MARSHALL LABORATORY TRAINING SEMINARS
1969

NOTE

Much of the material in this manual is confidential. Please see that the information is not released outside of the Fabrics & Finishes Department.

DU PONT'S ROLE IN THE PAINT INDUSTRY

Du Pont's position in the paint industry stems from its development of smokeless powder in 1894, for nitrocellulose was a basic ingredient of both that type of powder and of lacquers which the company introduced early in the 20th century. In fact, Du Pont's paint business resulted from the company's early desire for industrial diversification based upon sound research -- just as smokeless powder had been developed out of the black powder chemistry on which the company's corporate foundations were laid in 1802.

Paints of a crude type are, of course, almost as old as man himself, with the earliest recorded types having been used more than 20,000 years ago as a decorative medium in Cro-Magnon cave painting. Ancient Egyptian mummy cases were painted and varnished with crude but exceptionally long-lasting materials. Earth oxides mixed with oils and tree gums were compounded into painting materials by the Chinese as early as 1800 B.C., along with lacquer made from what was known in that ancient Oriental country as the Varnish Tree. And white lead, still an ingredient of some modern day paints, has been found in a Grecian pottery box dating from 400 B.C.

AMERICAN COLONIAL PERIOD

Paints, in fact, were one of the earliest commercial products of the American colonies. Thomas Child, a Bostonian, opened the first paint mill in this country in 1692. Far removed from the complicated compounding lines of today, Child's mill consisted of a granite trough in which a granite ball was rolled over various pigments and oils to produce paint.

White lead, still used as an ingredient of some exterior paints, was first produced in the United States in 1804, and the first American varnish is believed to have been made in 1815. Zinc oxide came into use as a pigment about 1850, and ready-mixed paint was developed during the period from 1860 to 1870.

DU PONT ENTERS LACQUER FIELD

Although it probably was not a consideration in the acquisition decision, Du Pont's introduction to the paint industry came in 1904 when the company, still concentrating upon smokeless powder and dynamite as its major products, purchased the International Smokeless Powder Company of Parlin, N.J. A minor part of

that company's business was production of solvents and lacquer-type materials, including a line of clear and pigmented nitrocellulose lacquers. Like most lacquers of the period, these were of exceptionally low solids content, with solvents forming about 95 per cent of the product. But, as the best materials of that type then available, they found a ready market for protective coating of such articles as brass beds, lamps, artificial leather and even the mantles of early gas lights.

Du Pont not only continued International's development of nitrocellulose lacquers but strengthened its background in the paint industry by acquiring the American Lacquer Company and Miller Company in 1907. Eight years later, it acquired the Arlington Company of Arlington, N.J., an aggressive manufacturer of pyroxylin plastics, lacquers and pigmented nitrocellulose enamels marketed under the trademark "Pyralin" for both spray and dip coating of small metallic and wooden articles.

HARRISON PURCHASE STARTS DU PONT IN PAINTS IN 1917

But Du Pont's real entry into the broad paint business came in 1917 when it purchased Harrison Brothers & Company, a major Philadelphia paint firm which had been founded in 1793 -- nine years before E. I. du Pont de Nemours, in fact, had built his first powder mills on the banks of the Brandywine near Wilmington. Harrison also was a major producer of sulfuric acid and pigments, both of which were to be important in other activities of the Du Pont Company.

The acquisition of Harrison Brothers was Du Pont's first major step in a chemical diversification program that has made the company today the nation's largest chemical manufacturer, with its original explosives business now accounting for an insignificant part of the company's business. And, perhaps more important, it marked the beginning of a scientific approach to paint formulation.

Science had scarcely touched the paint field in the decade prior to World War I. What few researchers there were, were connected with raw materials suppliers. Varnish making was almost a "black art," with formulations existing only in the heads of those in the industry, jealously guarded as "trade secrets" passed down by word of mouth from one varnish maker to his successor and never recorded in scientific fashion. Paint formulators "flew by the seat of their pants," adding pigments to varnishes whose chemical composition they could not obtain from the secretive varnish suppliers. Chemists, when they were employed by paint manufacturers, generally were used for control work only, with no real talent being devoted to paint formulation and research.

Little study had been started in those pre-World War I days on the fundamentals affecting such paint properties as flow, gloss, shelf stability, adhesion and chalking. The quality of the products left much to be desired, and, with the exception of asphaltic high-baking black enamels, no varnishes or varnish base materials had outdoor durability of as much as a year. Paints, generally compounded at the point of use by the painter, were of low solids content with consequent poor hiding power and very slow drying properties.

SCIENTIFIC CONTROL ENTERS PAINT PICTURE

With its dedication to research and chemical control, Du Pont embarked on a program of study designed to make paint manufacture a precisely controlled chemical process, rather than a "rule of thumb" business. Within a few months after acquiring Harrison Brothers, Du Pont purchased the Bridgeport Wood Finishing Company of Bridgeport, Conn., which not only made paints but also a line of specialties such as fillers and stains. In May, 1918, it acquired the Flint Varnish and Color Works, Flint, Mich., manufacturers of automotive and railroad coach finishes, and four months later, added by purchase the New England Paint and Oil Company of Everett, Mass. These acquisitions, along with that of the Chicago Varnish Company early in 1920, formed the nucleus of Du Pont's new Paint Division.

First major product of Du Pont's research in the new area was "Duco" nitrocellulose lacquer, developed by its Parlin laboratory and introduced in 1922. Its high solids content, in comparison with previous nitrocellulose type lacquers, provided a fast-drying film of superior durability and gloss and almost over-night captured a major share of the budding automobile industry's finish business. Its widespread adoption in the furniture and appliance industries, beginning with refrigerator manufacturers, was a logical extension of its success in the automotive industry.

"DUCO" FINISHES REVOLUTIONIZE AUTO INDUSTRY

The impact of "Duco" finishes on the automobile industry was tremendous, especially in the light of the mass production which was to come in the late 1920's, for it reduced finishing time from days to hours and provided finishes that would stand up for years instead of months. The best of the 1920 auto finishes, for example, required 26 days or more for application of up to a dozen coats of primers and varnishes, with their long drying times and hand rubbing requirements. "Duco" broke this bottleneck, introduced fast and efficient spray painting of far more durable finishes, and,

perhaps more than any other single factor, enabled the industry to develop its modern assembly line. Today, in fact, an automobile can be finished completely, from primer to top coat, in less than five hours.

In 1926, Du Pont began research on the synthesis of combinations of rosin and phenol-formaldehyde, which made possible the formulation of varnishes with much improved drying speeds for a given flexibility, as compared with the older fossil gum or rosin combinations. And, in the same year, the company introduced brush "Duco" lacquers both for household painting and in the industrial field, as a companion line to the spray "Duco" finishes, which six years earlier had revolutionized automobile finishing.

DU PONT LAUNCHES LABORATORY RESEARCH PROGRAM

Success of "Duco" finishes crystallized in Du Pont's mind the need for aggressive paint research, and in 1927, a Central Technical Laboratory was established in Philadelphia.

The Central Technical Laboratory, incidentally, is now the Marshall Laboratory, having been named in 1949 in honor of its first director, John Marshall. It is today the central research and sales development laboratory of the company's Finishes Division.

At that time, the Philadelphia plant of Du Pont's Paint Division had in its files formulas for about 22,000 paint, varnish and enamel products unclassified and filed only by date. One of the laboratory's first assignments was to review and classify this mass of data in a system which would make it usable as the basis of a planned research program and at the same time permit establishment of standard formulating practices. And while it may not sound glamorous by the usual standards of research work, that project provided the major building block for the company's future product development.

One of the laboratory's first research assignments was the development of new finishes based on modified alkyd resins and resulted in 1933 in the commercial introduction of a new line of "Dulux" alkyd enamels. These new film formers not only proved to have about the same weather resistance as the best nitrocellulose lacquers and drying speeds similar to the more brittle varnishes made from phenol-formaldehyde resin combinations, but were found to possess amazing toughness, flexibility and high luster without the rubbing required with older oleoresinous materials. Within 10 years, the "Dulux" alkyd enamels became one of the most important finishes used in the automobile industry, auto refinish trade, appliance manufacture, household equipment, marine, and structural

steel industries. Their outstanding whiteness and resistance to color change opened up a whole new area of use as the preferred architectural enamel.

1930's SPUR NEW DEVELOPMENTS IN AUTOMOTIVE FINISHES

The early 1930's also saw several developments which entrenched Du Pont finishes even more deeply in the automotive field. Early in 1934, Du Pont introduced its Calibrated Mixing Set, a series of small volumetric measures which enabled refinishers to mix in their own shops automotive colors to match factory color standards. For the first time, refinishers could duplicate the colors in the original car finish, and this simplified greatly the problems of paint touch-up and damage repair.

In 1935, Du Pont introduced "Preparakote" primers to the refinish trade, making "Dulux" finishes the preferred repaint system in upwards of 80 per cent of the refinishing of trucks, buses and other commercial vehicles. Here "Dulux" finishes displaced the older "Duco" nitrocellulose lacquers on an economy and ease-of-use basis.

"Duco" metallic colors were introduced in 1935 to provide a whole new line of sparkling, deep-sheen colors for automobiles. Two years later, "Pyralux" nitrocellulose finishes were offered for lower cost touch-up and over-all refinishing, although they were to be discontinued as a "wartime casualty" early in the next decade.

Expansion of manufacturing facilities continued during the 1930's with the company purchasing the Mountain Varnish & Color Works, Toledo, Ohio, in mid-1934, and building a new plant in San Francisco the following year. In 1937, construction was begun on a new plant in Fort Madison, Iowa, although it was 1940 before that facility began production, and in the same year, Du Pont introduced the first commercial finishes based upon urea-formaldehyde resins.

GROWTH OF INDUSTRIAL TRADE SALES FINISHES

After several years of field testing, Du Pont also introduced in 1937 an improved white paint for exterior use, based upon titanium dioxide pigment rather than the traditional white lead. About this time the company also introduced its well-known and now widely accepted Color Conditioning for Industry program, one of the most important factors in taking industrial painting out of the drab color stage and moving it into the scientific use

of color from the standpoint of area coding, safety designation, employee morale and maximum visual value.

Incidentally, until 1929 Du Pont had sold its consumer paints to retailers through wholesalers. At that time, the company decided to open its own retail-wholesale stores in five metropolitan centers -- Youngstown and Columbus, Ohio; Birmingham, Ala.; Syracuse, N.Y.; and Memphis, Tenn. By 1950 the number of Du Pont stores had risen to 60, remaining at that level until 1953 when the company abandoned its retail store operations and began paint distribution through Du Pont warehouses and independent retail dealers.

Alkyd resin primers and top coats pioneered by Du Pont in the 1930's were replaced about 1939 with alkyd-urea formaldehyde types which offered shorter bake times, better hardness and superior color retention as industrial finishes. The early 1940's saw introduction of polyvinyl formal resin wire coatings and nylon enamels as insulating materials.

EFFECTS OF WORLD WAR II

World War II represented a difficult period for both Du Pont and the rest of the paint industry. "Dulux" finishes virtually were abandoned due to a shortage of phthalic anhydride, and manufacture of "Duco" lacquers was curtailed sharply. War-caused shortages of labor, raw materials and equipment items continued to plague the industry through 1948, although by that time the paint industry had attained an annual sales volume of a billion dollars. Two years later, the outbreak of the Korean conflict again caused material shortages, and Du Pont was forced to give first priority to automotive finishes and temporarily cut back its development and production of other types of paints.

Perhaps the most significant changes throughout the paint industry in the post-World War II period were the entrance of many small companies into the paint business and the advance in technology on the part of all manufacturers. The combination of these factors made it difficult for the older, and especially the "quality," producers to maintain a rate of growth proportionate to the total industry.

DEVELOPMENTS FOLLOWING WORLD WAR II

First new products to come out of Du Pont's finishes laboratory after World War II were the "Metalli-Chrome" finishes in 1946. These were hard, durable lacquer enamels containing finely divided metal particles which gave to auto finishes a new, sparkling iridescence.

Another significant Du Pont development, at the paint manufacturing level, during this postwar period was the "47 Process," an improved method for pigment dispersions using fine sand as a grinding mechanism. Research work on the process, which sharply increased the capacity of pigment grinding facilities and resulted in better products, continued through 1954 when basic patents were finally obtained by Du Pont. Licensing arrangements were extended to other paint manufacturers and more than 250 other paint makers are now licensed to use the process.

Sprayable coatings based on "Teflon" fluorocarbon resins, which provided exceptional corrosion resistance and non-sticking characteristics, were introduced to the industrial finishes field in 1947-48.

The results of post-World War II research began to come to fruition in the 1950's.

Du Pont introduced its "Flow Kote" rubber-base interior wall paints for home use in 1952 and offered in the same year a new line of "Tufcote" alkyd enamels for heavy-duty industrial applications, along with odorless solvents.

ACRYLIC FINISHES INTRODUCED IN 1953

In 1953, the company's automotive customers saw the first field tests of "Lucite" acrylic lacquers, outgrowth of a research project whose objective was the development of an automotive finish having the low cost features of "Dulux" enamel, the styling and fast-dry features of "Duco" lacquer, and durability superior to either of those products. The following year, an improved "Dulux" enamel known as "Dulux" 100, was introduced for those automobile manufacturers who preferred an enamel to lacquer in their finishing process. But "Lucite" acrylic finishes rapidly gained in popularity, accounting for about 20 per cent of Du Pont's total topcoat sales to the auto industry by 1957, with General Motors adopting them as its "Magic Mirror" finish on all units beginning with the 1959 model year. In fact, acceptance of the "Lucite" finishes was so great that in late 1961, Du Pont released to the auto refinish trade a "blending service" on "Lucite" lacquers, similar to the mixing programs offered earlier for use with "Dulux" and "Duco" finishes.

An improved version of "Dulux" enamel was introduced in 1966. The newer product dries dust-free 50 per cent faster than its predecessor. Under identical exposure conditions, new "Dulux" looks as good after three years' exposure as the previous product does after two.

Du Pont's acrylic resin finishes spread to the appliance industry in 1958, and in the same year the company introduced "Duco" Spray Magic aerosol paints for touch-up purposes, along with a new Color Master paint mixing machine which permitted retail paint dealers to mix, in their own stores, any of hundreds of scientifically matched shades of paint and enamel.

"LUCITE" HOUSE PAINT

"Lucite" acrylic house paints -- first of the water-emulsion type products with superior resistance to blistering -- made their appearance in 1959, being recommended initially for use only over bare wood with a specially formulated primer. The following year marked the introduction of "Lucite" interior wall paint, a creamy thick, no-drip, thixotropic, emulsion type paint.

Combining all the advantagesof emulsions -- easy application, touch-up and clean-up -- "Lucite" wall paint climaxed more than 20 years of Du Pont research into utilization of acrylic resins. For the "do it yourself" home market, it provided a wall paint that not only was much less messy than earlier oil-base paints, but spread fast and evenly, acting as its own primer over almost any type of surface. Users liked its extremely low sheen, outstanding color uniformity, and long color retention, and within a year or two after its introduction it had become the most popular interior wall paint in the Du Pont line.

Meanwhile, exhaustive consumer tests in the 1959-62 period indicated that "Lucite" exterior house paint need not be limited to use over primed new or bare wood, but could be applied successfully over any sound substrate, offering much longer life than conventional oil-base exterior house paints. As a result of the studies, 1963 marked the first year of aggressive, large scale promotion of "Lucite" acrylic paint as a superior exterior house coating.

Two early-1967 refinements included: a no-primer "Lucite" house paint for use on bare or previously painted wood, masonry, metal, and -- in fact, every surface except staining woods; and for such woods as redwood, cedar, mahogany, and fir plywood -- an all new latex primer, the introduction of which gives Du Pont an all-emulsion house paint system.

OTHER DEVELOPMENTS OF THE '60's

Polyimide wire enamel and insulating varnish, products of Du Pont's broad polymer research program, were introduced on a commercial scale under the trademark "Pyre-ML" in 1962. Retaining

good mechanical and electrical properties over a temperature range of minus 310 degrees to 650 degrees Fahrenheit, they are among the most fire-resistant of organic polymers and are finding wide application in the electrical and electronic fields.

"Flintflex" lining, an unusually tough, flexible organic coating so smooth that few materials will stick to it, was introduced in the early 1960's and is being used widely as a chemically resistant lining for covered railroad hopper cars, food processing tanks, and industrial storage containers for dry bulk materials, including foodstuffs. It is a urethane-type product.

Also introduced by Du Pont in the early 1960's were "Budium" polymerized butadiene coatings for the metal container field. Low in cost, with outstanding resistance to nearly all types of foods, such coatings impart no taste to can contents and are expected to be adopted widely as an interior can lining in the food field and as a superior base coating for the interior of beverage cans.

The introduction of "Du-Lite" fluoropolymer enamel in 1965 brought unprecedented durability and color retention to the precoated metal siding industry.

The finish is designed for application to conversion coated aluminum and primed galvanized steel where exterior durability is vital, as in building panels.

"Du-Lite" has been used on numerous buildings from as far south as Florida to as far north as Alaska, including the huge Jones & Laughlin Steel Corporation complex in Hennepin, Ill.

Another area of large growth is the use of "Teflon" TFE non-stick finishes in both the cookware and kitchen appliance fields, where non-stick characteristics of the coatings eliminate the need for soaking and scouring of cooking utensils and other housewares. The anti-stick properties of "Teflon" finishes also have valuable applications for food, textile, paper, plastics, and other industrial processing equipment, as well as on gaskets, molds, and a variety of other articles.

In early 1967, Du Pont introduced a group of new coatings, along with a new trademark -- "Teflon-S" stratified non-stick and self-lubricating finishes. These coatings combine sufficient hardness for heavy-duty service with the non-stick property already familiar to users of "Teflon" TFE and FEP non-stick finishes. They also offer other advantages, including easier application methods, lower baking temperatures, and the use of only one coat for many types of applications. "Teflon-S" finishes were not designed for use on cookware, but they quickly

became useful on other consumer products, such as range hoods, snow shovels, and hand saws. Their potential applications by industrial and commercial firms are myriad, including conveyors, chutes, hoppers, and other bulk handling equipment; electrical equipment; valves, tanks, and linings; molds of many types; and other manufacturing machinery.

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Du Pont's plants for the production of paints, enamels, and other types of protective coatings marketed by the Fabrics and Finishes Department are located in Chicago, Ill.; Everett, Mass.; Fort Madison, Iowa; Flint, Mich.; Parlin, N.J.; Philadelphia, Pa.; South San Francisco, Calif.; Toledo, Ohio; and Tucker, Ga. Principal research facilities are located at the Marshall Laboratory in Philadelphia and the Flint Development Laboratory in Flint, Mich. Basic research also is conducted at the company's Experimental Station near Wilmington.

Du Pont's consumer paints are marketed through the Consumer Products Division of the Fabrics and Finishes Department. This group, established in 1962, reflects the company's intention to increase its emphasis upon the manufacture and marketing of finished consumer products -- a sharp departure from its first 150 years as primarily a supplier of chemical products for use and further fabrication by other firms. Product lines other than paints being marketed by this division include anti-freeze, the No. "7" line of automotive specialties, cellulose sponges, adhesives, and plastic toiletries.

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May, 1967

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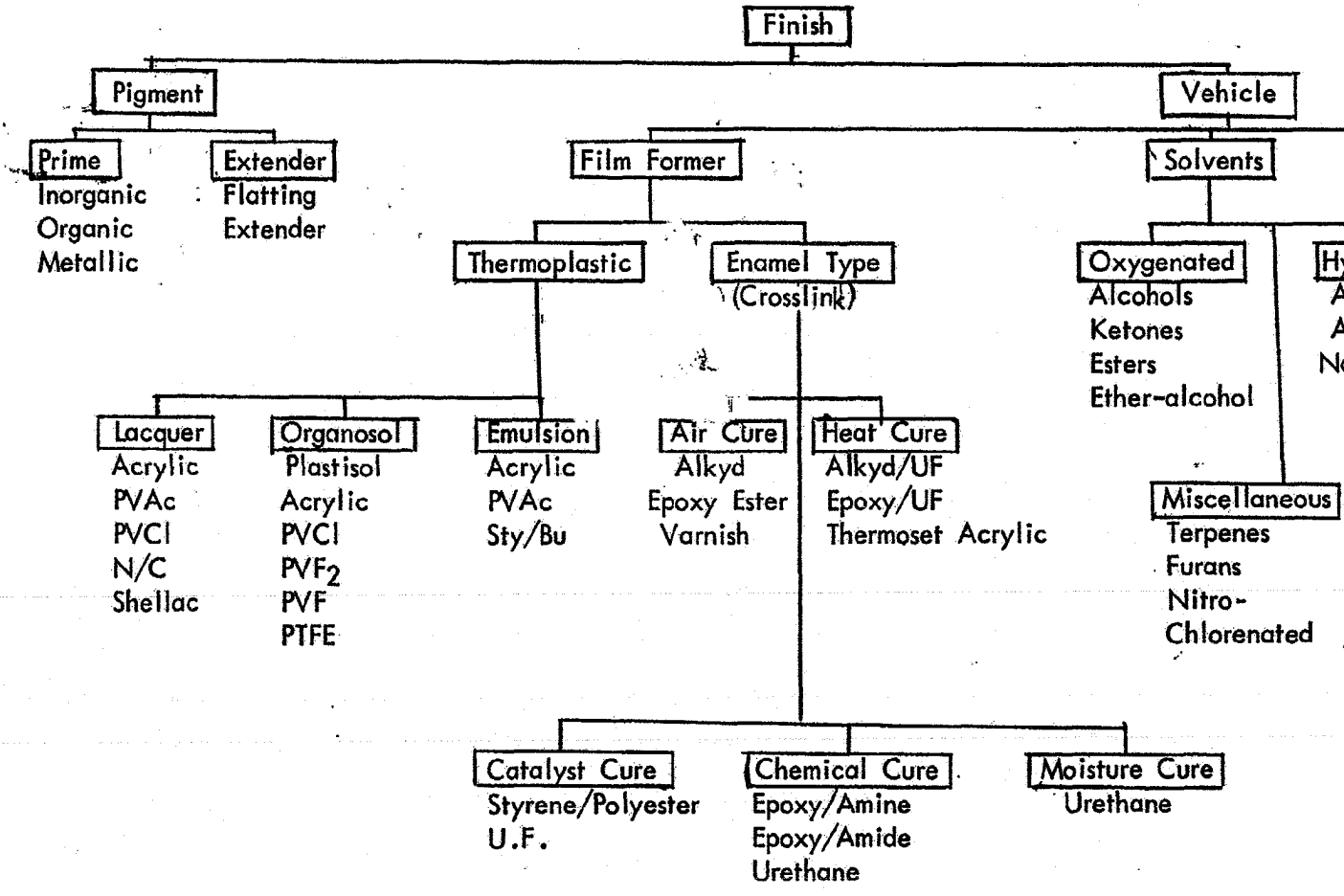
E. I. du Pont de Nemours & Co., Inc.

COMPOSITION OF FINISHES



MARSHALL LABORATORY
TRAINING SEMINAR
SEPTEMBER 1969

FORMATION, CHARACTERIZATION AND PROPERTIES OF COATING POLYMERS

Philip Heiberger

Formation, Characterization & Properties of Coating Polymers

A coating is a solution or dispersion of polymeric resinous materials plus pigments, additives and volatiles.

Our discussion will be confined to the preparation of the polymers used in coatings and the mechanisms by which these coatings form films.

