteri Measurement & Particle Size Properties.
1/9/76	Chestnut Run (Lg. Confr. Rm.)	9:00 AM	BHP	6, 11	General Pigmer Particle Size
1/23/76	Exptl. Sta. (2nd Fl. Confr. Rm.)	1:00 PM	GT/IHH	17, 18	X-ray Diffrac Microscopy.
2/6/76	Newport	9:00 AM	JJ	10, 15	Particle Size Methods, Surfa Agents.
2/20/76	Chestnut Run	9:00 AM	HM	12, 13, 16	Pigment Purif persion & Rhe
3/5/76	Exptl. Sta.	1:00 PM	PAW	14	Photochemical Lightfastness Durability.
3/19/76	Newport	9:00 AM	RCB/RDN	7, 22A	Light Absorpt and Inorganic
4/2/76	Chestnut Run	9:00 AM	JFH	22, 22A	Pigment Class Inorganics, K
4/23/76	Exptl. Sta.	1:00 PM	Mktg.	19, 20, 21, 26	Evaluation of Pigments, Ser Facilities El Pigment Stand

Date	Location	Time	Leader	Redbook Sections	Topi
5/7/76	Newport	9:00 AM	PHG/WEM	22D	Phthalocyanin
5/21/76	Chestnut Run	9:00 AM	EAS	22B & C	Azo Pigments Lakes.
6/4/76	Newport	9:00 AM	EEJ	22E	Quinacridones
9/3/76	Exptl. Sta.	1:00 PM	RJG	22F-H	Dioxazines, I Vat Dyes and Pigments.
9/17/76	Chestnut Run	9:00 AM	Mktg.	25	Pigment End U Competitive P
10/1/76	Exptl. Sta.	1:00 PM	WHS	27, 28	Process Scale Semiworks Fac
10/15/76	Newport	9:00 AM	JFM	29	Process Engin
10/29/76	Chestnut Run	9:00 AM	Inf.Serv. Div.	-	DuPont Inform
11/5/76	Exptl. Sta.	1:00 PM	Legal	-	Patent Propos
11/19/76	Newport	9:00 AM	WHS/WEM	30, 31	Manufacturing
12/3/76	Chestnut Run	9:00 AM	WSS	-	The Colors Pi