Rule: Film properties improve as molecular weight (MW) or molecular complexity increases.

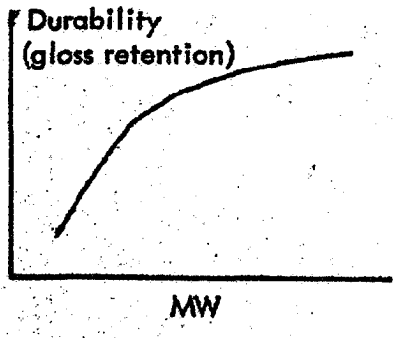
Methods:

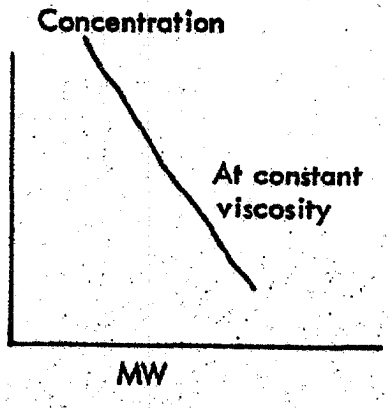
1. Use high MW polymers, these dry by evaporation with or withour coalescence. e.g. thermoplastics, lacquers, latexes.
2. Create complex structures via chemical reactions in film. e.g. thermosets, enamels, 2 component systems.

Product formulation is a process of compromise.

Required property balances, price, durability, solids, hardness, color, etc., will dictate choice of system. Selection will require knowledge of composition, reactivities, M.W. etc. which in turn implies knowledge of polymer chemistry, mechanisms, measurements, etc.

Examples





Polymer Preparation

Polymers are derived from simple organic molecules known as monomers, via

1. Stepwise reactions (condensation)
2. Chain reactions (addition).

Condensation polymers include the alkyds, phenol, urea and melamine formaldehydes, epoxies and polyurethanes.

Addition polymers include acrylics and vinyls.

Condensation Reactions

Polymeric reactions are completely analogous to the simple reactions of organic chemistry.

monofunctional: $ROH + R'COOH \rightleftharpoons R'COOR + H_2O$

bifunctional: $n\ HOROH + n\ HOOCR'COOH \rightleftharpoons HORO[COR'COORO]_{n-1} COR'-COOH + nH_2O$

which lead to linear polymers

polyfunctional:

CH_2OH
$CHOH$,
CH_2OH
glycerol

$C(CH_2OH)_4$ etc.
pentaerythritol

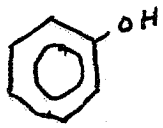
These polyols lead to 3 dimensional structures.

Polymer preparation is partly science and partly art. Kinetically, the rate of esterification is same for OH and COOH whether the reaction is monomeric or polymeric ------- BUT

in practice there are many complications---

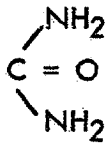
e.g.
1) Initially, the acid functionalities catalyzes reaction, this catalytic effort is lost as the acid groups are consumed.
2) Increased complexity leads to steric hindrances and to increased viscosities. This lowers the probability of random OH and COOH contacts.
3) Need for low product acidity requires excess OH's.
4) All OH's and COOH's are not necessarily equivalent.

Other Polycondensations



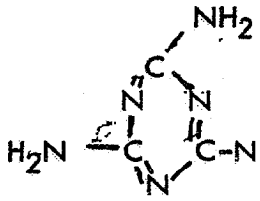
+ HCHO ⟶ phenolics

phenol + formaldehyde



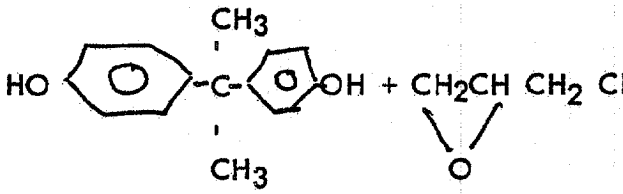
+ HCHO ⟶ ureas

urea + formaldehyde

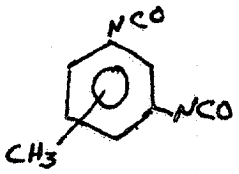


+ HCHO ⟶ melamines

melamine + formaldehyde



bisphenol A epichlorhydrin ⟶ epoxies



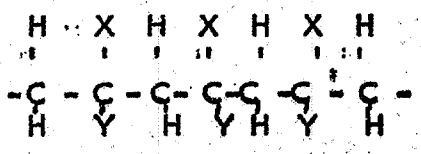
+ R'OH ⟶ urethane

tolylene diisocyanate + alcohol

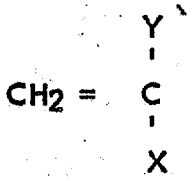
It would be instructive to complete these equations and recognize how complex the end products are.

Addition Polymers

Most addition polymers are substituted polyethylenes---



Most monomers are substituted ethylenes---



where X = H, CH_3, halogen,.....

Y = H,COOR,OCOR, Halogen, -C=N, Ø,COOH

Mechanisms:

Chain or addition polymerization operates when monomers are converted to polymers. These monomers are susceptible to chain polymerization by a number of mechanisms,

Free radical

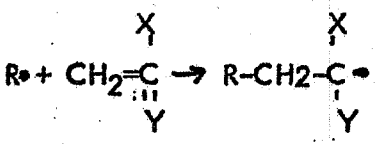
anionic

cationic

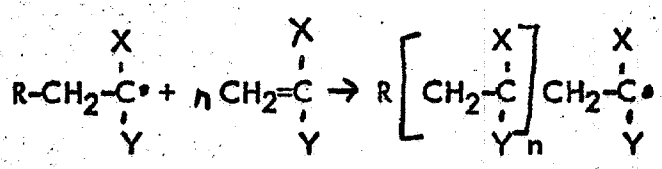
Of most significance to coatings is the free radical mechanism - e.g.

Mechanisms for Free Radical Polymerization of Vinyl and/or Acrylic Monomers

Initation:

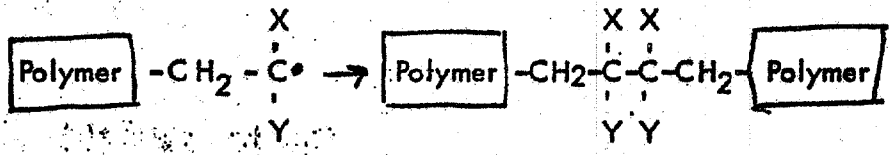


Propagation:

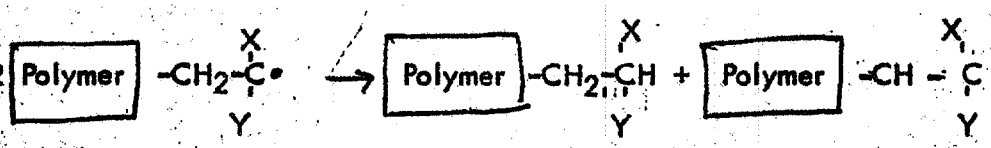


Termination:

(1) Combination or coupling



(2) Disproportionation:



Effect of Processing Variables on a Stepwise and a Chain Polymerization

Processing Variables	Stepwise Polymerization	Chain Polymerization
Time	The monomeric units are nearly all incorporated into larger molecules early in the reaction. The molecular weight increases with time. The yield of polymeric species is not a function of time in the latter stages of reaction.	High molecular weight polymer is formed immediately the reaction starts. The monomer concentration decreases steadily throughout the polymerization. The yield of polymer will increase with time.
Temperature	The rate of polymerization increases with temperature. However, the molecular weight of the final polymer is not appreciably affected.	The rate of reaction increases, but the molecular weight decreases, with increasing temperature.
Concentration of polymer-forming entities	Diluents usually slow down the rate of polymerization; the final molecular weight will not be appreciably affected.	The molecular weight decreases with increasing concentration of diluents.

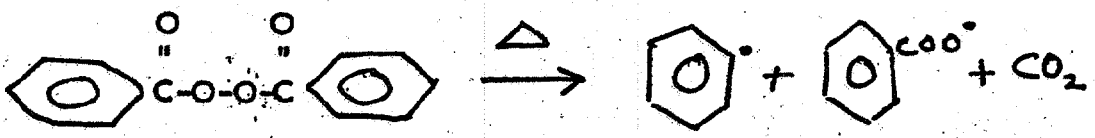
It is noteworthy that in chain polymerization, the presence of trace impurities or deliberate use of chain transfer agents or solvents have major effects on molecular weight and structure.

Initiation:

Mechanism involves generation of free radicals necessary to initiate polymerization, this may occur via

1. action of heat
2. irradiation
3. redox system
4. thermal decomposition of thermolabile organic molecules.

The latter is most common, e.g.

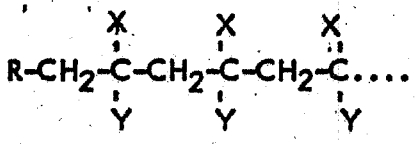


benzoyl peroxide.

each compound has a critical temperature -- selection of initiator is often an art.

Propagation

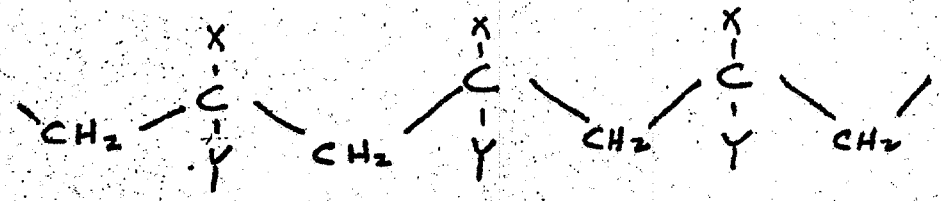
Monomers tend to polymerize in a regular fashion. Polymers with head to tail structures are quite common --



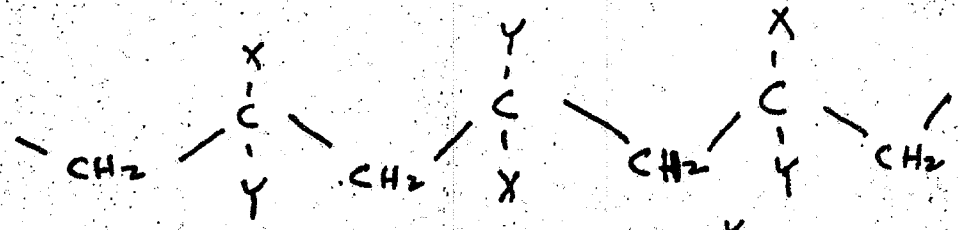
Note that every second carbon is asymmetric, therefore D or L arrangements are also possible. This is known as tacticity.

Most coating polymers are atactic. Stereoregularity is absent. Isotactic or syndiotactic polymers are less soluble, more crystalline, higher melting and more brittle.

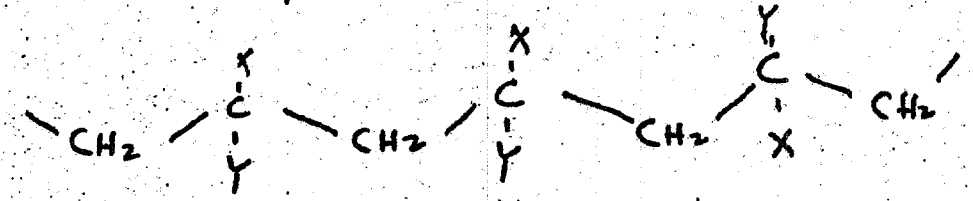
Isotactic:



Syndiotactic:



Atactic:



Termination Mechanisms

Two methods were shown, the preferred method is dimerization (styrene). Disproportionation is less desirable (MMA), because double bond is a potential breakdown center and because it activates neighboring groups leading to premature weathering or other environmental failures.

Termination may be controlled by

1. solvent, 2. chain transfer agent or 3. copolymerization.

Comparison of Polymerization Methods

There are several methods and the brief outline should charify the differences.

Polymerization Method	Characteristics of Technique
Bulk polymerization	Heat dissipation is difficult. The polymer is isolated as a solid that must be dissolved or dispersed before use. Not in general use for preparing surface-coating type polymers.
Solution polymerization	The polymerization temperature can be be controlled by the refluxing solvent. The polymer is obtained as a solution that may be used as such, and the method is widely used to prepare solution vinyl and acrylic polymers.
Suspension polymerization	Heat of polymerization is easily controlled. The polymer is usually isolated by coagulation and is contaminated with stabilizers, etc. Sometimes used for production of vinyl polymers subsequently used as organosols.

Emulsion polymerization (a) Aqueous continuous phase	Rapid polymerization to polymers with a higher molecular weight than is possible in solution polymerization at a comparable rate. The molecular weight distribution is usually narrower than that obtained in solution polymerization. Copolymers are possible from monomers that do not copolymerize easily in solution. The emulsion is usuable directly in some paint systems.
(b) Nonaqueous continuous phase	This method has the advantages listed for aqueous emulsion polymerization. In addition, the stabilizers and colloids are not water sensitive and the polymer is, therefore, obtained in a more hydrophobic form. The technique can be easily applied to the preparation of solutions of polymers by the addition of solvents for the polymer after the polymerization is complete. This method has advantages over solution polymerization - better viscosity control and heat dissipation, narrower molecular weight distribution, and control of the copolymerization tendency of monomers by the use of suitable monomeric or polymeric surfactants.

Copolymerization

Homopolymers are limited, they are either too soft or too hard, too inert or too reactive. Modifications are needed to achieve desired balance of properties or to provide appropriate crosslinking sites.

Simple blending is rarely adequate, many homopolymers are incompatible with each other, e.g. P (EMA) and P (MMA).

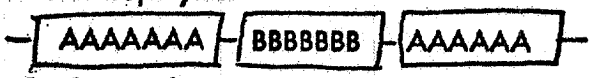
Approach is to prepare copolymers using monomers appropriately in order to obtain desired overall properties.

Copolymer types

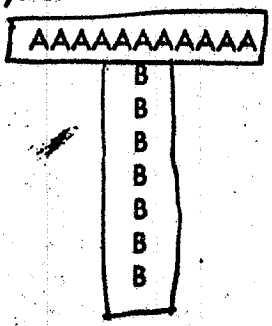
1. Random copolymer

A-A-B-A-B-A-A-A-B-A-A-B-B-A

2. Block copolymer



3. Graft copolymer



Random Copolymers

Listed are a few useful coating copolymers -

MMA/EA/MAA	S/BA/MAA
VCl/VAc	VAc/E
VCl/VAc/MA	AN/EA/MAA
S/Bu/MAA	

Resultant copolymers are rarely of same composition as starting materials,

e. g. 50/50 VCl/VAc on fractionation is known to vary from 75/25 to 42/58. Some monomers enter copolymer chains faster than others,

e. g. acrylics

Some monomers fail to homopolymerize but copolymerize readily,

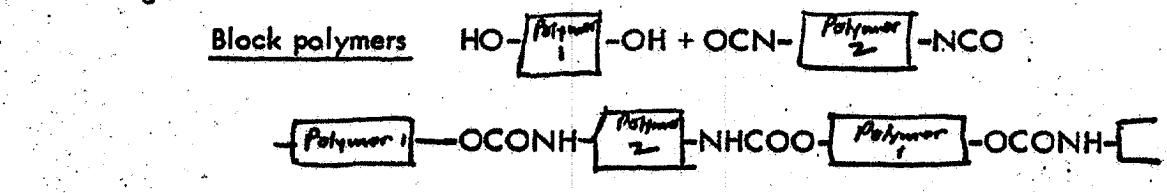
e. g. MA

Many rate studies are available and a wide variety of products exist.

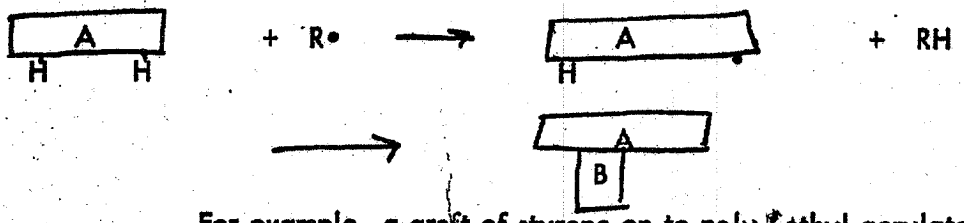
Block and Graft Copolymers

Although block & graft polymers are less commonly used in coatings, they are becoming more & more important - non-aqueous dispersions, can coating and urethanes -

Block polymers



Graft polymers



For example, a graft of styrene on to poly (ethyl acrylate) is more flexible, and softer, than a random copolymer of the same composition.

Polymer Characterization

The two main methods should be known -

1. End group analysis - (condensation)
2. Viscosity - (addition)

For I, acid no. is most common - though limited to low MW resins; accuracy decreases with increasing MW or complexity.

Measurement of viscosity is related to MW -

$$[\eta] = \lim_{c \to 0} \frac{1}{C} \ln \left(\frac{t}{to}\right)_c = \lim_{c \to 0} \frac{1}{C} \ln \left(\frac{t}{to}\right)$$

Intrinsic viscosity

where t = efflux time of polymer solution

to = efflux time of solvent

$[\eta] = KM^a$

where K = and a are constants and

M = molecular weight

A polymer is a mixture of molecules of different sizes and the MW is an average figure.

MW varies with the method - some determinations rely on the number of molecules, whereas, some depend on the weight of the individual molecules. Former are called number - average MW and the latter weight - average MW.

Number average	-	osmatic pressure end group analysis cryoscopic ebulliometric
weight average	-	light scattering ultracentrifugation viscosity (closer to weight - average)

Example: Equal No. molecules of 30M and 120M

$$\overline{Mn} = 30\,M \times 1/2 + 120M \times 1/2 = 75{,}000$$

$$\overline{Mn} = 30\,M \times \frac{30\,M}{150M} + 120M \times \frac{120M}{150M} = 102{,}000$$

when all molecules are equal, $\frac{Mw}{Mn} = 1$

thus ratio is a measure of distribution.

MW distribution is important because it influences solution viscosity, film strength, sprayability, drying time and other properties.

Glass Transition

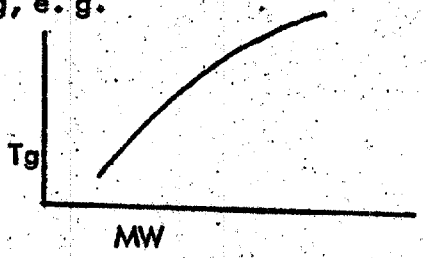
Some polymers are brittle or glassy, others are tacky or rubbery at a given temperature. The change from a glass to a rubber-like state takes place at specific temperatures called the glass temperature, Tg.

Tg corresponds to an abrupt change in a plot of physical properties versus temperature and is a reflection of the temperature above which segmental chain motion occurs.

Tg is important because flexibility, impact resistance, tensile strength, abrasion resistance, rate of cure, color, hiding, permeability and electric properties depend on relation between Tg and service temperature of coating.

Tg is a function of chemical composition, molecular weight, crystallinity and degree of crosslinking, e. g.

For given polymer



Variation of Tg With Polymer Composition

Polymer	Tg °C
Poly (methyl acrylate)	8
Poly (ethyl acrylate)	-22
Poly (n-propyl acrylate)	-55.5
Poly (n-butyl acrylate)	-54
Poly (methyl methacrylate)	105
Poly (ethyl methacrylate)	65
Poly (isobutyl methacrylate)	48
Poly (n-butyl methacrylate)	20
Poly (styrene)	100
Poly (vinyl choride)	75
Poly (vinyl acetate)	30
Isotactic PMMA	Tg = 115
Atactic PMMA	Tg = 104
Terephthalate polyester	melts at 265°
Isophthalate polyester	softens at 105°
Orthophthalate polyester	softens below room temp.

In general, the Tg of a copolymer is intermediate to that of the homopolymers.

An alternate method of modifying Tg is via plasticization.

Comparison of Internal and External Plasticization of a Polymer

Internal Plasticization	External Plasticization
The plasticizing component is chemically united into the film and is consequently not lost on exposure, etc.	The plasticizer may migrate from the film causing embrittlement on aging and/or poor adhesion by attacking the substrate. On the other hand, a temporary or fugitive plasticizer chosen so that it will volatilize after film formation can be an advantage for example, in latex systems.
The plasticizing comonomer is sometimes more expensive than a simple external plasticizer.	Modification of a formulation is easily achieved by use of different amounts of the plasticizer, or by a combination of plasticizers.
Mechanical properties often suffer at high comonomer contents.	Solvent release is often favored, since the plasticizer keeps the film surface mobile and relieves stresses set up during drying.
	External plasticizer is often effective over a wider temperature range.
	Less external plasticizer (on a weight basis) is usually required, and the desirable properties of the original polymer are not diluted as much as with internal plasticization.

MARSHALL DEVELOPMENT LABORATORY

TRAINING SEMINAR

PIGMENTATION

BY
P. M. CLINTON

PIGMENTATION

INTRODUCTION:

In the presentation today I will discuss several things about pigments; (A) how they are produced, (B) some of their physical properties, (C) what happens when a pigment is dispersed, (D) the appearance properties of pigments, and (E) typical pigment types.

Pigments are usually thought of as colored and opaque but many are actually almost colorless and transparent in paint vehicles. The colored opaque pigments are called prime pigments, the others extender pigments. Both serve a purpose in the film; the prime pigments to give color and opacity, and the extender pigments to control such properties as hardness, strength, sandability, gloss, and cost.

The vehicle of the paint includes the film former and the solvent. The definition of a pigment requires that it be essentially insoluble in the vehicle. This excludes such materials as dyes, which are soluble, from the definition. Some pigments are slightly soluble in certain vehicles and this is called "bleeding" and will be discussed more fully later.

SOURCES OF PIGMENTS:

Mineral or "earth" pigments are obtained from soil or rock deposits, for example, clay or limestone. They are crushed, ground (either dry or wet) and classified into various size ranges. They are usually irregular in shape.

Most synthetic pigments are produced by one of three methods:

1. precipitation
2. combustion
3. heat fusion

The formation of pigments by precipitation means that the pigment precursor is in solution and is precipitated from the solution to form the insoluble pigment. It is then washed, filtered and dried. Particle size and shape are determined by the precipitation conditions. Both inorganic pigments, such as "synthetic" iron oxides and organic pigments, such as phthalocyanines are produced this way.

A number of pigments are produced by combustion. Titanium dioxide, TiO_2, is largely made by combining titanium tetrachloride with oxygen, recovering the pigment in a water wash and drying it. Carbon blacks are produced by the partial combusion of carbonaceous materials such as oil or gas and recovering the finely divided pigment. Zinc and lead oxides are produced by heating the metal or its ores in the presence of oxygen and recovering the oxide. Operating conditions in each case have a large bearing on the particle size.

The heat fusion of materials is accomplished by subjecting the intermediates to high temperatures for extended periods of time, grinding and then classifying the finished pigment. Ultramarine blue is produced this way.

PHYSICAL PROPERTIES:

The gallon weight of the pigment is the density expressed as pounds per gallon. This is a true density (not a "bulk" density) in which the air voids are eliminated.

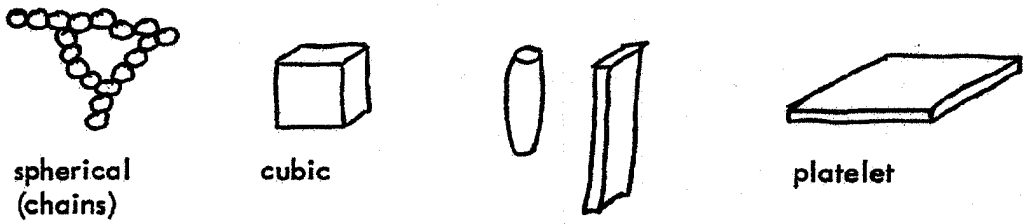
The particle size of a pigment is dependent on its method of manufacture.

A distribution of particle sizes is produced in all pigment manufacturing processes. The reaction conditions and classifying operations control the size distribution. During the reaction and drying stages the pigment particles form clusters or aggregates which must be broken apart before particle size can be measured. The average diameters of the pigments we work with can vary by at least two orders of magnitude.

Type of Pigment	Average Diameter in Microns
Carbon Black	0.01 - 0.10
Organic	0.1 - 0.5
Synthetic Inorganic	0.1 - 1.0
Mineral Inorganic	1.0 - 25.0

The particle size of many pigments is often inexactly specified as the fraction retained on a 325 mesh screen (44 micron holes). This only gives an indication of the upper limit of the particle range and not even a true measure of that for pigments of non-uniform size or those which are agglomerated.

Pigments also vary in particle shape. The shape of a pigment particle is determined by its crystal structure and the type and amount of grinding. Carbon blacks are spheroidal in shape, but they frequently are bound together in chain-like structures. Inorganic pigments are often cubical or acicular in shape. Acicular pigments are needle or rod shpaed. Some pigments are available as platelete. Aluminum flake and mica are of this type and they can exert a reinforcing effect on the paint film by making it less permeable when the "plates" are aligned across the substrate being painted.



spherical (chains) cubic acicular platelet

The particle shape can be modified by the grinding operation. "Wet" ground pigments usually have a smoother shape than "dry" ground pigments, and "micronized" pigments are usually the smoothest and most uniform in particle size. "Micronized" pigments are produced by comminution in a fluid-jet mill using compressed air or steam.

dry grinding wet grinding micronizing

The oil absorption of a pigment is the minimum amount of a vehicle required to wet a specified amount of the pigment. When a pigment is properly dispersed in a vehicle, air is displaced from the pigment surface by vehicle. The amount of vehicle needed to do this gives an indication of the pigment's surface area and character. Also, oil absorption represents, in volume units, the ratio of pigment to binder under conditions of closest packing. This can be converted to a pigment volume concentration (PVC) expressed as Critical Pigment Volume Concentration (CPVC). This is the pigment volume concentration above which you have air interfaces due to lack of vehicle. This is the concentration at which physical and optical properties of a paint film undergo large changes. Fine particle size organic pigments, with large surface area and high energy surfaces, require much more vehicle to "wet" them than a larger particle size inorganic pigment and consequently have much higher oil absorption value and lower critical pigment volume concentrations.

Pigment	Oil Absorption Value (OA)
TiO_2	18
Talc	45
Silica (Diatomaceous)	160
Red Iron Oxide	25
Chrome Yellow	22
Phthalocyanine Green	38
Carbon Black	100

$$\text{Oil Absorption (OA)} = \frac{\#\text{'s Linseed Oil}}{100\#\text{'s Pigment}}$$

$$CPVC = \frac{100\ P_b}{P_b + 0.01\ (OA) P_p}$$

P_b = Density Linseed Oil (0.935 g/cm^3)

P_p = Density Pigment (g/cm^3)

For Carbon Black:

$$CPVC = \frac{100 \times 0.935}{0.935 + 0.01\ (100)\ 1.82} = \frac{93.5}{2.755}$$

$$= 35$$

For TiO_2:

$$CPVC = 55$$

The reactivity of a pigment is its tendency to react with the vehicle. Basic pigments such as zinc oxide can react with acidic vehicles. This will usually result in an increase in viscosity. The very small pigments such as carbon black, iron blue and organic types may exhibit a physical or colloidal attraction in which pigment/pigment and pigment/vehicle interactions set-up an associated three dimentional structure in the paints. These can sometimes be controlled through the use of additives or broken down by high shear.

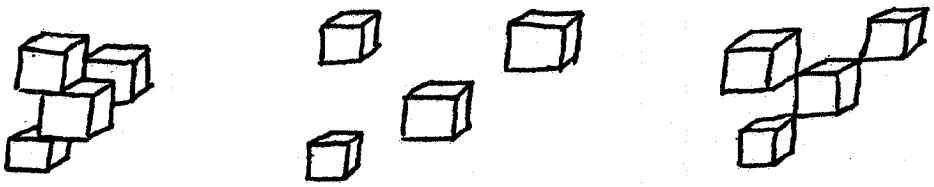
Pigments in emulsion paints can be affected by the ionic content of the mixture, also, a pigment that is water soluble can liberate ions in sufficient amounts to coagulate emulsions. Aluminum flake and zinc dust pigments are reactive with water ane evolve hydrogen gas. The reactivity of pigments points up the necessity of picking the right one for the vehicle you will be working with. In addition, the pigment has to be chosen with an eye toward the environment in which it will be used. The environment can react with the pigment also.

DISPERSABILITY:

The subject of dispersions will be covered in next talk. The treatment I am giving it here is done so that you can relate dispersion per se to pigments.

Dispersion is the action of forcing the pigment agglomerates apart (this is sometimes called deagglomeration) and replacing gases on the particle surface with vehicle. This often requires considerable energy. Pigment surfaces vary considerably in their affinity for liquids. Some are hydrophilic and others are organophilic. The character of the surface must be considered in making good dispersions. Additives may sometimes modify the surface character and aid in the dispersion process.

Once the pigment is deagglomerated in the dispersion process it may reform in a loose clump of pigments. This is called flocculation. It is point contact between a number of pigment particles caused by surface energy on the particles. These flocculates or clumps are soft and can be broken up easily, although they may form again if the driving force of attraction is still there.



agglomerate dispersion flocculate

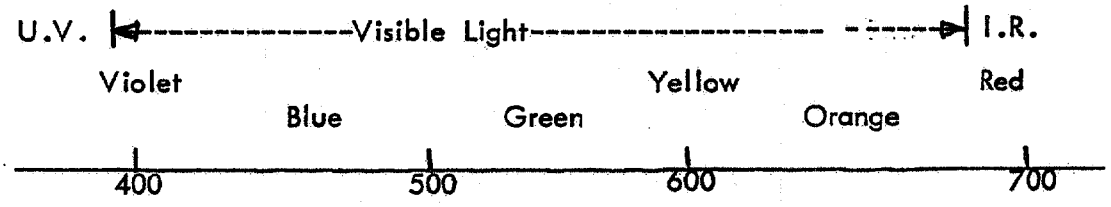
In water-based paints, ionic repulsion is used to stabilize the individual particles from flocculating. Surfactants give this charge to the pigment in the dispersion step. As long as the surface charge remains strong enough to keep the pigments far enough apart to prevent the attractive forces of the pigments from causing flocculation, they will be stable. In solvent based paints the dielectric of the medium is too high to provide charge densities adequate to stabilize pigments by ionic replusion. Here, pigments are stabilized by polymer adsorption of a magnitude sufficient to stop the close approach of the particles.

Flocculation can have both beneficial and undesirable effects. Flocculation can prevent hard settling of dense pigments in the paint can. It can also decrease sagging of wet films.. Adverse effects on color, hiding and gloss can be attributed to flocculation.

Color and hiding are affected because each floc behaves as a single particle and the number of effective particles in the paint decreases. Gloss is affected because the pigment clump is liable to interfere with the reflective surface of the paint.

APPEARANCE IN COATINGS:

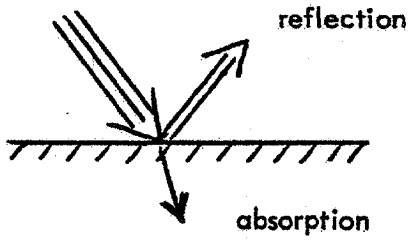
The primary reason for pigments in paints is to impart color and/or opacity to the film. Color is a sensation in the brain from stimulation of nerve endings in the eye caused by light of different wave lengths and intensities. The visible wave lengths range from about 400 nanometers, blue through green, yellow, orange to red at 700 nanometers.

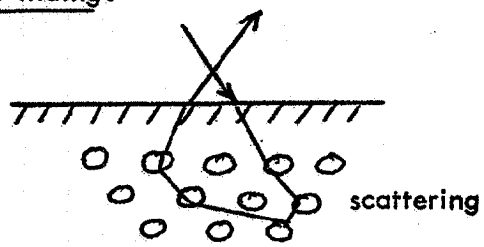


In opaque pigmented coatings light may be absorbed or reflected. White pigments reflect most of the incident light. Black pigments absorb most of the incident light. Colored pigments absorb some and reflect others, and the color you see depends upon the wavelengths reflected. A blue film would reflect, primarily, the blue wavelengths and absorb the others.

The color that a pigment reflects depends on its basic structure, b ut also such things as particle size, vehicle quality and the presence of air interfaces. Color as we see it, use it and measure it will be covered more fully in one of the later talks.

In addition to absorbing and reflecting light, pigments may also scatter light by reflecting and refracting it within the paint film. The light is thus returned to the observer before reaching the substrate. This is called hiding and when enough pigment is present in the paint to prevent light from reflecting from the substrate we have complete hiding.





The primary factor affecting hiding is the refractive index. The hiding power of a pigment is a function of the difference in refractive indices (R.I.) between the pigment and its surrounding, be it vehicle or air.

The following table shows some typical values:

Media	R.I.	Pigments	R.I.
Air	1.00	TiO_2	2.72
Water	1.33	Zinc oxide	2.08
Solvents	1.4-1.6	Calcium carbonate	1.58
Resins	1.4-1.6	Talc	1.49

When a pigment such as talc (R.I. 1.49) is dispersed in a resin (R.I. 1.5) the refractive index difference and the hiding are nil. Talc in air (1.49 vs. 1.00) is more opaque, however. Titanium dioxide gives opacity in both air (2.72 vs. 1.00) and resin (2.72 vs. 1.5) because of the large difference in R.I.'s.

Two other factors have an influence on hiding, pigment concentration and particle size. When a pigment is reduced in size it increases in opacity due to an increase in the number of interfaces present for refraction. When the particle is reduced beyond about 0.2 micron, however, it cannot adequately interact with the wavelengths of light and opacity falls off. It has been shown that TiO_2 has maximum opacity when its particle size distribution is centered around 0.2 microns.

Another factor affecting hiding and color is the degree to which the pigment is dispersed in the film. If the paint contains aggregates or flocculates of pigment these clumps behave opitcally as a single particle and the efficiency of the individual particles is lost.

It is often desired to lower the gloss of a coating. Pigments known as flatting agents have the property of causing large decreases in gloss when used in small amounts. These pigments have low refractive indices but a complex structure with high surface area. The incident light is scattered but not absorbed by multiple reflections among these internal surfaces. The structure set-up in the film also projects into the upper layer thus interfering with the reflection of light from the surface. The flatting pigments with the R. I. closest to that of the vehicle will give the clearest ("non-milky") flat film. Because of their high surface ares, flatting pigments have high oil absorption or vehicle demand causing an increase in viscosity. This does not usually cause a problem because they are so efficient they are used in small amounts.

PIGMENT TYPES:

I will now discuss some of the more important pigments we use, broken down into five categories: white hiding pigments, extenders and flatting pigments, colored pigments - inorganic and organic, black pigments and metallic pigments.

White hiding pigments can be divided into two headings, titanium dioxides and others. Since TiO_2 gives the greatest whitness and opacity it has largely replaced other white hiding pigments except in cases where the other pigments are used for a specific property; such as the use of zinc oxide to help retard the oxidation of oils during aging. Only TiO_2 will be discussed here.

All of our TiO_2 is supplied by Pigments Dept. and comes in a number of grades. Various treatments on the TiO_2 surface give the grades various properties. Three of the more important grades are W-123, W-185 and W-131. W-123 is designed as a general purpose grade, and is used in high gloss finishes. W-185 has an excellent balance of chalk resistance and hiding is designed for coatings on exterior exposure. W-131 is a highly treated pigment designed for the ultimate in weathering resistance at some sacrifice in hiding power and possibly some initial gloss lowering in a high gloss finish. Other TiO_2's designed specifically for emulsion finishes are becoming commercial. These TiO_2's are rutile crystal modifications produced by the "chloride" process. In addition, we use an anatase crystal modifications, W-16, in our trade sales products as an aid in "chalking" to promote self-cleaning of exterior paints.

Extender and flatting pigments are the second general class and are similar in character but perform different functions. Extenders are added to paints primarily to reduce costs. Extenders can, however, often control properties such as consistency, leveling and pigment settling. Mechanical reinforcement of the film and resistance to vapor or liquid permeation is also possible with certain extenders. Because the R.I. of extenders is so low, 1.4-1.8, they do not contribute significantly to hiding.

Calcium carbonate pigments such as W-90 and W-1004 are naturally occurring pigments of an alkaline nature. They react with acidic vehicles and affect alkaki sensitive pigments such as iron blue. They impart "hold-out" over porous substrates and increase the consistency of paints. They are slightly water soluble.

Barium sulfate known as barytes or blanc fixe is typified by W-12 (barytes-the natural pigment) and W-125 (blanc fixe - the precipitated pigment). These pigments are dense with low oil absorption and are used where a minimum effect on gloss by the extender is desired. It has a neutral pH and is chemically resistant. It tends toward hard settling and suspending agents may be needed.

Silicas of the crystalline type, W-31, and amorphous type, W-139 and W-1011 contribute toughness to paint films but are abrasive. The amorphous type is also called diatomaceous earth and is discussed later as a flatting pigment.

Magnesium silicate or talc, W-132 and W-135, is an important extender. Its acicular and lamellar shape gives soft settling in wet paints and offers some reinforcing in dried films to retard checking and cracking.

Mica, W-88, is a complex potassium - aluminum silicate of lamellar shape. The particles of mica consist of thin sheets which can overlap in a film thus decreasing the permeability of the film. It can also retard checking and cracking through film reinforcement.

Diatomaceous silica W-1011 and W-139, is a very effecient flatting agent. This is a function of the high surface area of the pigment, which is a calcined fossil of diatoms. This type of pigment is also used in primers as an aid in sandability and intercoat adhesion and in some coatings to increase blistering resistance possibly through increased porosity.

Chemically prepared silicas such as W-176, Cab-O-Sil, and W-1021, super fine, super-floss, are very fine in particle size and form three dimensional structures in the films. These are extremely efficient flatting agents and also cause the consistency of the paint to increase when used in moderate amounts.

Inorganic colored pigments form an important color class of which a few of the more important are mentioned here. In general, they are lower in cost than organic colored pigments, larger in particle size, quite opaque, and easy to grind.

The red iron oxides, W-362, W-355, W-366 and the yellow hydrated iron oxide, W-630, form one family of inorganic pigments. They are red to yellow in color, are permanent to light, low in cost, opaque, and easy to disperse. They are one of the more important pigment types we use. Their main drawback is their rather dull color.

Chrome yellows, W-686 and W-687, are precipitated lead chromates of bright yellow color, good opacity, low cost and easy dispersability. They darken on exposure and are sensitive to alkali, Since they contain lead they are toxic if ingested and must be kept out of paints children may come in contact with.

Molybdate oranges, W-622, W-652 and W-655, are similar to chrome yellow in properties. They contain lead molybdate and vary in shade from orange to red. They are sometimes blended with red and violet organic pigments to produce vivid intermediate red shades. They are also potentially toxic.

Cadmium reds, W-382, and W-384, are mainly cadmium sulfides. They are fairly light fast but sometimes difficult to grind. They have good heat and alkali resistance but are potentially toxic.

Iron Blue, W-582, is a deep blue pigment of extremely fine particle size. It is difficult to disperse but has high tinting strength and good lightfastness especially in masstone. It is very alkali sensitive.

Chromium Oxide, W-754, is a pigment inert to light, heat, acid and alkali and is easy to disperse. It is a dull green in color and has been largely displaced in most formulations by the organic phthalocyanines which are much stronger and more intense in shade.

The organic colored pigments as a class can be considered higher in price than inorganics, brilliant in color, and of high tinting strength and relative transparency. Some of them "bleed" in certain solvents and some are not lightfast or resistant to acids, alkali or heat but each pigment must be considered separately. Organic pigments are low in density, high in oil absorption and of fine particle size. They are generally more difficult to disperse than inorganics.

There are a number of pigment classes but I will only mention a few of the more important classes and examples here.

Acid-azo pigments such as W-300, BON red, and W-612, green gold, are insoluble dyestuffs which are slight bleeders. They are quite lightfast in light tints, have good tinting strength and are acid resistant. They are alkali sensitive.

The thioindigoid class is represented by W-312, thiofast red, a violet pigments of high strength and excellent lightfastness.

Phthalocyanine blues, W-537, W-552, W-577, and greens, W-750, W-785, W-764 are the most widely used organic pigments. They produce brilliant tint colors, are very strong, have excellent lightfastness and chemical resistance and are non-bleeders. Because of their superior balance of properties they are practically the only blue and green pigment types in use today. These pigments are supplied as Monastral® Blue and Green pigments from Pigments Department. They can be difficult to disperse and sensitive to flocculation.

Another class of pigments pioneered by the Pigments Department is the quinacridone family. These are also sold under the "Monastral" trade name. The pgiments range from an orange through reds to violets under such codes as W-818, W-819 and W-830. These pigments are lightfast, non-bleeders, heat, acid and alkali resistant, have high tinting strength and when well dispersed are quite transparent. Like the phthalocyanines they are of small particle size and somewhat difficult to disperse. They are also sensitive to flocculation in some vehicles.

The use of black pigments in paints means the use of carbon black pigments (except for a few pigments of specialized use which won't be mentioned here). Carbon blacks are the smallest particle size pigments used and have a very high surface energy. They are produced from incomplete combustion and are highly agglomerated and difficult to disperse. The color characteristics of a black depends on particle size, how well it is dispersed and the method of manufacture. The "high color blacks" are the finest particle size and are usually post-treated to increase "jetness" and aid dispersion. An aqueous carbon black stablized with surfactants, W-247, is also in use. W-205 is a large particle size carbon black, easy to disperse and blue in tone. It is used in shading paint where a blue tone is needed. An analog of this, W-225, is available in pelletized form to cut down on dusting and reduce bulk for handling. W-224 is a brown toned black of medium jetness used as a general purpose tinting black. W-253 is a carbon black precipitated on an inert carrier, aluminum benzoate. This is called "laking" and this laked pigment is easier to disperse and more stable to flocculation in certain vehicles. The laking procedure reduces strength. W-253 is a brown toned black of intermediate strength. W-259 and W-279 are "high color" blacks. They are of the smallest particle size and are chemically treated during manufacture to give the greatest "jetness". These pigments are used in automotive finishes to give depth and intensity to the black lacquer finishes.

Metallic pigments consist mainly of aluminum and bronze flake and zinc powder.

Aluminum flake is usually supplied as a paste in solvent or solvent and an additive such as stearic acid. The two types are "leafing" and "non-leafing". Leafing means that the stearic acid on the flake surface causes it to float to the surface of some vehicles causing a layer of flakes to orient themselves horizontally at the surface. This gives a smooth, brilliant surface to the film which is heat reflective and protects the film beneath. Of course, all aluminum flakes are very opaque. The non-leafing aluminum does not float on the surface of the film but does tend to orient itself horizontal to the substrate during film shrinkage. All aluminum flakes are sensitive to water in the packaged can and react (called gassing) to liberate hydrogen. Water, therefore, must be avoided in formulating with aluminum flake. Aluminum flake of the non-leafing type is graded according to its particle size distribution. The largest size, W-103, gives the most brilliant and reflective film but it also tends to project through the film causing roughness in a high gloss finish. W-105 is the finer grade. It is less brilliant and duller in appearance but gives smoother films. W-110 is an intermediate grade suitable for general purpose work. The leafing grade of aluminum is W-64.

Bronze powder, W-149, is similar to aluminum flake in appearance and behavior.

Zinc dust, W-180 and W-122 is a finely powdered zine metal used chiefly for corrosion protection. This is accomplished by cathodic protection of a steel substrate when the zinc is available in very high concentrations in the paint film. Zinc being higher than iron in the electro-chemical series becomes an anode to the iron or steel cathode and is corroded preferentially thus protecting the substrate.

This talk has only scratched the surface of pigments and their technology, but I hope I have given you a foundation to understand and apply pigments in your future work.

Thank you.

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MARSHALL DEVELOPMENT LABORATORY

TRAINING SEMINAR

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TITLE: PAINT FORMULA CALCULATIONS

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PAINT FORMULA CALCULATIONS

In discussing the composition of paints, we use terms expressing the weight and volume relationships of the ingredients. This lecture covers the definition of these terms, methods of calculating them, and some of the implications of the relationships.

The translation of weight of ingredients to volume ratios and vice versa used to take up a large portion of a chemists time. This work is now done by computer here at the Marshall Laboratory and it is seldom necessary for us to make the calculations ourselves. Nevertheless, it will help us to understand paint behavior and performance if we know how these formulating parameters are calculated, what they signify, and how they are used in practical formulating work.

Raw material suppliers give us the gallon weight in pounds per gallon of our raw materials. In some cases, they may report the density (grams per milliliter) rather than the gallon weight. Density can be converted to gallon weight by multiplying it by 8.32 (the number of pounds of water in a gallon at 75°F).

$$\text{Gal. Wt.} = 8.32 \times \text{Density}$$

The bulking value or gallons per pound of a material is the reciprocal of its gallon weight

$$\text{Bulking Value} = \frac{1}{\text{Gal. Wt.}} = \text{gallons per pound}$$

Note that with pigments, both gallon weight and bulking value refer to the solid pigment (no voids). Sometimes these values are designated as wet gallon weight or wet bulking value. While this does not clearly emphasize that it is the weight or volume of the solid pigment that we are talking about, it does distinguish these values from the dry gallon weight or dry bulking value which refer respectively to the weight and volume of the dry pigment including the voids. The dry values are used in relation to the space requirements for shipping or for loading dry pigment into ball mills.

Knowing the gallon weight and/or bulking value of the materials in a paint, we can calculate a number of weight and volume relationships between the ingredients.

One area where weight and volume considerations are particularly important is in figuring costs. We normally buy our raw materials by the pound, but we sell them by the gallon. This practice tends to conceal their true price.

For example, W-655, molybdate orange, costs $.542 per pound and W-865, toluidine red costs $1.57 per pound. It looks as though W-655 is cheaper, but, when we consider the cost per gallon it is not.

	Cost/Lb.	x	Lbs./Gal.	=	Cost/Gal.
W-655	$ .542	x	47.55	=	$25.75
W-865	$1.57	x	11.62	=	$18.23

Of course, many other considerations would influence our selection of either of these pigments. Cost per gallon is not the whole story, but it is important that we are not misled by the cost per pound figure.

We use a number of parameters to describe paint systems. One is the percent solids by weight, or, simply, weight solids. This is the weight of non-volatile material in the formula divided by the total weight of the paint times 100.

$$\% \text{ Weight Solids} = \frac{\text{Weight of Non-Volatile}}{\text{Total Weight of Paint}} \times 100$$

We say solids even though the non-volatile may be liquid before it is cured.

Weight solids is often used as a control test because it is easily determined by evaporating the volatile portion from a weighed sample of paint. Any gross loading error will be revealed by a discrepancy between the theoretical and the measured weight solids.

Weight solids, however, provides little information about the properties of either the paint or the film.

The percent solids by volume, or volume solids, on the other hand, is a more useful figure. Volume solids is the volume of non-volatile material in a paint divided by the total volume of paint times 100.

$$\% \text{ Volume Solids} = \frac{\text{Volume of Non-Volatile}}{\text{Total Volume of Paint}} \times 100$$

Knowing the volume solids, we can calculate other parameters. The theoretical coverage for example is given by the formula:

$$1604 \times \% \text{ Solids by volume} = \text{square feet covered at 1 mil dry film thickness.}$$

(1604 is the number of square feet one gallon of liquid will cover to a depth of one mil.)

It is called theoretical coverage because it assumes no losses by over-spray, cleavage, etc., and because the actual film may be applied at a higher or lower film thickness.

Knowing the coverage and the cost of the paint, we can calculate the cost per square foot of coverage.

$$\text{Cost per square foot} = \frac{\text{Cost Per Gallon}}{\text{Square Feet of Coverage}} = \text{Cents per sq.ft.}$$

This is a legitimate basis on which to compare paints for cost. Cost per gallon by itself is a misleading figure.

Another parameter is the pigment-to-binder ratio, P/B. This is the ratio of the weight of pigment to the weight of binder, expressed as pounds of pigment per 100 pounds of binder.

$$\frac{P}{B} = \frac{\text{Pounds of Pigment}}{\text{Pounds of Binder}} \times 100 = \frac{\text{Pounds of Pigment}}{\text{100 Pounds of Binder}}$$

The P/B level of a paint is selected on the basis of experience as ro what level will give adequate hiding, gloss and film properties.

The P/B ratio is often used to specify a desired hiding level in a product. We have to use a different P/B specification for different pigments, however, because they differ in hiding power. Pigment-to-binder thus indicates the relative hiding power of two paints only if they are made with the same pigment or pigment blend. For the comparison to be valid, though, we must be sure the formulas are not too dissimilar in their other components. Between really dissimilar formulas, the P/B level may show almost no correlation with hiding,even though the prime pigment is exactly the same in each.

Consider for example, a medium gloss fluoropolymer coil coating finisn which has adequate hiding at 0.7 to 0.8 mils with a TiO_2 P/B of 54/100 as compared with a low gloss thermosetting acrylic coil coating enamel which requires a TiO_2 P/B of 105/100 to get adequate hiding at 0.9 to 1.0 mils. The fluoropolymer paint has high hiding because of the low refractive index of the polymer while the acrylic paint has low hiding because the coarse extender particles act like "windows" through the film.

Comparing the P/B levels of an extender pigmenr in similar paints will given an indication of the relative gloss of the two paints, but as with prime P/B comparisons, we must be sure the paints do not differ too greatly in their other components.

We should not use P/B level as a guide for substituting one pigment for another unless the gallon weights of the pigments are nearly equal. If the pigments differ considerably in gallon weight, the physical properties of the paint and paint film will change because of the difference in volume of pigment in the two paints.

A parameter which has better correlation with the physical properties of the paint is the pigment volume concentration or PVC. This is the volume of pigment divided by the total volume of solids in the paint times 100

$$PVC = \frac{\text{Volume of Pigment}}{\text{Volume of Pigment + Volume of Binder}} \times 100$$

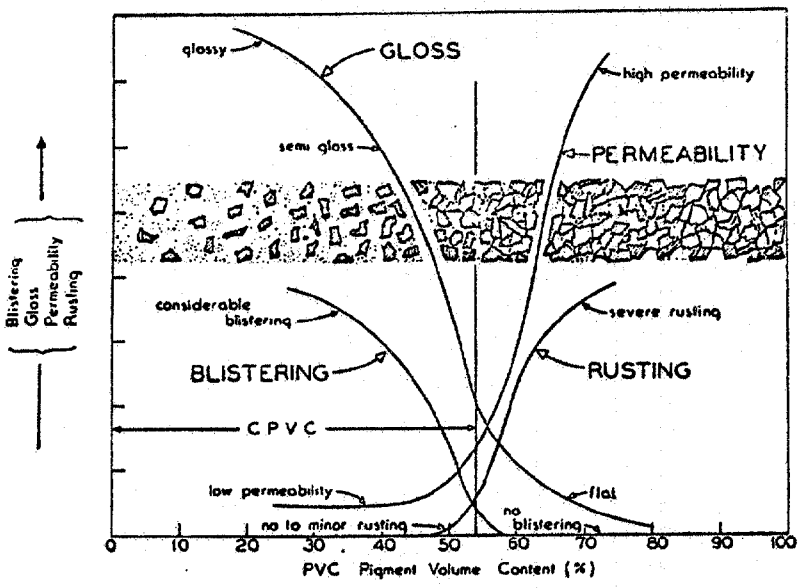
or

$$PVC = \frac{\text{Volume of Pigment}}{\text{Volume of Total Non-Volatile}} \times 100$$

The PVC shows reasonably good correlation with the physical properties of a paint, especially in highly pigmented products containing extender pigments. If extender pigment substitutions are made by replacing one pigment with an equal volume of another, the PVC is held constant, and the gloss, flow, viscosity and coverage of the paint will show relatively little change from the original formulation. This holds true regardless of differences in gallon weight of the pigments.

Wide differences between the pigments in particle shape, size, or size distribution, however, do cause some change in paint properties even when PVC is held constant.

If we take a given pigmentation and ladder the PVC of the formulation over a wide range we will find that there is a point at which the physical properties of the paint and the paint film show dramatic changes. This point is the critical pigment volume (CPVC). At the CPVC there is just enough binder present to wet the pigment and fill the voids between the particles. At higher PVC's the film is porous and will be flat, poorer in flow, poorer in corrosion resistance, but more resistance to moisture blistering and higher in hiding. At lower PVC's the film will show higher gloss, improved flow, improved corrosion resistance, poorer moisture blistering and lower hiding.



* - Graph illustrating the sharp breaks that occur in many film properties at the critical pigment volume concentration (CPVC).

The CPVC differs for each pigment or pigment blend. It can be determined by making a PVC ladder and checking the properties or, for single pigment products, it can be calculated approximately from the oil absorption data on the pigment.

The CPVC represents for static packing what PI represents for dynamic packing - the minimum binder content that will fill the voids. The CPVC, of multi-pigment system cannot be calculated with accuracy because we have no good mathematical method of allowing for the effects of interpacking and particle shape differences.

Let's now look at a practical problem in paint formulation and see how the calculations are made. The following problem and its solution show one method of laying out the work and using the given data to calculate a 100 gallon formula and determine its contents.

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PAINT FORMULA CALCULATIONS

PROBLEM:

I. Build a formula based on the following criteria:

A. a 3/1 weight ratio of W-123/W-189, TiO_2/Aluminum Silicate Extender

B. 30% total PVC

C. volume solids of 30%

D. 0.5 lbs. of G-782, Balab bubble breaker, per 100 gallons of paint

E. 100 lbs. of H-550, propylene glycol, per 100 gallons of paint

F. Use RC-11014, acrylic emulsion, for binder

II. Determine the following for the above formula:

A. gallon weight

B. weight solids

C. pigment/binder ratio

D. theoretical coverage at one mil

CONSTANTS FOR INGREDIENTS

Code	Name	Gal. Wt.	% Solids Weight	% Solids Volume	Wt. % Pigment
H-506	Tap Water	8.34	-	-	-
H-550	Propylene Glycol	8.59	-	-	-
RC-11014	Acrylic Latex	8.63	44.01	42.08	-
G-782	Balab Bubble Breaker	7.52	100.00	100.00	-
W-123	Titanium Dioxide	34.25	100.00	100.00	100.00
W-189	Aluminum Silicate	21.50	100.00	100.00	100.00
548-961	W-123 Dispersion	17.97	72.45	41.01	70.00
548-980	W-189 Dispersion	13.28	63.63	42.27	60.00

PAINT FORMULA CALCULATIONS

Pigment	Lbs. Pigment	Gals. Pigment
W-123	300 (1)	8.75 (2)
W-189	100 (1)	4.65 (2)
Totals:		13.40 (6)

Ingredient	Ingredient Lbs.	Ingredient Gals.	Gals. Solids
548-961	428 (3)	23.8 (4)	9.76 (5)
548-980	167 (3)	12.6 (4)	5.33 (5)
			15.09 (8)
RC-11014		70.4 (10)	29.6 (9)
Totals:			44.7 (7)

Ingredient	Gal. Solids/ 100 gal. Paint	Gal. Ingredient/ 100 gal. Paint	Wt. Ingredient/ 100 gal. Paint	Wt. Solids/ 100 gal. Paint	Lbs. Pigment/ 100 gal. Paint	Gals. Pigment/ 100 gal. Paint
548-961	6.55 (11)	16.0 (13)	288 (16)	209 (18)	202 (20)	5.87 (21)
548-980	3.58 (11)	8.52 (13)	113 (16)	71.8 (18)	67.8 (20)	3.14 (21)
RC-11014	19.8 (12)	47.1 (13)	406 (16)	179 (18)	-	-
G-782	0.1 (12)	0.1 (13)	0.5(given)	0.5 (18)	-	-
H-550	-	11.7 (14)	100.0(given)	-	-	-
H-506	-	16.6 (15)	138 (16)	-	-	-
Totals:	30.0 (given)	100.0 (given)	1045.5 (17)	460.3 (19)	269.8 (20)	9.01 (21)

(19) weight solids = 460/1046 = 44.0%

(20) P/B = 270/(460 - 270) = 270/190 = 142/100

(21) PVC = 9.01/30.0 = 30.0%

(22) Theoretical Coverage .30 X 1604 = 482 sq. ft./gal. at 1 mil

SOLUTION:

(1) With the established 3/1 ratio, 100 lbs. W-189 requires 300 lbs. W-123.

(2) Determine gallons of pigment: $\frac{\text{Wt. of Pigment}}{\text{Gal.Wt.of Pigment}}$

(3) Establish weight of dispersion giving required wt. of pgt.

300 lbs. W-123 = .70x, where x = lbs. 548-961.

(4) Determine volume of dispersions: $\frac{\text{Wt. of Dispersion}}{\text{Gal.Wt.of Dispersion}}$

(5) From this calculate gallons of solids: gal. x percent volume solids of the mill bases.

(6) Total volume of pigment.

(7) Since paint must be 30% PVC, volume of pigment = .30x, where x = total volume solids; 13.4 = .30x; x = 44.7 gals.

(8) Total gallons of solids from dispersion.

(9) Therefore, the gallons of solids contributed by the latex must be (total gallons solids required) - (gallons solids already present): 44.7 - 15.1 = 29.6.

(10) Determine the volume of latex needed for the required volume of latex solids: gallons of latex solids divided by percent volume solids of the latex:

29.6 = .421 x where x = gallons latex; = 70.4 gallons.

(11) The final 100 gallon formula must be 30.0% volume solids or 30 gallons of solids per 100 gallons of paint. Therefore, the volume of ingredient solids must be multiplied by a fraction to reduce it to 30.0 gallons holding all previously calculated ratios. Multiply gallons of ingredient solids by the fraction: (gallons volume solids required)/(gallons volume solids presently available) i.e. 30.0/44.7 = .672.

(12) Note that there is a requirement of 0.5 lbs. G-782 per 100 gallons. Since this is 0.1 gallons solids, the gallons of latex solids alone must be reduced by 0.1 gallons to adjust for 30% PVC and to keep 30.0% volume solids.

(13) To find the gallons of each ingredient per 100 gallons of paint, divide the gallons of solids of each ingredient by the percent volume solids of that ingredient: e.g.,

$$\text{gallons of latex} = \frac{19.8}{.421} = 47.1$$

(14) There is a requirement of 100 lbs. of H-550 per 100 gallons of paint. Determine the volume of H-550:

$$\frac{\text{Wt. of H-550}}{\text{Gal. Wt. of H-550}} = \frac{100}{8.59} = 11.7 \text{ gals.}$$

(15) To determine the number of gallons of water required to make 100 gallons, add up the gallons of ingredients so far and subtract from 100 gallons.

(16) Determine the pounds of each ingredient in the 100 gal. formula, multiply the gallons of the ingredient by its gallon weight.

(17) The gallon weight is the weight per 100 gallons divided by 100.

(18) Determine the wt. solids of each ingredient by multiplying weight of the ingredient by its percent weight solids. Lbs. Ingredient x % Wt. Solids = lbs. of Solids.

(19) The % weight solids is the total weight solids divided by the total weight multiplied by 100.

(20) Determine weight of pigment by multiplying weight of dispersion weight fraction as pigment e.g. lbs. W-123 = .70 (wt. of 548-961); weight of binder = total weight solids - weight of pigment.

(21) To recheck % PVC, take total gallons of pigment, divide by total gallons of solids, and multiply by 100.

(22) The theoretical coverage is the percent volume solids of the paint times 1604. .30 x 1604 = 482 sq. ft./gal. at 1 mil.

PROPOSED PRESENTATION FOR

COATINGS TECHNOLOGY COURSE

SPONSORED BY
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TITLE:

PRINCIPLES OF FORMULATION

AUTHOR:

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PRINCIPALS OF FORMULATION

You have by now a good technical background on many of the raw materials and intermediates that go into a coating.

Today we will survey the process of selecting these ingredients and combining them into a coating. We will consider how we can design or engineer this coating to meet the specific performance requirements of a particular end use.

One scheme for approaching this problem is the following:

I. Define the critical functional and appearance properties required of the coating.

II. Define the substrate requirements and limitations.

III. Define the service conditions and service life of the coating.

IV. Define other restrictions (manufacturing, application, labeling, Rule 66 compliance, FDA compliance, cost, etc.).

V. Select ingredients most likely to meet the specific requirements of the coating.

VI. Combine ingredients using formulating principles and balance properties.

VII. Test performance.

You will notice that this scheme emphasizes defining the problem. I think this is important. We are dealing with an extremely complex subject with multi-multi-variables. We have to know exactly what it is that we want to do before we have the slightest chance of doing it.

Let's see what is involved in defining and solving paint problems.

1. Define the critical functional and appearance properties required of the coating.

The only reason for putting a coating on a surface is to modify the properties of the surface. The surface must perform some function that it could not perform without the coating.

The two most obvious and well-known functions that a coating performs is to improve the appearance and the durability of the surface. I have a list of some 40 or so additional functions that coatings can provide. Here are a few of them with examples of end uses:

1. Heat Control (roofs, instruments, space capsules)
   a. By reflection
   b. By absorption
   c. By insulation
   d. By radiation
2. Light Control (homes, light fixtures, advertising displays)
   a. By reflection
   b. By absorption
   c. By color
   d. By texture
   e. By opacity
   f. By transparency
   g. By fluorescence
3. Electrical Conductivity (printed circuits, heating panels)
4. Electrical Insulation (wire coating, potting compounds)
5. Lubrication (electric cables, rifles, irons)
6. Friction (non-skid deck paints)
7. Adhesion (masking tape, fly paper)
8. Release (non-stick cookware, mold release agents)
9. Water Repellancy (rain wear and other clothing)

10. Wettability (primers for emulsion paints, towels)

11. Flammability (impregnants for matches and charcoal)

12. Fire Retardance (paints that won't burn, or paints that insulate other materials to retard ignition)

13. Toxicity (anti-fouling paints, mildew resistant coatings)

14. Non-toxicity (toys, juvenile furniture, food containers)

15. Permeability ("breathing" paints that transmit water vapor)

16. Impermeability for liquids and gasses (barrier coats on food wrappers)

17. Shatter Resistance (coating on flash bulbs)

I leave the listing of additional functional properties to you as a homework assignment.

Usually a coating must serve a number of functions rather than just one. Some of these functions are direct opposites of one another. The coating, of course, cannot serve both functions at once and it is up to the formulator to decide what intermediate level is adequate and practical for the job at hand.

I have included a number of functions and end uses that are not normally associated with paint. This is deliberate. The paint industry today has evolved into the coatings industry, and we should no longer restrict ourselves to so narrow a field of opportunity as paint.

Understanding the functional purpose of a coating helps in formulating it. It defines the real reason for using the coating, clarifies the technical requirements, places performance and physical property specifications in perspective, and focusses attention on what is actually sold.

II. Define the substrate requirements and limitations

The properties of the surface to be coated influence the design of the coating. Each substrate has its own problems:

Wood

- Rots
- Mildews
- Is non-uniform in porosity, does not uniformly absorb paints and stains
- Is not dimensionally stable to heat and moisture
- Is degraded by ultra violet light
- Contains water soluble materials that stain paint or react with it
- Contains oils and pitches that inhibit oxidation, stain paints, and mar their surface (knots, cypress oils)
- Must be held in place with nails which rust
- Has built in stresses that cause it to warp
- Shows fiber lifting
- Develops hydrostatic pressure under the coating by capillary attraction
- Transmits water vapor
- Is easily dented and scratched

Iron and Steel

- Corrode by oxidation (rusting)
- Form electrolytic cells when in electrical contact with other metals
- Form electrolytic cells between crystal domains within the metal itself
- Structural members are coated with mill scale that is contaminated with salts and is difficult to remove
- Once cleaned, it must be coated immediately to prevent corrosion
- Needs chemical treatment for best adhesion and corrosion resistance

Copper and Brass

- Form salts that stain paints
- React with film degradation products to form brown discoloration
- Are often used with a high polish which emphasizes coating defects

Zinc

- Reacts with vehicle acids and degradation products to form zinc soaps that destroy adhesion
- Reacts with cadmium sulfide pigments and discolors them
- Is a sacrificial metal in electrical contact with less reactive metals
- Is difficult to clean of oils used in processing and of white rust developed in storage
- Needs chemical treatment for best adhesion and corrosion resistance

Aluminum

- Is protected by its own transparent oxide layer
- Needs chemical treatment for best adhesion and corrosion resistance
- Chemical color treatments may affect coating adhesion

Masonry (Stone, brick, stucco, asbestos shingles, etc.)

- Contains alkali
- Transmits moisture
- Contains water soluble materials (Calcium sulfate efflorescence)

Plaster

- High water content when applied
- Contains alkali
- Is easily chipped or scratched

Each of the other substrates you may encounter will have its problems too.

Something else we must know in order to formulate satisfactory coatings is the service conditions to which they will be exposed.

III. Define the service conditions that the coating must withstand

The service conditions of the finish are pretty well defined by the end use of the article that is coated. Each end use will require a different set of film properties.

Let's discuss some of the more critical service conditions encountered in various end uses:

Houses - Exterior

- Extremes of climate
- Moderate mechanical abuse
- Mildew organisms
- Dirt and chemical contamination
- Stain from iron and copper fittings

Automobiles

- Extremes of climate
- Moderate to severe mechanical abuse
- Exposure to gasoline, oils, brake fluids, anti-freeze
- Polishes and waxes (abrasives)
- Tree sap
- Bird dung
- De-icing salts
- Smoke, soot, dust
- Must be repairable and recoatable in the field

Washing Machines

- Water and high humidity
- Detergents
- Bleaches
- Dyes

Electrical Insulation

- Electrical voltage
- High temperature
- Oils
- Ozone

Non-stick Cookware Coating

- High temperature
- Hot food acids
- Moderate abrasion
- Detergent
- Hot grease

Don't overlook any of the critical service conditions. I know of a case where a chemist developed a green coating to be sprayed on dead grass to improve its appearance. It was color-fast to sunlight, did not look artificial, and did not damage the grass. But in the first field trial, it proved to be water soluble.

Service life of the coating, of course, need not exceed the requirements of the article being coated. A license plate that is discarded after a year's use does not need five year durability. A casket finish must have a high quality initial appearance, but long term appearance is not essential.

On the other hand, long lived articles call for the maximum service life that can be put into a coating. Houses, industrial structures, ships, and automobiles are examples. Usually a high priced, long lived coating can be justified for these end uses because the labor cost of surface preparation and re-painting with low cost paints at frequent intervals exceeds the cost of painting at less frequent intervals with more expensive paint.

Having defined our problem in terms of functional properties, substrate properties, and service requirements, there are still other limitations within which we must formulate.

IV. Define other restrictions

Here are some of the factors we may need to consider:

- Manufacturing Equipment

Our formulation must be suitable for manufacture in the equipment available to us.

If reduction of the crystal size of the pigment is necessary, we need a ball mill. If we need the utmost in clarity and intensity of a transparent color for automotive metallics, we need a 2-roll mill. If we need a high pressure vessel for a polymerization step, we must have it. If we don't have the necessary equipment, we must develop an alternate formulation that we are equipped to make.

- Application Method

There are many ways of applying coatings:

Brush	Silk Screening
Hand Roller	Doctor blade
Spray	Squeegee
Dip tank	Air knife
Curtain coating	Tumbling
Roller coating (strip coating)	Fluid bed
Electrocoating	

It is the method of application that largely determines what the physical properties of the liquid product must be.

A brushing paint must have the right balance of drag and slip, enough slip to make it easy to apply and enough drag to keep the painter from spreading it too thin. It must flow enough to level out brush marks, but not so much that it runs or sags on vertical surfaces. It must set-up quick enough to prevent marring from dust and insects, but not so fast as to create lapping difficulties.

For rolling, it must not spatter or foam excessively, and must have adequate hiding even in thin areas of texture pattern.

Spray paints must atomize properly, must cover the ware without too heavy an orange peel pattern, must not pit or dimple from foaming or overspray, must not pull away from sharp edges, must set-up fast enough to avoid sagging, etc.

For dip tank application the paint must be resistant to foaming, and stable in viscosity and dry potential on long term exposure to air. It must coat the ware smoothly and uniformly without pulling away from sharp edges. It must flow without sagging or silking and it must leave the minimum bead at the bottom of the piece.

Not only does each application method place special requirements on the formulation, but each modification requires special treatment. For spray painting alone many variations in the formulation are necessary to adapt it to spraying by suction cup, pressure pot, hot spray, steam spray, airless spray, and several types of electrostatic spray.

There are modifications of other application methods as well, and each of these requires its special formulation.

- Labeling

Labeling laws influence our formulation in that, for some toxic ingredients, special warning labels are required - even up to the skull and crossbones poison label. To avoid adverse customer reaction, our Sales Department may demand alternate formulations.

- Rule 66 Compliance

Rule 66 is a section of the Los Angeles County Air Pollution Control District's Solvent Emissions Control Law that places severe restrictions on the amount and kind of solvents that may be released to the atmosphere during coating operations. Other localities are expected to adopt regulations similar to Rule 66 though perhaps less stringent. Wherever such rules are in effect, compliance is, of course, compulsory.

In cooperation with air pollution control goals (and in anticipation of more wide spread adoption of regulations) many coating manufacturers are converting their products to Rule 66 compliance for general sale in all areas.

- FDA Compliance

The Food and Drug Administration places restrictions on what coating materials may be used in contact with food.

Toxicity

When toxic ingredients are required you are obligated to take all necessary precautions during manufacture and application, and to warn the ultimate consumer of the risks in the use and mis-use of the finished article.

Shelf Life

A shelf life of as little as six months may be adequate for an industrial product while a trade sales product may require a minimum life of two years.

Royalty and Patent Considerations

Both cost and legality are factors to consider.

Cost

The goal is minimum cost, but with all the required properties.

Bearing all the previous factors in mind, we are now ready to begin selecting ingredients.

V. Select ingredients most likely to meet the specific requirements of the coating

To do this job well, requires a thorough knowledge of raw materials. We must know their strong points and their weak points and how they interact with one another. No one can carry all this information in his head. Purchase specifications, suppliers literature, technical books, technical journals, test record files and your own data files, are a few of the sources for this information.

We have to know all kinds of things: that chrome yellow darkens on exposure but that there is a pre-darkened grade of it; that yellow iron oxide turns to red iron oxide in 450°F or higher bakes; that vinyls are soluble in ketones but that acetone is not a particularly good solvent for them; that the tails (the residue of very slow evaporating components) of a solvent may lower gloss if they leave the film after it is cured; that a polymer dissolved in a true solvent often shows a greater drop in viscosity with the addition of a diluent than it does with the addition of more solvent; that polymers and plasticizers that are compatible in solution may not be compatible in the cured film and vice versa; that a flocculating agent added to improve settling resistance may also lower or raise gloss, lower hiding, and decrease flow etc. etc. etc. The list is interminable.

We do have some general guidelines, however.

Usually the component of our formulation that has the most influence on its performance properties is the binder. The binder contributes many of the functional properties to our coating. It largely determines the chemical resistance, flexibility, adhesion and durability of our film. Selection of the binder then is the most critical step in our program.

The pigmentation affects such properties as hiding, hardness, gloss, color, corrosion resistance, durability and to some extent affects flexibility, adhesion, sandability, etc.

The solvent or volatile component of the coating has the sole function of making the mixture of ingredients liquid enough for manufacturing and application processes. It affects quality in that poor solvent formulation leads to paint film defects such as popping, low gloss, poor film integrity, sagging, etc. The technical ideal is to use the minimum amount of the lowest cost solvents in the paint.

In addition to the binder, pigment, and solvents, most formulations contain modifiers or additives. These are materials which, used in small amounts, modify the properties of the paint or film. Often the effect is profound. Additives provide many of the functional properties of the coatings.

Typical additives and the properties they affect are driers, skinning inhibitors, fungicides, flow control agents, dispersing agents, wetting agents, UV screening agents, anti-foaming agents, etc.

VI. Combine ingredients using formulating principles and balance properties

Once we have selected a set of ingredients that are likely to meet the functional and appearance requirements of the coating, on the substrate we must coat, under the service conditions it will be exposed to, and under whatever other restrictions are involved, we must then combine the ingredients to get the best balance of physical properties of the coating both as wet material and as a cured film.

To do this, we must determine what ratios of ingredients give the desired properties. We will be concerned with what ratios of polymers give the desired level of crosslinking; what ratios of prime pigment-to-binder give adequate hiding; what ratios of total pigment-to-binder give the desired gloss level, what ratios of solvents are needed to give the desired solids level and evaporation rate, etc.

In discussing the composition of paints, we need to use terms expressing the weight and volume relationships of the ingredients. This portion of the lecture covers the definition of these terms, methods of calculating them, and some of the implications of the relationships.

The translation of weight of ingredients to volume ratios and vice versa used to take up a large portion of a chemist's time. This work is now done by computer in many organizations and it is seldom necessary for us to make the calculations ourselves. Nevertheless, it will help us to understand paint behavior and performance if we know how these formulating parameters are calculated, what they signify, and how they are used in practical formulating work.

Gallon Weight, Density and Bulking Value

Raw material suppliers give us the gallon weight of our raw materials in pounds per gallon. In some cases, they may report the density (grams per milliliter) rather than the gallon weight. Density can be converted to gallon weight by multiplying it by 8.32 (the number of pounds of water in a gallon at 75°F).

$$\text{Gal. Wt.} = 8.32 \times \text{Density}$$

The bulking value or gallons per pound of material is the reciprocal of the gallon weight.

$$\text{Bulking Value} = \frac{1}{\text{Gal. Wt.}} = \text{gallons per pound}$$

Note that with pigments, both gallon weight and bulking value refer to the solid pigment (no voids). Sometimes these values are designated as wet gallon weight or wet bulking value. While this does not clearly emphasize that it is the weight or volume of the solid pigment that we are talking about, it does dintinguish these values from the dry gallon weight or dry bulking value which refer respectively to the weight and volume of the dry pigment including the voids. The dry values are used in relation to the space requirements for shipping or for loading dry pigment into ball mills.

Knowing the gallon weight and/or bulking value of the materials in a paint, we can calculate a number of weight and volume relationships between the ingredients.

Cost per Pound, Cost per Gallon

One area where weight and volume considerations are particularly important is in figuring costs. We normally buy our raw materials by the pound, but we sell them by the gallon. This practice tends to conceal their true price.

For example, molybdate orange pigment costs $.542 per pound and toluidine red costs $1.57 per pound. It looks as though molybdate orange is cheaper, but, when we consider the cost per gallon, it is not.

	Cost/Lb.	x	Lbs./Gal.	=	Cost/Gal.
Molybdate Orange	$ .542	x	47.55	=	$25.75
Toluidine Red	$1.57	x	11.62	=	$18.23

Of course, many other considerations would influence our selection of either of these pigments. Cost per gallon is not the whole story, but it is important that we are not misled by the cost per pound figure.

Percent Solids by Weight

We use a number of parameters to describe paint systems. One is the percent solids by weight, or, simply, weight solids. This is the weight of non-volatile material in the formula divided by the total weight of the paint, times 100.

$$\% \text{ Weight Solids} = \frac{\text{Weight of Non-Volatile}}{\text{Total Weight of Paint}} \times 100$$

We say solids even though the non-volatile portion may be liquid before it is cured.

Weight solids is often used as a control test because it is easily determined by evaporating the volatile portion from a weighed sample of paint. Any gross loading error will be revealed by a discrepancy between the theoretical and the measured weight solids.

Weight solids, however, provides little information about the properties of either the paint or the film.

Percent Solids by Volume

The percent solids by volume, or volume solids, on the other hand, is a more useful figure. Volume solids is the volume of non-volatile material in a paint divided by the total volume of paint, times 100.

$$\% \text{ Volume Solids} = \frac{\text{Volume of Non-Volatile}}{\text{Total Volume of Paint}} \times 100$$

Theoretical Coverage

Knowing the volume solids, we can calculate other parameters. The theoretical coverage for example is given by the formula:

$$1604 \times \% \text{ Solids by volume} = \text{square feet covered at 1 mil dry film thickness.}$$

(1604 is the number of square feet one gallon of liquid will cover to a depth of one mil.)

It is called theoretical coverage because it assumes no losses by overspray, cleavage, etc., and because the actual film may be applied at a higher or lower film thickness.

Material Cost per Square Foot

Knowing the coverage and the cost of the paint, we can calculate the cost per square foot of coverage:

$$\text{Theoretical Cost/square foot} = \frac{\text{Cost Per Gallon}}{\text{Square Feet of Coverage}} = \text{Cost/sq.ft. at 1 mil DFT}$$

This is a legitimate basis on which to compare paints for cost. Cost per gallon by itself is a misleading figure.

If we know percent losses by overspray, cleavage, etc. we can calculate actual cost per square foot.

Actual cost per square foot =

$$\frac{\text{Cost Per Gallon}}{\text{Square Feet of Coverage}} \quad (1.00 - \%\ \text{Losses}) = \text{Cost per sq. ft.}$$

Pigment to Binder Ratio

Another parameter is the pigment-to-binder ratio, P/B. This is the ratio of the weight of pigment to the weight of binder, expressed as pounds of pigment per 100 pounds of binder.

$$\frac{P}{B} = \frac{\text{Pounds of Pigment}}{\text{Pounds of Binder}} \times 100 = \frac{\text{Pounds of Pigment}}{\text{100 Pounds of Binder}}$$

The P/B level of a paint is selected on the basis of experience as to what level will give adequate hiding, gloss and film properties.

The P/B ratio is often used to specify a desired hiding level in a product. We have to use a different P/B specification for different pigments, however, because they differ in hiding power. Pigment-to-binder thus indicates the relative hiding power of two paints only if they are made with the same pigment or pigment blend. For the comparison to be valid, though, we must be sure the formulas are not too dissimilar in their other components. Between really dissimilar formulas, the P/B level may show almost no correlation with hiding, even though the prime pigment is exactly the same in each.

Consider for example, a medium gloss fluoropolymer coil coating finish which has adequate hiding at 0.7 to 0.8 mils with a TiO_2 P/B of 54/100 as compared with a low gloss thermosetting acrylic coil coating enamel which requires a TiO_2P/B of 105/100 to get adequate hiding at 0.9 to 1.0 mils. The fluoropolymer paint has high hiding because of the low refractive index of the polymer while the acrylic paint has low hiding because the coarse extender particles act like "windows" through the film.

Comparing the P/B levels of an extender pigment in similar paints will give an indication of the relative gloss of the two paints, but as with prime P/B comparisons, we must be sure the paints do not differ too greatly in their other components.

We should not use P/B level as a guide for substituting one pigment for another unless the gallon weights of the pigments are nearly equal. If the pigments differ considerably in gallon weight, the physical properties of the paint and paint film will change because of the difference in volume of pigment in the two paints. See below.

Pigment Volume Concentration

This parameter has better correlation with the physical properties of the paint. The PVC is the volume of pigment divided by the total volume of solids in the paint, times 100

$$PVC = \frac{\text{Volume of Pigment}}{\text{Volume of Pigment + Volume of Binder}} \times 100$$

or

$$PVC = \frac{\text{Volume of Pigment}}{\text{Volume of Total Non-Volatile}} \times 100$$

The PVC shows reasonably good correlation with the physical properties of a paint, especially in highly pigmented products containing extender pigments. If extender pigment substitutions are made by replacing one pigment with an equal volume of another, the PVC is held constant, and the gloss, flow, viscosity and coverage of the paint will show relatively little change from the original formulation. This holds true regardless of differences in gallon weight of the pigments.

Wide differences between the pigments in particle shape, size, or size distribution, however, do cause some change in paint properties even when PVC is held constant.

Critical Pigment Volume Concentration

If we take a given pigmentation and ladder the PVC of the formulation over a wide range we will find that there is a point at which the physical properties of the paint and the paint film show dramatic changes. This point is the critical pigment volume (CPVC). At the CPVC there is just enough binder present to wet the pigment and fill the voids between the particles. At higher PVC's the film is porous and will be flat, poorer in flow, poorer in corrosion resistance, but more resistance to moisture blistering and higher in hiding. At lower PVC's the film will show higher gloss, improved flow, improved corrosion resistance, poorer moisture blistering and lower hiding.

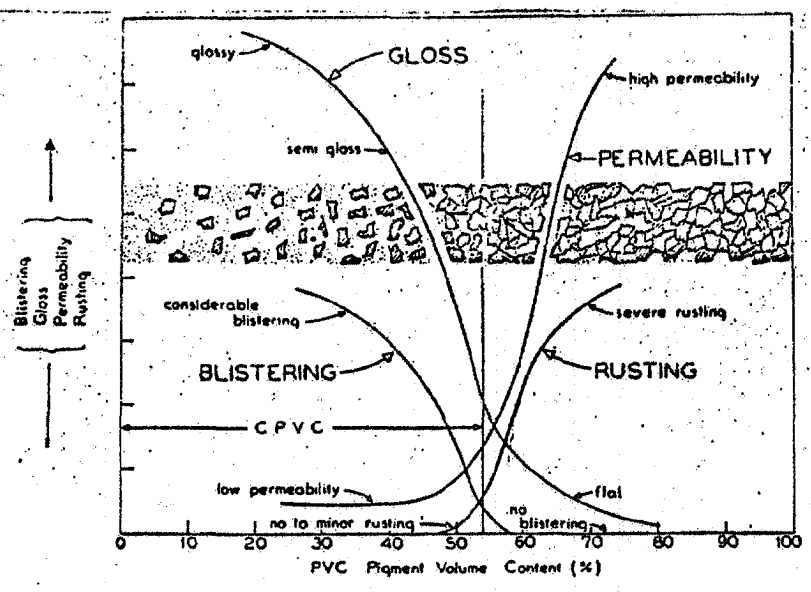

Fig. 7-1. Graph illustrating the sharp breaks that occur in many film properties at the critical pigment volume concentration (CPVC).

The CPVC differs for each pigment or pigment blend. It can be determined by making a PVC ladder and checking the properties or, for single pigment products, it can be calculated approximately from the oil absorption data on the pigment.

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*-Patton, Temple C. Paint Flow and Pigment Dispersions, John Wiley & Sons, 1964 New York, N.Y. Page 187.

$$CPVC = \frac{100}{1 + OA_m}$$

where OA_m = oil absorption in milliliters of oil per milliliter of pigment by the oil rub-out method. (ASTM-D-281-31).

In multiple pigment systems such as house paints or flat wall paints which contain both coarse and fine pigments there is an interpacking effect. The fine particles fit in the voids between the coarse particles and the CPVC is higher than for the single pigments alone.

Patton discusses mathematical and graphical methods of allowing for this interpacking effect. Both methods, however, depend on having packing data on the particular type and grade of pigments used and this information is not readily available.

With regard to crosslinking resins in binder composition there are no generalizations to offer. The ratio of polymers needed to provide a given level of film properties varies from type to type, and within types, there is generally a wide range of permissable ratios.

When we do reach the point of having made a formulation using our knowledge of formulating parameters, we will probably find that it does not meet all the requirements we have set for it.

At this point we use the art of compromise and in collaboration with Sales and/or the customer we concentrate on optimizing the most important properties, making sacrifices where necessary in the less essential properties.

Testing of the final formula is the next step.

VII. Test performance

Testing of your final product can be anything from routine control tests, if we are making a minor modification in an already established product, on up to many months of detailed characterization and performance testing, if an entirely new quality for a large volume end use is involved.

Many laboratories have specific check lists of tests for architectural finishes, appliance finishes, automotive finishes, etc.

In some cases customers require that your paint pass a battery of qualifying tests before they will approve it. In this situation it is extremely important that both you and your customer are using the same testing technique and equipment.

We have pointed out a number of factors to be considered in paint formulation, and have indicated some of the formula parameters we can manipulate to modify the film properties.

Now let's try to design some coatings for specific end uses, using the problem defining approach we have outlined.

At this point I shall solicit suggestions from the class as to what functional properties, substrate requirements, ingredients, and formula ratios might apply to formulating such products as (1) an interior semi-gloss architectural enamel, or (2) a low gloss coil coating finish, or (3) an exterior emulsion house paint, etc.

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MARSHALL DEVELOPMENT LABORATORY

TRAINING SEMINAR

SERIES

1969

TITLE: DISPERSIONS

AUTHOR: W. J. MC CONEGHEY

DISPERSIONS

The next two training talks are on dispersions. This is a complex subject and we will concentrate mainly on just two aspects of it; the packing index concept and the types of dispersion equipment available in F&F.

First, let's review the definition of dispersion:

DISPERSION - DEFINITION

Dispersion encompasses the process of wetting the pigment particles with vehicle to displace the layer of air and moisture on them, the process of breaking up the agglomerates into discrete crystals, and the process of stabilizing the mixture to control flocculation. Thinking of dispersions in these terms of wetting, de-agglomeration, and stabilization helps in identifying and solving dispersion problems.

We use the word dispersion for both the process and for the mill base that is the result of the process. The term dispersion is preferred to grinding because grinding implies fracture of the pigment crystals and, in most dispersion methods, the amount of crystal fracture is insignificant.

IMPORTANCE

The design of good dispersions is an important part of a formulator's work. The quality and cost of a dispersion strongly affects the quality and cost of the finished product. Some dispersions are manufactured almost daily over a period of years and are used in many different finished products. Any errors in formulation are multiplied many times over. Conversely, efficiently made, trouble-free dispersions provide multiple savings and benefits. The incentive for proper formulation is high.

There are many factors to be considered in dispersion formulations. The table on page 2 lists some of these considerations. That we discuss only two of them in this short training program is <u>not</u> to imply that the others are unimportant and can be neglected.

FACTORS AFFECTING DISPERSION FORMULATION

Pigment

Hydrophilic or lipophilic nature
Flocculation tendency
Hardness of crystals
Hardness of agglomerates
Particle size and size range
Particle shape
Packing index
Cost

Vehicle

Viscosity
Solvent composition
Polarity of components
Hydrophilic/Lypophilic Balance (HLB)

Additives

Wetting agents
Dispersing agents
Anti-settling agents
Viscosity control agents
Tackifiers
Defoamers

Equipment

"47 Process" Sand Mill
"48 Process" Mixer Dispersion
"49 Process" Slurry Dispersion
Ball and Pebble Mills
2-Roll Mills
Other Dispersion Equipment

Mill Base Requirements

Optimum Color Development
Color Stability
Viscosity Stability
Settling Resistance
Freedom from Seeding
Fineness
Miscibility with Finished Product

Finished Product Requirements

Color Stability
Viscosity Stability
Gloss
Flow
Color Brightness
Transparency
Hiding
Settling Resistance

Of these factors, the two we have selected for discussion are of particular value to DuPont formulators. One is the DuPont developed packing index concept. The other is the types of dispersion equipment available in the F&F plants.

Neither of these topics can be covered fully in the time allotted. However, we hope to give you an appreciation of the usefulness and versatility of the tools available to you. This, together with diligent use of the supplementary and reference materials, should help you to develop your formulating skills.

We will consider the packing index concept first because understanding it will help us to understand how each type of dispersion equipment works, what its advantages and limitations are, and how it may be used most effectively.

The packing index concept was developed by DuPont engineers and is confidential information. Maintenance of this confidential status gives DuPont a valuable competitive advantage over other manufacturers.

The packing index* itself is simply a number expressing the volume ratio of pigment to liquid under specified conditions of packing and shear. Later we will go into this definition more thoroughly, but first let's see what we gain by using the packing index concept. This formulating tool predicts the physical effects of pigments in dispersions and paint films. Knowing these effects in advance, we can greatly reduce the amount of costly trial and error work in designing products for optimum performance and optimum processing.

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*-For reasons to be explained later, packing index applies only to pigments greater than 0.2 microns in diameter.

Here are a few of the specific areas in which the packing index concept is useful:

(1) In estimating the optimum pigment concentration for formulating a mill base for a particular pigment using sand-mill, mixer, or ball mill dispersion equipment.

(2) In calculating the interpacking effect in multi-pigment systems so that they too can be dispersed at the optimum pigment concentration.

(3) In defining the formulating limits for any pigment or pigment system in our dispersion equipment

(4) In converting a mill base from one dispersion method to another.

(5) In predicting the effect a pigment change will have on the gloss, hardness, elasticity, sandability, porosity, etc. of the finished product film.

(6) In selecting pigment blends to get the maximum concentration of low cost extender pigments in low gloss products.

(7) In substituting one pigment for another in either a mill base or a finished paint while maintaining the physical properties of the original product.

(8) In understanding what is actually happening inside a dispersion or a paint film so that we can better define our problems and objectives.

PACKING INDEX, DEFINITION

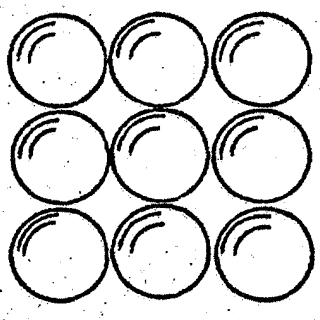
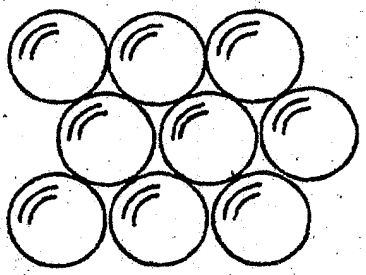
The packing index (PI) of a pigment is the ratio of the volume of the fully dispersed pigment to the volume of the liquid at which the pigment/liquid system will be dynamically packed when under high shear.

$$\text{Packing Index} = \frac{\text{volume of pigment}}{\text{volume of liquid}} \quad \text{or} \quad PI = \frac{P}{L}$$

(Note: PI is sometimes written as an overprint: $\overset{f}{P}$)

"Dynamically packed" for our purpose is defined as that concentration of dispersed pigment in liquid at which, under normal dispersion process shear rates, there is some mechanical interference between particles but the mixture is still fluid. In this situation, the mixture is right on the borderline between a dilatent and a non-dilatent condition. Addition of more pigment would greatly increase the interference between particles making it dilatent. Addition of more liquid would greatly reduce the mechanical interference between particles making it non-dilatent.

In a system consisting of uniform size spheres, dynamic packing is illustrated by cubic packing and a dilatent condition by ortho-rhombic packing.

Dynamic Packing	Static Packing
	
Cubic Packing	Ortho-rhombic Packing
* $\frac{P}{L} = 1.11$	* $\frac{P}{L} = 1.56$

*-The 1.11 $\frac{P}{L}$ shown for cubic packing is in fact the packing index for uniform size spheres, but the 1.56 $\frac{P}{L}$ shown for ortho-rhombic packing is merely the pigment to liquid ratio for that type of packing. It is not a packing index. Packing index refers only to dynamic packing conditions.

DYNAMIC PACKING VS. DILATENCY

If shear is applied to a cubic (dynamically) packed system, the spheres can move past one another with relatively little mechanical interference.

Systems more densely packed than cubic are dilatent. In these systems the packing is still loose enough to allow flow at low shear rates, but is tight enough that resistance to flow becomes increasingly greater as shear rate is increased.

At low shear rates the particles are moved a few at a time and slowly. There is time and room for them to weave past one another. However, at high shear rates, they are all moving at once and there is no time or room for the weaving movement to occur. The particles jam up and interlock. The mixture becomes "dry" in appearance because there is not enough liquid to fill the extra void space created when the particles are moved toward the dynamic packing configuration.

Let me show you what I mean:

DEMONSTRATION OF DILATENCY

Here is a dilatent dispersion of pigment in liquid. Note that it can be stirred slowly and that it flows off of the spatula. Yet when I jerk the spatula from the container quickly it comes out clean and the container is actually lifted by the resistance to flow. Note also that when I shear a little of the mixture between two spatula blades, it flows when I move the blades slowly, but "tears" or "breaks" when I move them rapidly. The fluid mixture seems to become dry under high shear

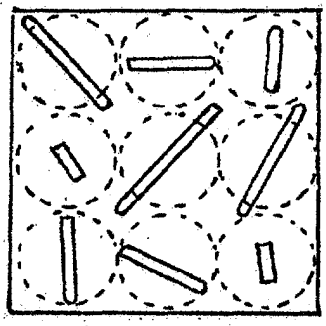
We have spent quite some time on dynamic packing and dilatency because an understanding of these terms is essential to understanding dispersion processes. For convenience we have used uniform-sized spheres to illustrate the ideas we are talking about. Now let's consider the problem of real pigments.

PACKING INDEX OF REAL PIGMENTS

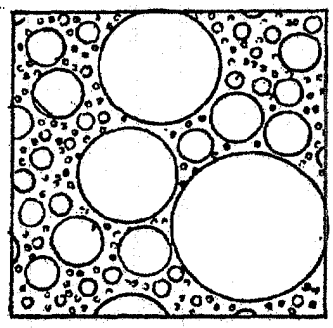
The packing index of uniform sized spheres is 1.11 but the packing index of real pigments depends on the particle shape and on the particle size distribution.

Under dynamic packing conditions, a non-spherical (needle-like, plate-like, cubic, or irregular) particle tumbles end for end as it is carried through the medium. It requires much more space for this tumbling action than its own physical volume. Such particles give low packing indexes - less volume of pigment and more volume of liquid under dynamic packing.

A wide range in particle size distribution, on the other hand, gives a high packing index - more pigment and less vehicle under dynamic packing. The fine particles fit into the voids between the coarse particles without interfering with their movement.



Non-spherical Particles
(Rods tumbling in three dimensions)
Low PI



Spherical Particles.
(Wide size distribution)
High PI

The packing index of all real pigments results from some combination of these two factors. In those packing indexes that are higher than 1.11, the particle size distribution effect predominates. In those that are lower, the particle shape effect predominates. Both effects are significant. Packing indexes range between 0.17 for W-895, iron oxide red, to 1.63 for W-120, barytes extender.

HOW PACKING INDEX IS MEASURED

The PI of a pigment is not a theoretical figure. It is a physical measurement. We determine the dynamic packing level of a pigment by first making a dilatent dispersion. Then, while the dilatent dispersion is under shear, we add liquid dropwise until the tear effect disappears. At this point the mixture is, by definition, dynamically packed and, knowing the volume of the pigment and the volume of the liquid, we can calculate the PI.

This measurement of PI is accurate to ± 5%. Details of the test are given in TM-450-A, but it is not necessary that you learn to run the test. The PI's for most commonly used pigments are listed in Formulating Practice 01-A, (FP-01-A). The PI of new or experimental pigments will be determined by the Marshall Laboratory Physical Testing Group on your request.

Note that the PI of a pigment is measured under the same shear conditions as occur in actual dispersion processes. Hence, it is more directly applicable to practical dispersion formulation than other common measurements of pigment characteristics. For dispersion work, properties such as oil absorption, void volume, critical pigment volume, and surface area are of much less significance than PI.

So far we have been talking about the PI of individual pigments. What happens though when we have to disperse a blend of two or more pigments?

PACKING INDEX OF MULTI-PIGMENT SYSTEMS

We could, of course, measure the PI of the blend but it is easier and quicker to calculate the PI. We can do this with sufficient accuracy if we know the PI of the individual pigments and have an estimate of their relative diameters.

Since pigments are irregular in shape and vary in size distribution, the "diameter" of a pigment is really a fictitious number. We can, however, make a reasonably accurate estimate of the effective diameter (ed) of a pigment. The effective diameter is the estimated diameter of a sphere equivalent to the volume requirements of the average size and shape of particle in the pigment when under shear.

We use this effective diameter number to define the size relationship between the two pigments:

$$\text{Size Ratio} = \frac{\text{ed of Coarse Pigment}}{\text{ed of Fine Pigment}} \quad \text{or} \quad SR = \frac{ed_c}{ed_f}$$

When the SR is less than three, the interpacking effect is negligible. For SR> 3 the packing index of the systems (PI_s) is the volumetrically weighted average of the pigments in the system.

$$PI_s = \frac{\text{Vol. Pig. A} + \text{Vol. Pig. B}}{(\text{Vol.pig. A}) \times PI_A + (\text{Vol. Pig. B}) \times PI_B}$$

When the SR is as high as 3, however, there is a slight interpacking effect. This effect becomes increasingly significant with increasing SR.

The method of calculating the PI of these high SR systems is explained in detail in FP-01-A and in M. E. Wall's 12/18/62 condensation of these practices. Computer Program ML-1049 also provides this calculation. It would be well worth your while to understand how these calculations are made, but we haven't time to study them today. Let's do try though to get some idea of what happens when pigments of significantly different effective diameters are mixed.

SIZE RATIO AND INTER PACKING EFFECT

First we must eliminate from consideration those pigments finer than 0.2μ (1μ = 1/1000 mm) in diameter. With these fine pigments, the effective diameters are appreciably altered by the absorption of a layer of polymer from the vehicle. This volume effect, high surface area effects, the cushioning effect of the polymer, and the small forces exerted on any one particle place these fine pigments outside the scope of dynamic packing measurements. In our packing index calculations, we count these pigments as part of the vehicle.

The effective diameters of the remaining commonly available pigments then range from 0.2μ to about 15μ, giving a top SR of 15/0.2 or 75. If we compare these ed's on a scale where 0.2μ= 1 inch, then the ed of the coarse particle is more than six feet! Actually some of the coarser particles may be as much as 200μ in diameter giving a size difference of 1000 to 1 between the coarsest and finest particles. On the 0.2μ= 1 inch scale, the coarsest particle would have a diameter of 83 feet!

There is plenty of room for the fine particles to pack between the coarse particles.

Where the SR of blends is only slightly greater than three, the interpacking effect is slight. At higher SR's, it is greater. So far as the movement of the coarse particles is concerned, the fine particles behave somewhat like vehicle. The greater the SR, the more like vehicle the fine particles behave. The nomograph in FP-01-A and B takes this SR dependency of interpacking and vehicle-like behavior into account.

Let's look at an example of this interpacking effect.

DEMONSTRATION OF INTERPACKING

Here are two dilatent dispersions which differ in particle size. Note that each tears under high shear on the spatula test. If they were of the same particle size, there would be no interpacking when they were mixed and the mix too would be dilatent. But they do differ in particle size and a one-to-one mixture of the two is quite fluid and is non-dilatent. The pigment and liquid in the fine particle size dispersion has spread the coarse particles farther apart and they no longer show mechanical interference. The liquid in the voids of the coarse dispersion has spread the fine particles farther apart and they too no longer show mechanical interference. We could add both more fine pigment and more coarse pigment to this system to bring it up to the dynamic packing level.

Another example of the interpacking effect is these two dispersions. Here is a dilatent dispersion of a coarse pigment, and here is the same dispersion with fine pigment added. Adding more pigment has made it non-dilatent!

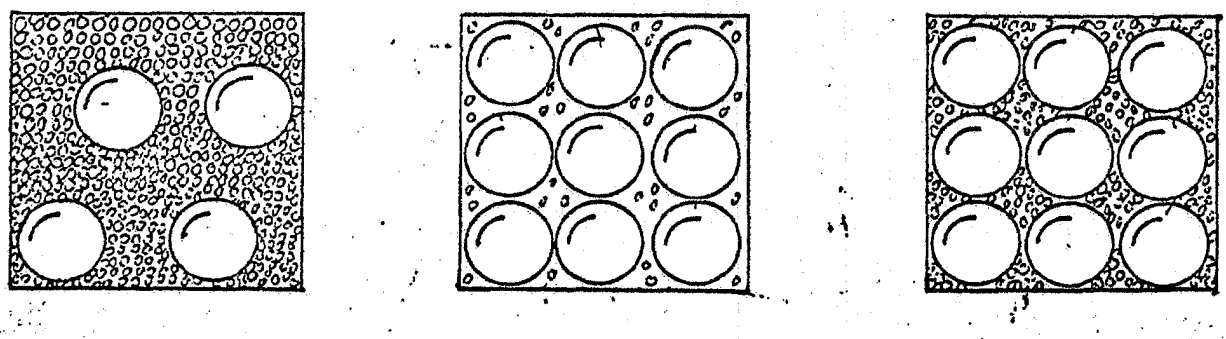
You can see that interpacking has a significant effect on dispersion behavior and on the amount of pigment that can be dispersed in a mill base.

The multi-pigment PI calculation is a tool with which we can predict and allow for these effects in our dispersion work without going through an expensive time-consuming trial and error process.

The PI calculation also gives us additional information about the particle size distribution in multi-pigment packing systems.

TYPES OF PACKING SYSTEMS

The packing index calculation identifies the type of packing system as excess fine, excess coarse, or balanced. Idealized diagrams of these systems are shown below:



Excess Fine Excess Coarse Balanced

Knowing the type of packing system helps us to identify the cause of some dispersion problems and to predict the performance of films. Here are a few of the implications of the different types of packing systems.

The type of packing system affects suitability for different dispersion methods. A balanced system provides a good dispersion of both the coarse and the fine pigment by any dispersion method. It is the preferred system for "48 Process" where particle-particle interference provides the dispersive force. The excess fine system is best dispersed by sand mill or ball mill, though even with these the dispersion effect on the coarse pigment in the system will be less than optimum. The excess coarse systems can be dispersed by any method,but the "48 Process" must be done in two-stages for best dispersion of the finer pigment. In the first stage the fine pigment is loaded together with just enough coarse pigment to make a balanced system. When that stage is dispersed, more vehicle and the remainder of the coarse pigment is added and dispersed.

Multi-pigment finished products with different pigment packing systems have different film properties. Assuming that the volume of pigment/volume of binder ratio is equal to the same % of PI for each system, the properties will generally vary as follows. A balanced system gives harder, stronger, smoother, more easily sanded films than the others. An excess fine system is likely to look gritty but has better hiding than the others. An excess coarse system will be lower gloss and lower hiding, but more flexible than the others.

The structure of a paint film made from a mixture of prime and extender pigments is not too different from that of concrete aggregate where the size ratios of sand and crushed stone are of about the same magnitude as the pigment SR. The paint film gains rigidity and strength from its coarse particles in the same way that the concrete does from the crushed stone.

PIGMENT SUBSTITUTIONS:

Occasionally we need to replace one pigment with another in a dispersion without altering the dispersion properties. This can be done with the greatest possibility of success by setting the P/L of the new system equal to the same % of its PI as the P/L of the old system is of its PI. (Replacement at equal % of PI). Percent PI =(P/L /PI)x 100. A pound-for-pound substitution or a volume-for-volume substitution is far less likely to work.

The same technique may be used when replacing one pigment with another in a finished product while holding film properties constant. Here, however, it is the volume of pigment/volume of binder rather than P/L which should be set at the same % PI in the two systems.

In substituting pigments in finished products, we must also consider other factors such as differences in particle shape or in degree of flocculation. Substitution of pigments at equal % of oil demand would perhaps be a better method to use for finished products (though not for dispersions), but we do not yet have a convenient mathematical system for predicting the static interpacking of multi-pigment systems in the oil absorption test. We have to make a physical measurement of the oil absorption of the pigment blend.

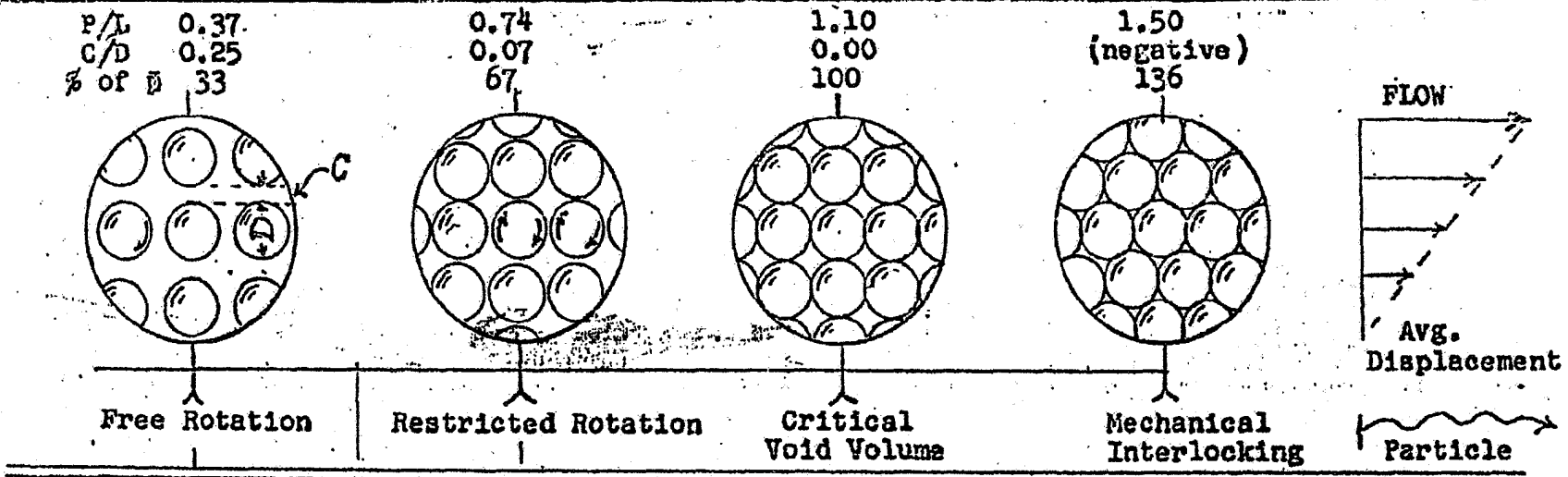
PERCENT PI AND DISPERSION METHOD

The chart on page 13A shows the preferred range of percent PI for each dispersion method. These preferred ranges should be adhered to in all dispersion work. Formulas outside these ranges will not give optimum dispersion.

The chart also shows the way the behavior of pigmented systems changes as the percent PI is varied.

I will explain the chart in more detail when we discuss dispersion equipment in the next class.

BEHAVIOR CHANGE WITH RELATIVE PARTICLE CONCENTRATION IN SYSTEMS



FLOW BEHAVIOR

Fluid → Semi-fluid → Solid

Increasing mixture viscosity (increasing shear rate on fluid) → increasing dilatency

Increasing sensitivity to pigment or liquid adds → shear rate sensitivity

Increasing stress transfer efficiency → increasing mechanical reaction

MILLING

"48 PROCESS" BASE

"47 PROCESS" BASE

"47P" SAND

BALL MILL BASE

(Attrition) (Mulling)

FILM

CRITICAL PACKING

Low flocculation

Gloss — Semi-Gloss — Flat — Film Porosity

High flocculation

25 33 50 67 75 100 125 140 P/L as % D

F. & F.
DISPERSION EQUIPMENT

In the last 20 years or so there has been a very rapid evolution in F&F toward more efficient dispersion methods. From heavy dependence on 3-roll, 5-roll, and ball mill dispersions we have shifted largely to "48" and "47" process equipment, supplemented by a few ball mills and some special purpose machines.

Most of this evolution has come about through internal studies of equipment design and formulation variables. The "47 Process" sand grind is an F&F invention, "47 Process" mixer dispersion equipment is a special F&F design, and several of the formulation techniques that promote the exploitation of these and other dispersion methods are F&F developed.

That considerable progress has been made is evident, but a great deal remains to be done. Studies of dispersion stabilization have been made and further work on stabilization and dispersion improvement is being done. Other types of equipment and equipment modification are considered by Process Engineering when appropriate.

In the meantime it is highly desirable that we use our current knowledge to the fullest. That is what this training session is about.

The information in this talk provides only a broad outline of the principles, operation, performance, formulating parameters and recommended areas of use for the different types of equipment. To understand and use the equipment properly, you must study the appropriate formulating practices and related references.

The following table lists the types of dispersion equipment available in F&F plants:

F. & F.

DISPERSION EQUIPMENT

1) "47 Process" Sand Mill
2) "48 Process" Mixer Dispersion
3) "49 Process" Slurry Dispersion
4) Ball and Pebble Mill
5) 2-Roll Mill
6) Other Dispersion Equipment

"47 PROCESS", SAND GRIND
FP-01-A

PRINCIPLE:

In the "47 Process" method of dispersion, the pigment is dispersed in the vehicle by the shear forces between rapidly moving sand particles.

OPERATION:

The dispersion is accomplished by passing a pre-mix of pigment and liquid thru a mill containing sand. In the mill, the pre-mix and sand are subjected to high shear by a series of rotating discs. The pre-mix is fed into the bottom of the mill and the dispersed base flows out at the top thru a screen that holds back the sand. Out-put is regulated by controlling the input of pre-mix.

PERFORMANCE CHARACTERISTICS:

This dispersion method is fast, economical to operate, low in initial cost, adaptable to a wide range of products and batch sizes. With two pre-mix tanks it can be used for continuous production. It will not give the maximum dispersion to very fine pigments less than 0.1 micron in diameter, nor will it appreciably reduce the size of coarse pigment crystals. Very hard large agglomerates are also difficult to disperse.

The dispersion of difficult pigments can be improved by making the pre-mix in two stages with the first stage adjusted to "48 Process" conditions. Undispersed agglomerates in the "47 Process" base indicate the need for this type of pre-dispersion.

FORMULATING PARAMETERS

Selection of the proper P/L is important and should be made on the basis of the percent PI recommended for "47 Process " in the chart on page 13A. A P/L in the lower percentage range will give relatively higher dispersion effect on the fine particles together with a higher thru-put if desired. A P/L in the higher percentage range will give relatively higher dispersion effect on the larger particles. Most products disperse well when the P/L is 25% to 35% of PI_s.

Vehicle composition is usually 20 to 30% solids by weight and should contain any wetting agents, dispersing agents, or defoamers required by the formulation.

The vehicle viscosity should be adjusted to the particle size involved.

Particle Size in Microns	Viscosity in Poises
0.1 to 2	0.5 to 2
2 to 10	2 to 5
Over 10	5 to 10

The dispersion base viscosity should be between 100 and 1000 centipoises (1000 CPS = 85 KU, Stormer). This viscosity should be measured at the operating temperature of the mill.

RECOMMENDED AREAS OF USE:

The "47 Process" is preferred for all bases which cannot be adequately handled by the cheaper "48 Process", or which do not require the special treatment provided by "49 Process" or the exceptionally high dispersion of ball or 2-roll milling.

"48 PROCESS" MIXER DISPERSION
FP-01-B

PRINCIPLE:

In the "48 Process" dispersion method, the pigment is dispersed in the vehicle by virtue of the close spacing of its own particles. This results in a combination of forces: hydraulic shear between counter-rotating pigment particles, mechanical transmission of shear force by inter-locked pigment particles, and crushing action on fine particles and agglomerates caught between coarse particles (coarser particle attrition).

OPERATION:

This process requires a high-powered mixer with an impeller specially designed to provide good turnover of a heavy paste-like material and high shear between the impeller blades and the tank wall.

The procedure consists of the step-wise loading of pigment into the dispersion vehicle while the mixer is running. Pigment is added until the power limit of the mixer is approached. As the mix becomes paste-like, the pigment must be sprinkled in slowly to avoid lumping and power overload. At full power load the pigment particles are very close together and shear stresses are high enough to rupture the agglomerates. After a few minutes operation, the power requirement drops as the agglomerates are broken. When the drop in power requirement begins to level off, more pigment is added. This procedure is repeated until the full pigment add is made. The mill is then run for a specified period after the last add (usually 30 minutes) and the dispersion is complete.

After the dispersion step, the base is let down either to the finished product or to liquid consistency for transfer to a regular letdown tank. In reducing the paste, liquid is added very slowly at first to allow time for complete mixing with the heavy paste. As the mix becomes more fluid, the rate of addition may be increased.

The usual order of addition for multi-pigment systems is a large portion of the coarse pigment, then the fine pigment followed by the remainder of the coarse pigment. As fine pigment is added to a heavy paste of coarse pigment, the viscosity will first drop as the volume of fines added spreads the coarse pigments far enough apart to prevent particle interference. Then, as further fine pigment is added, the viscosity increases somewhat as the fine particles begin to interfere with one another. Addition of the remainder of the coarse pigment brings the mix back up to the heavy paste consistency.

PERFORMANCE CHARACTERISTICS:

The "48 Process" is low cost. One operator can tend it, initial investment is low, it requires no pre-mix tanks and, if the letdown is made in the "48" mixer, no letdown tank or transfer pumps. Manufacturing flexibility is increased because there is less need to coordinate scheduling of auxiliary equipment and manpower. Batch size can be varied between 60% and 100% of the nominal capacity of the equipment.

The "48 Process" is limited to breakdown of low to moderate strength agglomerates. It works best for multi-pigment systems where the size ratio is greater than three and the pigment system is balanced, but other types of systems can be handled.

An excess fine pigment system or a fine single pigment base can be dispersed if the strength of the agglomerates is not too great and the degree of dispersion required in the finished product is not too high.

An excess coarse pigment system can be handled easily by using two dispersion stages in which the first is balanced and the second is excess coarse.

Hard-to-disperse pigments may be given extra dispersion by putting them in an extra tight first stage. On the other hand, if limited particle breakdown is desired as with some flatting pigments, a friable pigment may be held out and dispersed in a loose final stage.

FORMULATING PARAMETERS:

Selection of the proper P/L is critically important in "48 Process". The dispersive action is directly dependent on the spacing between particles. Over the practical "48 Process" P/L range, the liquid shear rate between particles varies from 100 to 10,000 times the overall mixture shear rate between the blade and vessel walls. The normal P/L range for "48 Process" is 100 to 120% of PIs, but some pigments for some end uses may be dispersed at a much lower P/L. For example, TiO_2 for low gloss emulsion paints is dispersed at 50% of PIs.

To keep flow resistance within bounds, the vehicle viscosity must be kept low. The preferred vehicle viscosity range for solution finishes is 0.05 to 0.5 poises measured at the normal operating temperature (140°F to 150°F). A viscosity up to one poise can be tolerated where there is a need for more polymer to prevent excessive flocculation or where the overall binder/solvent composition of the finished product forces the use of a higher viscosity vehicle. One poise, however, is about the maximum practical value for vehicle viscosity.

Wetting, dispersing, and defoaming agents, if required, are usually included in the base.

RECOMMENDED AREAS OF USE:

The "48 Process" is the preferred process for large volume items where the degree of dispersion meets the end use requirements. Low to medium gloss Trade Sales interior and exterior paints are the principal products made by this method.

"49 PROCESS" NITROCELLULOSE OR VINYL
FP-01-C or D

The "49 Process" is limited to nitrocellulose (Px)* and vinyl formulations. In this method of dispersion, pigment is dispersed in a high viscosity slurry of solid polymer in non-solvent. With Px the non-solvent is a blend of a latent solvent such as alcohol and a diluent such as aliphatic or aromatic solvent. With vinyl a blend of aliphatic and aromatic solvents is used. In each case a thick gummy fibrous mixture results. Pigment stirred into this mass is subject to high shear because of the high viscosity. The viscosity is too high to allow pigment loading to the point of particle interaction, hence packing index considerations are of little significance in this process.

OPERATION:

The "49 Process" formulas vary in the number of manufacturing steps. However, the essential steps are to (1) make a high viscosity slurry of all the solid polymer in non-solvent plus dispersing aid; (2) add the pigment and mix until it is wetted and deagglomerated; (3) add solvent to dissolve the polymer and deflocculate the pigment; and (4) add the remaining ingredients to make the finished product. With some pigments, steps 1 and 2 can be combined and with some step 3 requires two stages.

A "49 Process" mixer requires about five to six times the power of a conventional letdown mixer and requires a water jacket to control temperature.

PERFORMANCE CHARACTERISTICS:

The "49 Process" is simpler and lower cost than dispersing the pigment in plasticizer by other dispersion methods and adding clear Px or vinyl solutions to make the lacquers. It does not give quite as high a degree of dispersion but it is satisfactory for most Px and vinyl products.

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*-Px, abbreviation for nitrocellulose (pyroxylin).

When bases for Px or vinyl products are made in other than "49 Process" equipment, plasticizers are usually used in the base vehicle. Px solutions should not be used because of the danger of fire or explosion if it is overheated and a vinyl solution makes a poor dispersion vehicle because the polymers high viscosity and poor wetting. The "49 Process" mixer circumvents these problems because its design allows little chance for overheating and it is powerful enough to handle high viscosity solutions. The "49 Process" thus avoids the limitations on plasticizer selection and concentration that are imposed by other dispersion methods.

Separate pre-mix and letdown tanks are not required, and batch size may be varied from 60% to 100% of the nominal mixer capacity.

FORMULATING PARAMETERS:

Selection of the non-solvent/dispersing aid blend for the first stage dispersion vehicle and attaining sufficiently high viscosity of the dispersion mix are the most critical factors in "49 Process" dispersion.

The vehicle for this stage must be a non-solvent for the Px or vinyl polymer, and should contain dispersing aids such as oils, synthetic resins, natural gums, plasticizers, or surfactants whenever possible. Usually there is a choice of several non-solvents and dispersing aids in the overall formula and the most suitable combination must be determined by experiment for each pigment.

From the non-solvents and dispersing aids available in the formula, select those that cause the minimum flocculation of the pigment. Then make pigment slurries in a ladder of dispersing aid in non-solvent. Generally the slurries will be high viscosity at the low solids end of the ladder (because of flocculation) and high viscosity at high dispersant content (because of vehicle viscosity) with a minimum point between.

For maximum dispersion effect, use the concentration that gives the minimum viscosity. Most fine organic pigments require this type of vehicle.

For faster wetting and higher overall production rate, use a lower concentration of dispersing aid - the minimum concentration that will still give a liquid first stage. This type of vehicle is suitable for most inorganic pigments.

The minimum viscosity formulation is referred to as a "45 Process" first stage, and the minimum concentration formulation as "46 Process", after the similar vehicle types used in ball milling. Whenever it will provide adequate dispersion, use the higher production rate "46 Process".

After the pigment is dispersed, the polymer must be dissolved. Doing this in two steps gives improved deflocculation of fine pigments. With a small addition of solvent, the polymers will swell and become gummy. Mixing for a period at this consistency breaks up the flocculate and stabilizes the dispersion.

RECOMMENDED AREAS OF USE:

The "49 Process" dispersion method is the preferred method for Px and vinyl formulations wherever the degree of dispersion is adequate.

BALL AND PEBBLE MILLS
FP-01

PRINCIPLE:

Ball and pebble mill dispersions are made in horizontal rotating cylindrical tanks partially filled with steel balls, flint pebbles, or manufactured ceramic balls. The dispersion is accomplished by the combined shearing and crushing action of the balls as they cascade down the side of the mill.

Mills with steel grinding media are called steel, unlined, water-cooled (SUW) mills. Ceramic-lined mills with pebble or ceramic media are called pebble, lined, water-cooled (PLW) mills. We will use the term ball mill to include both types.

OPERATION:

Ball mill dispersions are usually made in three stages. In the first stage, the grind stage, the pigment is added to a low binder content vehicle and the mill is rotated until the desired fineness is reached. Second is an add-and-grind stage in which additional binder is added to deflocculate the pigment and stabilize the base. Grinding this stage for 1000 to 4000 cycles breaks up the strong flocculates that are generally found when resins are added to the low binder content grind stage. When properly stabilized, the dispersion will contain enough binder to prevent further flocculation when the base is letdown with more resin in the finished product. The mill is drained at the end of the add-and-grind stage. The third stage is a 1 or 2% thinner or resin add to rinse the mill. The rinse is drained into the base and thoroughly mixed in to complete the batch.

Ball milling allows individual treatment of pigments in composite pigment systems. Loading a hard-to-disperse pigment as a separate first stage grind gives it the extra dispersion it needs. Conversely, loading a coarse flatting pigment after the other pigments are dispersed avoids overgrinding and loss of flatting efficiency.

PERFORMANCE CHARACTERISTICS:

Ball milling is a relatively high cost dispersion method. Maintenance and operator costs are low, but initial investment is high and production rate is low.

SUW mills are more efficient than PLW mills because of the higher density grinding media. However, the steel worn off of the balls discolors light pigments and limits SUW mills to use with black and dark colors. PLW mills are satisfactory for light colors and products that cannot tolerate contamination with steel, but the wear from the ceramic media decreases the intensity of the clean bright transparent colors that are used in metallic glamour finishes.

Except for these restrictions, ball mills will disperse almost any kind of pigment, fine or coarse, soft or hard.

Ball milling is one dispersion method that will significantly reduce the particle size of coarse pigments though it is nearly always better to buy a grade of pigment in the desired particle size range and disperse it by a lower cost dispersion method.

Ball mills have many advantages. They are simple to operate, require no pre-mix, have minimum volatile losses, are free from contamination, and give good reproducibility.

Their limitations are cost and lack of flexibility in volume and scheduling. For a given formulation and mill, only one size of batch and only one production rate is possible. Varying either the batch size or the grinding cycles causes poor reproducibility.

They are very noisy in operation.

FORMULATING PARAMETERS:

For the grind stage choose a P/L in the recommended % PI range shown for ball mills on the chart on page 13A. Hard-to-grind pigments, strongly flocculated bases, highly viscous bases, and high density bases indicate a P/L toward the lower end of the range. For the opposite conditions, a higher P/L is appropriate.

Remember that pigments below 0.2μ in diameter are beyond the scope of packing index measurements. These pigments require very low P/L ratios. Lamp black for example is dispersed at a P/L ratio of 0.06 to 0.08 in ball mill formulas.

Composition of the grind stage vehicle markedly affects efficiency. The ideal vehicle is determined by making pigment slurries in a ladder of solvent, binder, and wetting agent blends. Such ladders generally show a high viscosity at high solvent content and a high viscosity at high binder content with a minimum point between. The preferred solvent, binder, and wetting agent blend is on the solvent-rich side of the minimum viscosity point. With most resins, this results in a grind stage vehicle with about 5% to 10% binder solids.

Bases made with the solvent-rich vehicle are called "46 Process" bases. Bases made with the higher resin content vehicle which gives the minimum viscosity are called "45 Process". Grinding in still higher resin content and hence higher viscosity vehicle is called conventional grinding.

Though pigments disperse with less flocculation in the "45 Process" vehicle, the "46 Process" solvent-rich vehicle is preferred because it wets the pigment faster and gives a faster overall production rate. The flocculation is then broken down in the add-and-grind stage.

Conventional grinds are much slower than "46 or 45 Process" grinds. (One five-day conventional grind was reduced to less than 8 hours when reformulated to "46 process"). Although "46 Process" is the preferred method, both "45 Process" and conventional grinds are necessary in those cases where there is not enough free solvent to make a "46 Process" grind.

When the formulation allows a choice of solvents, use the ones having the minimum flocculation effect on the pigments.

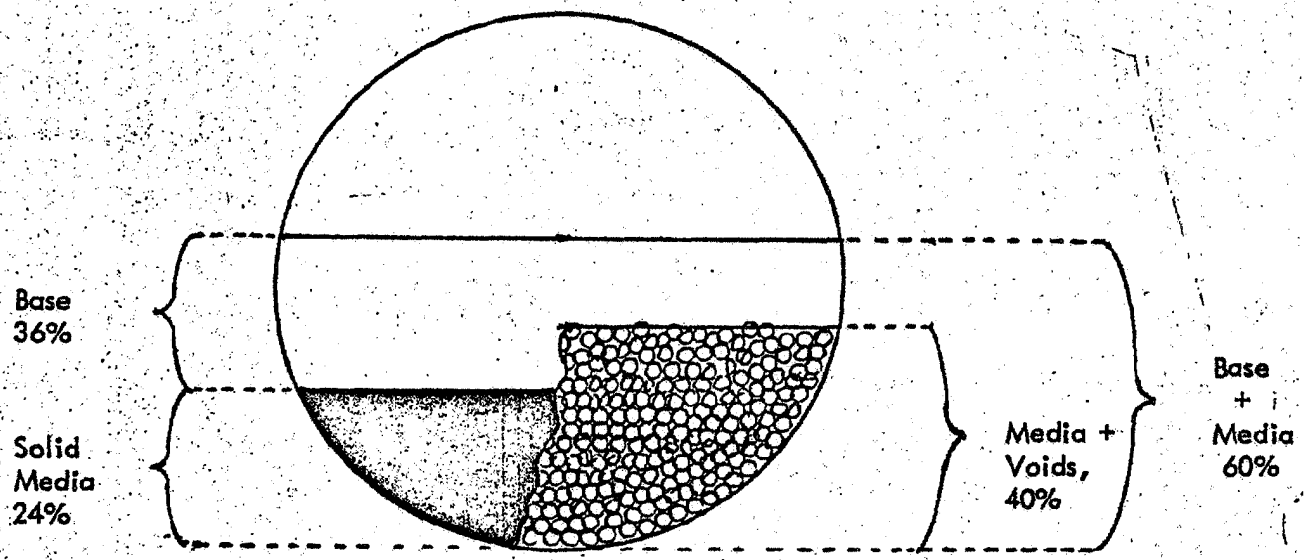
A mill filled to the half-way mark with bulk grinding media and with just enough mill base to fill the voids would give the shortest grinding time. However, this gives small batches and neglects loading and unloading time. The optimum production rate is approached with the loadings shown in the chart of Volume Relationships in Ball Mill Formulations on page 27.

VOLUME RELATIONSHIPS IN BALL MILL FORMULATIONS, SHOWN AS % OF MILL CAPACITY

Grind Stage		Steel Mill	Pebble Mill
(1)	Grinding Media + Voids	40%	60%
(2)	Solid Grinding Media	24%	36%
(3)	Mill Base	36 to 56%	34%
(4)	Total Grind Charge	60 to 80%	70%
(5)	Grind Ratio (Line 1 ÷ Line 4)	40/60 to 40/80	60/70
Add-and-Grind Stage			
(1)	Total Charge	90% max.	90% max.

The diagram below illustrates a 40/60 grind stage loading:

40/60 GRIND STAGE



The grind ratio is the ratio of the grinding media plus voids to the total grind charge. The limits shown in the chart are based on theory confirmed by experience and represent a compromise between the amount of pigment dispersed per batch and grinding time. The 40/80 ratio is preferred because it disperses more base per batch. However, if the pigment is hard to disperse, the grind time will be excessive. For hard-to-grind pigments, a lower mill base charge,down to as low as the 40/60 ratio,shortens the grind time and gives a better production rate.

Lower mill base charges are also used if more resin is needed to stabilize the base than can be added to a 40/80 grind, or if there is so little free vehicle in the final product that the mill base must be made at high consistency.

Never load ball mills to more than 90% of capacity. The 10% air space is needed for expansion as the grind heats up.

RECOMMENDED AREAS OF USE:

Ball milling is recommended for (1) expensive pigments which require a high degree of milling for full color development, (2) pigments such as carbon blacks which need a high degree of milling to meet finished product quality requirements, and (3) coarse pigments where reduction of crystal size is necessary.

Use ball mills only where less expensive dispersion methods will not do the job.

2-ROLL DISPERSION

PRINCIPLE:

Two-roll milling consists of working a plastic mass of resin, plasticizer, and pigment between two temperature controlled rolls rotating at different speeds.

OPERATION:

Resin, plasticizer, pigment and sometimes a little solvent are pre-mixed in a heated W & P sigma blade mixer for about two hours. Then, by chilling and adding a non-solvent, the mix is broken up into granular form. The granules are worked into a sheet on a heated two-roll mill. The sheet is milled for about 30 minutes and is then removed, cooled, and broken into chips for use in the finished product.

The heat of milling and static electricity build-up may cause a flash fire, so the mill is grounded, hooded, and equipped with a CO_2 extinguisher system.

PERFORMANCE CHARACTERISTICS:

Two-roll milling provides a high degree of dispersion with none of the steel or ceramic contamination of ball mills. Bright transparent colors for automotive metallics have maximum clarity when 2-roll milled.

This method is very expensive. The mills are costly and require the operator's full attention and the batches are quite small.

FORMULATING PARAMETERS:

We have no written formulating practice for 2-roll milling. Problems in this field should be referred to C. D. Rickabaugh at Parlin or W. Balloon at Flint.

RECOMMENDED AREAS OF USE:

Use 2-roll dispersions only when high clarity colors are absolutely necessary. If the volume required is very small or the order not likely to be repeated, it may be less expensive to purchase a 2-roll dispersion rather than develop our own formula. However, compatibility of the purchased product with our binder system must be ascertained.

OTHER DISPERSION METHODS

There are many more types of dispersion equipment on the market. A few are listed below:

- Flush base dispersion equipment
- Ultrasonic devices
- High shear mixers
- Three-roll and five-roll mills
- Kinetic dispersion mills
- Stone and carborundum mills

Some of these offer advantages for specialized uses, but none is inherently more useful for large scale day-to-day production of a wide variety of products as the types of dispersion equipment now available to you in F&F Plants.

We hope that this introduction to the subject of dispersions will help you in learning to use this equipment skillfully and efficiently.

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MARSHALL DEVELOPMENT LABORATORY

TRAINING SEMINAR

SERIES

TITLE: FORMULATING EMULSION FINISHES

BY:

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ORV/smw

Emulsion finishes represent one of the more recent developments in the coatings field. These coatings are characterized by the presence of water in place of solvent. However, the binder in emulsion finishes is not in solution. The binder is present in the form of small discrete spherical particles suspended in water, and in modern paints these binder dispersions are termed latexes.

This condensed presentation on latex paints will touch briefly on the components of such paints, and also the function that each component plays in the film formation and service requirements of the paints. Latex paints contain the following ingredients:

1. Latex
2. Hiding Pigments
3. Extender Pigments
4. Pigment wetting and dispersing aids
5. Emulsifier
6. Thickener and protective colloid
7. Coalescing aid
8. Defoamer
9. Preservative
10. Freeze-thaw stabilizer
11. Water

As you can see, there are many ingredients in a latex paint and they are all needed to insure the proper performance of the latex paint. Many times latex paint formulas require several different types of each of the individual ingredients shown abcve. However, in order to convey more explicitly the formulation of latex paints, each of the ingredients mentioned above will be described as to its composition and function in a general way, and then several latex formulas will be shown and you will be able to see the composite makeup, functions, and interactions that enter into the formulation of latex paints.

1. Latex: In describing the latex binders used in our present finishes, and their merits and deficiencies, it might be well to spend just a few minutes to review the history of water paints. In the early ages the Greeks and Egyptians used sour milk and freshly burned lime plus coloring agents such as ground iron oxides, ochres, lampblack, etc., to make their paints, which were used mainly for decorative purposes. The binder in this case was Calcium Caseinate. In the middle ages, artists used tempera colors for portraits, decorations, etc., and the binder in this case was egg white.

Around 1900 powder paints containing glue, whiting, and chalk were made. Also casein powder paints were introduced, containing casein as the binder, hydrated lime, preservative, hiding pigments and lime proof colors. The casein reacted with the lime to form a Calcium Caseinate gel after the addition of water. This type of paint was widely used, and in fact is still used tody, but when first introduced they were tricky to use because the paint when mixed with water had to stand until the casein reacted with the lime. However, if allowed to stand too long they would gel completely.

The British made the next advance with the introduction of distempers which were the forerunners of the paste emulsion paints. They used glue as the protective colloid in the aqueous phase and bodied oil as the oil phase. Pigmentation was with lithopone and the usual extender pigments. These paints were not widely used in this country.

In the early 1920's, a paste type of casein paint was introduced. It used an alkaline casein dispersion as binder. These paints had poor stability, were subject to putrefaction and enzymatic degradation. CO_2 was sometimes given off which would cause cans to explode. The paint film itself was poor due to poor washability and these unplasticized casein paints tended to peel. By 1939, emulsions of alkyd resins and protein used as binder was growing in favor and were replacing casein paste paints, and also oil base paints for interior walls. Speed-Easy, still sold today by Du Pont is an example of such a paint.

During World War II there was a tremendous growth of the synthetic rubber industry because of the shortage of natural rubber latex. After the war ended, the plants used in the production of the synthetic rubber were idle. By changing the ratio of the butadiene and styrene in making synthetic rubber, a latex was produced that was suitable as the film forming binder in paints. This was the start of the technology of present latex paints. Also during the war, the Germans exploited the use of PVAc paints because of the shortage of other film forming materials. As a result the good exterior durability of these water based paints was noted.

After World War II the rapid rise in the number of home owners and the higher costs of labor tended to promote the growth of the "do-it-yourself" market. Latex paints, because of their ease of application and clean-up, lack of a strong paint odor, fast dry, and no fire hazard, became a popular product in the consumer market. Also, these paints could be used over relatively fresh plaster walls without reaction with the alkali in the plaster. Since the films were somewhat porous the water could escape through the paint film without the formation of blisters. This brief history covers the evolution of water based paints up to the present time.

The most important latices in use today are the acrylic copolymers, vinyl acetate, vinyl acrylic copolymers, styrene-butadiene. By definition a latex is a fine stable dispersion of rubber, or natural or synthetic polymer in water. The dispersed particles have a diameter in the range of 0.1 - 0.25 microns. As made the latex polymer has a very high molecular weight but being in dispersed form the viscosity of the latex is lower. The same polymer in solution (same molecular weight) would give a very high viscosity at low solids. The high molecular weight results in good tensile strength, toughness, and durability.

An emulsion has two liquid phases, a continuous liquid phase (in the case of the latices being discussed this is water) and a discontinuous internal phase (the polymer). As made, latices are stabilized by the addition of surfactants. During the manufacture of the latex the surfactant functions (1) to solubilize the monomer to allow initiation of the polymerization reaction, (2) to prevent coagulation during polymerization by preventing particle coalescence, and (3) to stabilize polymer particles in the finished emulsion. The type and amount of surfactant (or surfactants) used, and the method of addition can effect the following variables in an emulsion polymerization process: (1) polymerization rate, (2) particle size, (3) molecular weight of the polymer, (4) percent conversion of monomers, (5) emulsion viscosity, and (6) emulsion stability.

An appropriate quantity of a surfactant, known as a post-stabilizer, is often added to a polymer emulsion after polymerization is complete. This increases resistance to coagulation by shear encountered in transporting, pumping, or coating operations. It also improves resistance to coagulation due to acids, and divalent and trivalent metal ions, or addition of pigments and extenders, and also improves freeze-thaw stability.

Latex properties are determined to a larger extent by the type and amount of the monomers used in its composition. A butadiene-styrene latex will contain these monomers in a ratio varying from 30/70 to 40/60. As the ratio of styrene increases the polymer becomes more brittle and more difficult to coalesce. As the ratio of butadiene increases the polymer becomes softer and more rubberlike, and, because of its unsaturation, it is susceptible to oxidation. This imparts water resistance to the dried films, but also causes yellowing which is undesirable when experienced in white and light tints.

PVA latexes are made as homopolymers or as copolymers. The homopolymers do not coalesce readily even at room temperature and they require the addition of an external plasticizer such as dibutyl phthalate to form a film. The copolymers are internally plasticized through use of Dibutyl Maleate, Vinyl Stearate, and acrylic esters, etc. They have good adhesion to many surfaces including glass, and they also have good exterior durability.

PVA latices, in general, impart better flow to latex paints than do the butadiene-styrene or acrylic latices. They have a relatively high density, and on a solid-volume basis are more expensive than styrene-butadiene or acrylic latices.

Acrylic latices are made as copolymers from monomers such as methyl methacrylate, ethyl acrylate, 2 ethyl hexyl acrylate, butyl acrylate, and methacrylic acid. Polymethyl methacrylate is quite hard and by itself does not coalesce and is not sufficiently flexible to be usable for consumer latex paints. It is plasticized by incorporation of other acrylic esters and the flexibility and tensile strength can be tailored to suit the specific needs of the end paint product by proper choice of monomers and monomer ratio. The lower molecular weight esters produce harder polymers, and the converse is true of those with higher molecular weight.

Latexes are used as the binder or film forming component in emulsion paints. Small discrete particles of polymer are colloidally dispersed in water. When the water evaporates the latex particles are being crowded closer together and are losing Brownian motion. As they become tightly packed capillary forces set up by the evaporating water causes the latex to coalesce at the points of contact. (See Exhibit No. I) These points of contact become enlarged by deformation to roughly the shape of a dodecahedron. *(See Exhibit No. II)

Coalescence of a latex film is influenced by a number of factors. These factors can be identified as Environmental, Physical, and Compositional. Considerning environmental factors first, temperature controls the hardness of the latex particle. Each polymer has a temperature below which it cannot coalesce without the aid of some external aid. This is known as the glass transition temperature,or more accurately the minimum film forming temperature, of the latex polymer. Temperature also controls the evaporation rate of the water and other volatile components in a film. Relative Humidity of the atmosphere in which the film dries controls the rate of lossw of water. With low humidity there is a very rapid loss of water and the film coalesces rapidly influencing the flow and smoothness of the paint film. With high humidity, particularly when temperature/ humidity conditions are close to the dew point, evaporation of the water is very

slow and films have been observed to stay wet overnight under these conditions. This often results in poor film formation and subsequently poor film properties.

The porosity of the substrate also controls rate of coalescence since it causes either rapid or slow wicking of water from the latex and consequent build up and concentration of latex particles at the interface between the substrate and the paint film.

Under the Physical factors influencing coalescence, we can consider particle size and the quality of the dispersion. Other factors being equal, a latex with relatively large particle size will coalesce more difficultly than one with small particle size. Also, a latex with a wide range of particle size distribution will be more difficult to coalesce into a uniform film than one with a small size distribution. These generalizations are particularly true with highly pigmented paint systems.

Under Compositional factors, we have already mentioned the choice of monomer ratios in the various latices as influencing the hardness of the latex. In the Styrene Butadiene latices the high Styrene compositions are hard and do not coalesce. The same is true of Methyl methacrylate polymers and polyvinyl acetate polymers. However, when these are blended with ethyl acrylate, 2 ethyl hexyl acrylate, or butyl acrylate, the copolymers become softer with lower glass transition temperatures, and coalescence occurs.

Also the stabilization of the latex influences its tendency to coalesce. This is accomplished through use of surfactants and protective colloids and thickeners. The function of surfactants was previously mentioned, but it can be seen that addition of a pigment dispersion containing minimum dispersant to a latex having minimum surfactant concentration required for stability would cause problems. Mixing would reduce the concentration in solution of both surfactant and dispersant. Most pigments have high surface energy, while polymer particles are generally characterized by low surface energy. High energy interfaces adsorb more ions than low energy interfaces at equal ion concentration in solution. Also, high surface energy provides greater forces for holding ions at an interface. This, if the pigment had an affinity for adsorbing the latex stabilizing surfactant, it is possible that depletion of surfactant from solution, and consequent desorption of some surfactant from polymer particles, could produce some flocculation among polymer particles.

Another flocculating influence is also involved in pigment and latex mixing. Some slightly soluble pigments are a source of polyvalent cations (for instance Ca++ from $CaSO_4$) which could produce latex coagulation by disruption of the electric potential at the polymer/liquid interfaces.

2. Hiding Pigments: Hiding pigments are defined as those having a large difference in refractive index between the pigment and the medium in which it is dispersed. For latex paints the pigment normally used to impart white reflectivity is TiO_2. It is used because it is non-reactive, and has an index of refraction of 2.71, while most polymers have an index of refraction of 1.6. Lithopone which is essentially 29% Zinc Sulfide and 71% Barium Sulfate can be used but it does not compare favorably on a cost/hiding power ratio with TiO_2 pigment. None of the other white hiding pigments such as Zinc Oxide, Leaded Zinc Oxide, etc., are used in emulsion paints. The TiO_2 used in latex paints is specially treated to impart high opacity and to make it easily dispersible in the water system.

Colored pigments are also classified as hiding pigments. They are used to impart color to the paint film. There are many colored pigments suitable for use in water paints, red, yellow, and black iron oxides, burnt sienna, carbon black, chromium oxide, Monastral® Green, red, and blue, Dalamar® Yellow, etc. Most, if not all, of these pigments have been described in previous talks. It is only important that the pigment should be chemically stable i.e. acid and alkali resistant, lightfast, and dispersible in water systems. Pigment dispersions must be stable when intermixed with the latices to be used in paint formulations.

3. Extender Pigments: White extender pigments are mineral compounds of relatively low refractive index. They differ in composition, particle size, and shape. They develop very little hiding in gloss and semi-gloss paints, but they contribute high "flat hiding" (air/pigment interfaces) to latex flat paints at low cost. This can be demonstrated by soaking a piece of chalk in water for about an hour and then use it to make a mark on a blackboard. While the mark is wet, it has relatively little opacity and whiteness. However, when the water evaporates, thereby developing pigment/air interfaces, the opacity and whiteness improves tremendously.

Extender pigments are used to control gloss, texture, suspension, viscosity, and hardness of paint films. The main types of extenders used in latex paints are calcium carbonate, silicon oxide (in the form of Diatomaceous Earth), Silicates (in the form of Clay, Talc, and Mica) and Barium Sulfate (Barytes). The brightness of extender pigments varies from 70% - 98% depending on the amount and type of impurities which impart color and lower brightness.

Particle size varies from 50 to .01 microns, and shapes of extenders vary from spheres, to needles, and include fibers and plates. The particle shape influences pigment packing, flexibility of the film, bridging of cracks, etc. The particle size, and the particle size distribution, influence hiding, viscosity, film porosity, vehicle and surfactant demand, gloss, fineness, etc. Corrosion and blister resistance, and also stability, are dependent on the soluble salt content of pigments. For these reasons, it can be seen that extenders cannot be substituted for each other on the basis of equal weight or equal volume alone. Also in comparing the cost of extenders, it is important to consider the different bulking values and densities of the pigments. Since paint is sold by the gallon it is important to convert cost per pound into cost per gallon in order to make meaningful cost comparisons.

Since the price of TiO_2 is considerably greater than that of extender pigments, formulators try to utilize extenders to impart as much hiding as possible, thereby contributing to economy of formulation. As we will see, extenders differ somewhat from each other in their hiding power ability as well as in other properties, but they all can be used in a formulation to introduce air/pigment interfaces which greatly contribute to hiding in a paint film. When a formulation is loaded with pigment to the point where there is insufficient latex polymer to completely coat the pigment, a number of pigment/air interfaces are developed. These have a great deal more hiding power than the pigment/resin interface and, when accomplished with extender pigments, it is a cheap way of getting hiding power. We refer to the point at which pigment/air interfaces appear in number as the Critical Pigment Volume Concentration of that system. (As computed Pigment Volume is the volume of pigment contained in a 100 gallon formula, divided by the total volume solids of the formula.) Since each pigment has a certain size and shape, and therefore can pack efficiently or not, each pigment system will have its own distinct Critical Pigment Volume Concentration.

Calcium Carbonate: This is available in both natural and synthetic types. The natural grade is obtained from limestone, marble, or English chalk and it contains 95% - 99% $CaCO_3$ and has a refractive index of 1.63. The extremely coarse grades are not used in paints but in putties, caulks, undercoats, etc. The medium particle size grades 10 - 35 microns are used in interior flats, and the finer grades up to 10 microns are used in semi-glosses. The precipitated or synthetic pigment contains 98% - 99% $CaCO_3$ and they have a small particle size, small particle size distribution, high oil absorption, and are brighter than the natural product. However, the natural grades are lowest in cost.

Silica: SiO_2, Silica pigments are made in three distinct classes: (1) as ordinary silica, mainly by grinding and classifying quartz, with an index of refraction of 1.54; (2) diatomaceous silica, refractive index 1.4 to 1.5; and (3) synthetic silicas. The quartz type has little use in latex paints because it is difficult to disperse and settles rapidly. It is used only in paints where good abrasion resistance and inertness and "tooth" are required.

Diatomaceous Silica, occurring as the silaceous skeletons of aquatic diatoms, are extensively used for their very high flatting efficiency. The skeletons are porous, fragile, and have almost every conceivable geometric form. (See Exhibits III and IV). They contain between 83% and 95% SiO_2. The most useful grades are white but some are light gray, light pink, or buff colored. They have a high bulking value (Solid Gallon Weight only 16 to 18 pounds). They have a very high oil absorption which produces a high flatting effect, high thickening power, and good pigment suspension. They are widely used in interior latex flat wall paints. However, because of its porosity and friability it detracts from the ease of stain removal and scrubbability of flat paints and films are also subject to development of shiners when scrubbed or washed.

Synthetic Silicas are essentially pure silica and have extremely fine particle size, 10 microns or less in average diameter. They have high brightness and high oil absorption and are used to lower or control gloss of semi-gloss and flat finishes. The extremely fine grades are sometimes used to provide "spacers" for TiO_2 pigments to maintain their hiding power efficiency.

Magnesium Silicate-Talc: $2\,Mg \cdot 4\,SiO_2 - H_2O$. Talc is obtained from mineral rock and its crystalline form and resultant physical characteristics vary with the location of the rock. It has a refractive index of 1.59. Talc occurs in four basis types (1) fibrous, (2) platy, (3) annular, and (4) nodular, and generally occurs as a mixture of these types. The usefulness of any particular grade is determined by the mixture of types, average particle size, and particle size distribution. Most useful grades of talc for paint are predominately fibrous or platy. Fibrous talcs are good for exterior durability and for pigment suspension but they detract from flow and smoothness of the paint film. Platy talcs improve brushability, flow, smoothness of film, and enamel holdout of paints.

Talc has a relatively high brightness and it is easily dispersed in both water and oil systems. It has excellent suspension properties and helps to keep other pigments from settling. The biggest use for talc in emulsion paints is in exterior house paints where it is used to obtain good consistency control, application properties, suspension, and a satisfactory repaint surface.

Aluminum Silicate - Clay: $Al_2O_3 \cdot 2\,SiO_2 \cdot 2H_2O$.

Clay is obtained from mineral rock which is mined in the Carolinas, Georgia, and England. Particles are mostly laminar, hexagonal plates. The widely used grades have a top particle size of about 10 microns and a refractive index of 1.56. All grades are hydrophilic in varying degrees and are chemically neutral. Oil absorption ranges from 25 - 44 for the non-calcined grades to 48 - 58 for calcined grades. The brightness varies from 80% to 92% reflectance. Clay pigments weigh about 21.6 pounds per solid gallon, approximately one pound less than calcium carbonate.

Calcined clay is being used in latex interior wall paints because is has high dry hiding and produces smooth films. Because clays are hydrophilic they are easily dispersed, and have good suspension properties, and they impart good brushing and leveling.

Mica: $K_2O \cdot 3\,Al_2O_3 \cdot 2\,H_2O$

Mica is contained in several minerals but the usual source of extender pigments for paints is the muscovite type. Mica occurs in large sheets of crystal which are delaminated by compressed air and then ground (either wet or dry).

Particle size is relatively large, about 325 mesh, and it has a refractive index of 1.59. The particle is plate-like in structure (See Exhibit No. V) and it provides mechanical reinforcement of the paint film and increases the length of the path that water and moisture must travel to penetrate the film. It is also used in latex house paints to prevent cracking and to improve brushing properties. In exterior paints mica imparts a sparkle to films by reflected sunlight.

Barytes $BaSO_4$ Barium Sulfate

Barium sulfate extender pigment is available in two forms: a ground ore as barytes, and precipitated as blanc fixe. Both have good reflectivity and fineness and are very dense: - Gallon Weight is 37 pounds per gallon (almost twice that of calcium carbonate). It has a refractive index of 1.64. It has a low oil demand. Its high cost per pound, and its high density, makes this an unattractive pigment for use in latex paints. However, it is chemically inert and can be used if it is found to impart desirable properties in any particular formulation.

4. Pigment Wetting and Dispersing Aids: In an aqueous suspension of an ordinary pigment, there is a strong tendency for the pigment particles to adhere to each other when they collide. The attractive forces between the surfaces of the particles is large. Agglomeration or flocculation of particles results. It is possible to deflocculate such suspensions by adding surface active materials which adsorb strongly at the liquid-solid interface and which, at least in part, overcomes the strong interparticle attraction. When a pigment is dispersed in water, the air-solid interface is replaced by the liquid-solid interface. That is air atoms and molecules on the pigment surface are replaced by water molecules. The tendency for a pigment to disperse can be increased by: (1) reducing interfacial tension between pigment and water, and (2) reducing the force of cohesion holding pigment agglomerates together. Good dispersion is essential in emulsion paints for best hiding power, flow and leveling, color development, package stability, minimum color flooding and floating. Each pigment has its own optimum dispersant requirement and it is usually helpful to have a wetting agent (surfactant) in conjunction with the dispersant.

Two factors which determine the effectiveness of a pigment dispersant are the ability of the dispersant to (1) adsorb onto a pigment particle, and (2) impart a high charge density to the particle. Types of compounds used as dispersing agents include sodium polyphosphates, sodium salts of lignin and sulfonic acids, sodium salts of aryl alkyl sulfonic acids, and sodium salts of carboxylated polyelectrolytes.

Some fatty acid soaps, and certain polyampholytes, such as casein, also have dispersing properties.

Surfactants used in latex paints can be classed into four types: anionic, cationic, nonionic, and amphoteric. The non-ionic and anionic surfactants are most widely used. Structurally, a surfactant molecule (or ion) is characterized by the presence of a hydrophobic group and a hydrophilic group.

Anionic surfactants ionize in solution. After ionization, takes place, the anion is the surface active part of an anionic surfactant molecule and has both hydrophilic and hydrophobic groups in its structure. Common household soap is an anionic surfactant. It is usually a mixture of sodium salts of fatty acids. When ionized the carboxylate radical is the solubilizing or hydrophilic group. (See Exhibit No. VI). Among commercial anionic surfactants, four hydrophilic groups predominate: carboxylic, sulfate ester, sulfonic, and phosphate ester.

Nonionic surfactants do not ionize in solution. The hydrophilic portion of the surfactant molecule usually contains several hydroxyl groups or ether linkages. One of the most widely used materials for constructing hydrophilic segments for nonionic surfactants is ethylene oxide. It can be reacted with any hydrophobic compound having an active hydrogen, such as acid, alcohol, phenol, alkylphenol, amide, or amine. The more units of ethylene oxide the more hydrophilic the surfactant. Atlas Chemical Company has developed the HLB System to serve as a guide in selection of surfactant. For non-ionics it is a numerical indication of the percentage weight of the hydrophilic portion of the molecule. In actual calculation, the weight percent of the hydrophilic portion of the molecule is divided by 5 and this is the HLB number of the surfactant. A completely hydrophilic surfactant has an HLB of 20, a completely lipophilic one, a value of 0. Nonionic surfactants are generally compatible with anionic, cationic, and other nonionic surfactants, and are not affected by cations.

Cationic surfactants have molecules with surface active cations. Most solid surfaces (pigments, etc.) are either neutral or negatively charged and the positively charged cation of the surfactant is attracted to the [illegible] on these surfaces. Amines are the basis of all common cationic surfactants, including simple amine salts, quarternary ammonium salts, amino amides, etc.

An Amphoteric surfactant molecule has groups which permit it to act as either a cationic or anionic surface-active agent depending on pH. They are usually cationic in acid solution and anionic in alkaline solution.

5. Emulsifier: Emulsification is the process of dispersing one liquid in another (the liquids being mutually insoluble or sparingly soluble in each other). When water is one of the liquids, two types of emulsions are possible: oil in water (water is the continuous phase), and water in oil. The term oil describes any organic liquid sparingly soluble in water.

An emulsion is usually formed by physically extending one phase in the other by shaking, mixing, or stirring, in the presence of an emulsifier. The extended phase collapses into small spheres because of its instability. The emulsifier has two principal functions: (1) it decreases the interfacial tension between the liquids, and thus permits easier formation of the greatly extended interface, and (2) it stabilizes the dispersed phase against coalescence once it is formed.

In forming emulsions, it is necessary to bring about an enormous increase in interfacial area separating the two phases. Breaking up oil droplets into collidal particles involves a tremendous increase in surface areas. For example, dispersing 10 milliliters of oil into a fairly fine emulsion can produce more than a quarter-acre of surface.

To perform its function properly, an emulsifier must concentrate at the interface. This will happen if the hydrophilic portion of the emulsifier is sufficiently attracted by the water phase or repulsed by the oil phase, and if the hydrophobic portion is sufficiently attracted by the oil phase or repulsed by the water phase.

6. Thickeners and Protective Colloids: Thickeners are used to adjust viscosity of paint and to act as stabilizers for the latex system. As the viscosity of the external phase is raised, Brownian movement is inhibited. This improves pigment suspension and also provides improved application properties. Colloids coat surfaces of particles and prevent them from flocculating or coalescing. Examples of these are methyl cellulose, carboxymethyl cellulose, casein, etc.

7. Coalescing Aid: These help the latex particles to coalesce and then they leave the film also because they are volatile. They act as a temporary plasticizer for the latex particles, softening them so they can coalesce more readily. The best types are the water soluble ones such as Carbitol Acetate,

and Carbitol Ethyl Cellosolve and they improve freeze-thaw resistance as well as color development and color uniformity. Water insoluble types are Butyl Cellosolve Acetate, Butyl Cellosolve, Butyl Carbitol Acetate. Permanent types are Di butyl Phosphate and Tri Cresyl Phosphate and they act as plasticizers in the dried film.

8. Defoamers: In latex paints surface active agents are used to stabilize the latex, to stabilize pigment dispersions, etc., and these surface active agents contribute to foam stability by lowering surface tension of the continuous phase which is water. Specific surface active agents may also be used for defoaming. Defoamers adsorb preferentially at the air-water interface. Their exact mode of action is not known but it is believed that they tend to produce liquid films that are weak and easily susceptible to breaking by shock and deformation. Polyglycols are one type of defoamer. Thickeners tend to stabilize foams and they are usually added at the end of the paint making process to minimize foaming. Defoamers are also added at the end of the batch to increase their effectiveness.

9. Preservative: The continuous phase of latex paint is water which is a good medium for growth of bacteria. Many of the components of paints contribute food for bacterial growth. In order to prevent putrefaction of latex paints by this action, preservatives are added which inhibit growth of bacteria. The most common ones used are mercury salts such as phenyl mercury oleate, phenyl mercury acetate, phenyl mercury propionate, and also the Dowicides, such as pentachloro phenol, etc. Formaldehyde may be used as a preservative for latex storage.

10. Freeze-Thaw Stabilizer: When the water portion of a latex freezes, the small polymer particles are forced closer together due to the growth of the ice crystal. If the latex is not properly formulated with a suitable surfactant the emulsion will break and the latex will coagulate. Anti-freeze agents are generally added to latex paints to lower the freezing temperature of the continuous phase and prevent instability. They also act as coalescing aids when latex paints are applied at low temperatures. The common anti-freeze agents used are ethylene glycol, hexylene glycol, glycerine, etc.

11. Water: Water contributes the greatest volume of any of the ingredients used in latex paints. Since latex paints range between 25% and 40% solids by volume, it can be seen that water, the major component of the volatile phase, contributes at least half the volume of every gallon of latex paint sold.

Deionized water is generally used in making latexes for maximum latex stability but tap water is used for the balance of the water used in production of the paint.

Now that you know the type of ingredients used in latex paints, and their specific functions, let us look at a typical latex paint formulation and observe how these ingredients are used. Let us consider the formula for "Flow Kote®" Wall Paint #1406-C Roman White, 389-406 (See Exhibit VII) and its mill base 548-966 (See Exhibit VIII). The mill base 548-966 is made first in a "48 Process" dispersion mixer. W-165 a slight gray small particle size diatomaceous earth, which is used to provide "flatness" (low gloss) to the paint film, is added to the mixer along with G-1111 Methyl Cellulose which is the thickener in this formulation. These two ingredients are dry blended for 10 minutes and water is then added. The intimate dry mixing of the W-165 and G-1111 prevents the G-1111 from balling up and this shortens time required to solvate G-1111.

H-658 Polypropylene Glycol, a defoamer, is then added to prevent foaming. H-657, Sodium Polycarboxylate solution, a pigment dispersant is then added to aid in dispersing pigment agglomerates. G-796 Phenyl Mercury Propionate is added to prevent bacteria growth.

W-1011 a white grade of diatomaceous earth is added to provide flatness and some hiding through introduction of air/pigment interfaces in the paint film. H-514 Ethylene glycol is added to provide freeze-thaw stability to the paint. VM-5648 Potassium pentachlorophenate is added as a preservative against bacteria. It works with the G-796 and does a better job than either one could do alone, G-12 Soya Lecithin is added as a pigment dispersant.

W-1002 Aluminum Silicate is next added along with W-1004 Calcium Carbonate. These are medium fine particle size extender pigments and are added to provide flatness, hiding, washability, etc., to the paint film. W-129 Ti Pure® R-901 a TiO_2 pigment with a surface treatment of 2.0% SiO_2 and 4.0% Alumina is added as the main hiding power pigment. It provides most of the opacity to the paint film. Additional water and H-284 Ammonia hydroxide solution are then added to increase pH prior to the addition of the finished mill base to the latex.

The finished paint is made in a large mixing tank. RC-11008 is first added. This is a latex made from Methyl Methacrylate/2 Ethyl Hexyl Acrylate/ Methacrylic Acid in the ratio 44/54/2. It is stabilized with 5% H-609 Triton X-100 nonionic surfactant and 1% Du Ponol Anionic surfactant. This is the binder for the

paint and it holds the pigment particles together in a coherent film and holds that film to the surface to which it is applied. G-747 Nopco 1497-V a defoamer is added to control foaming and help break bubbles which develop during application of the paint.

The mill base is then added to the mixing tank and the "48" mixer is washed with water and it also is added to the mixing tank. VM-5751 a mixture of Methyl Cellulose and Ethylene Glycol is added to increase viscosity. Tinting Colors are added to adjust color and water is added to complete the batch, thereby adjusting volume solids of the finished paint. pH and viscosity are then adjusted with H-284, VM-5751 and H-506.

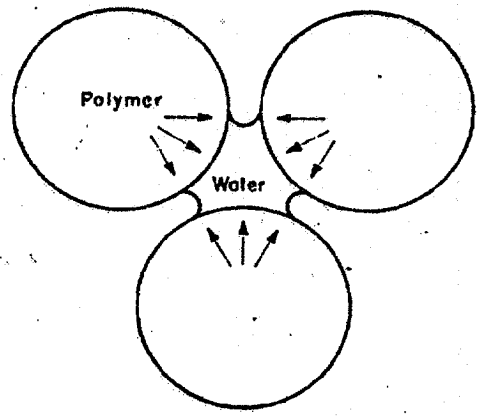
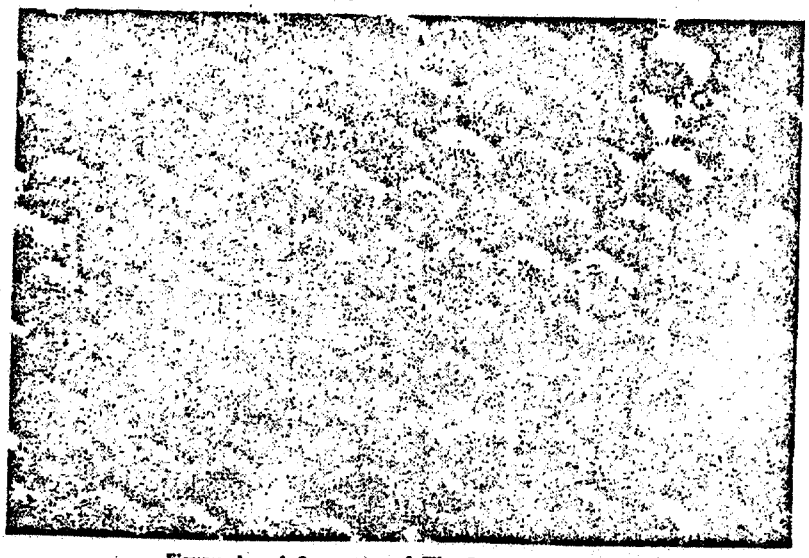


Fig. 18.42 Contracting forces resulting from capillary water in interstices between polymer particles. From Talen[20].

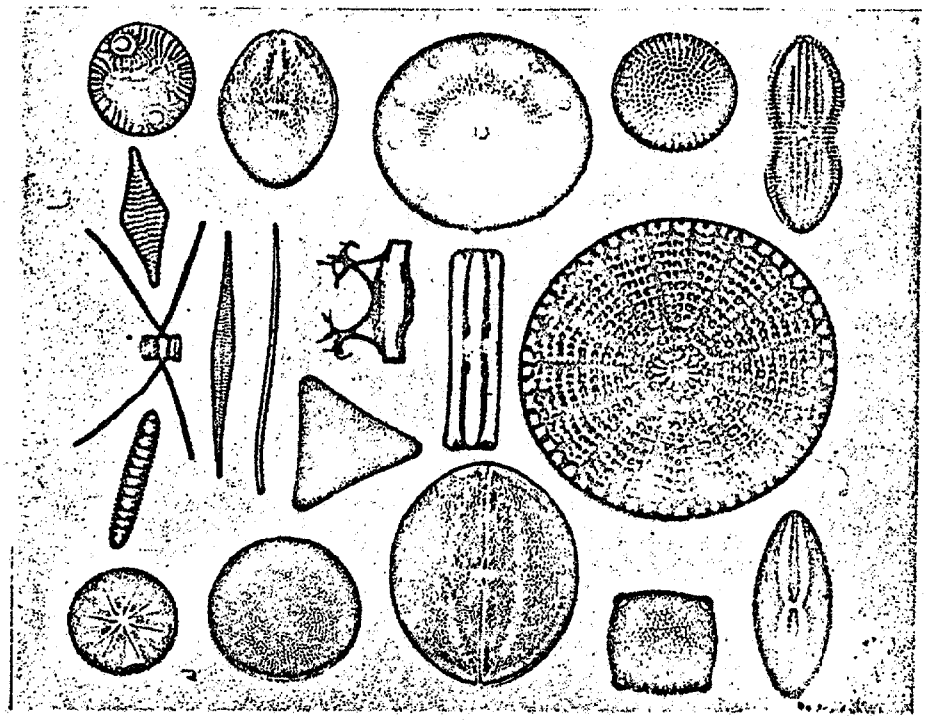
EXHIBIT NO. 1



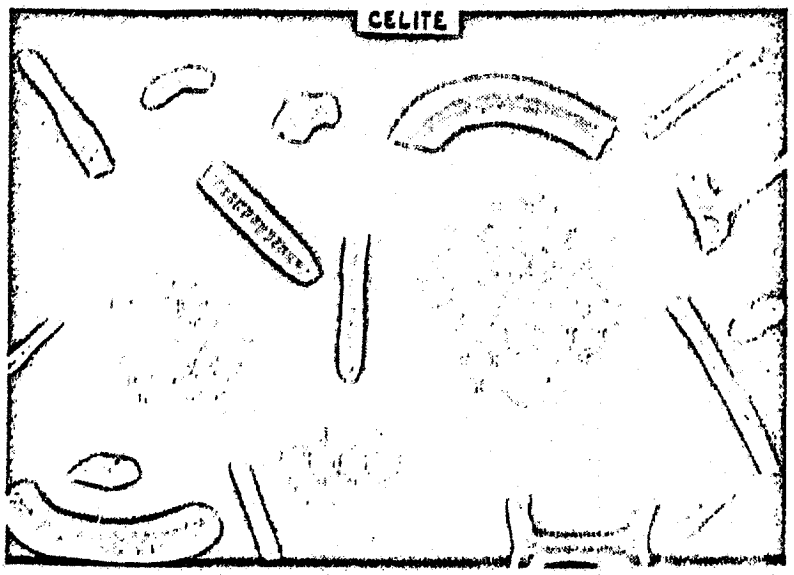
Figures 1 and 2 courtesy of The Dow Chemical Co.

Figure 2—Unpigmented latex. Magnification 28,580X

EXHIBIT NO. 11



DIATOMS FOUND IN DIATOMACEOUS EARTH
EXHIBIT NO. III



Celite is a registered trademark of Johns Manville Corp.

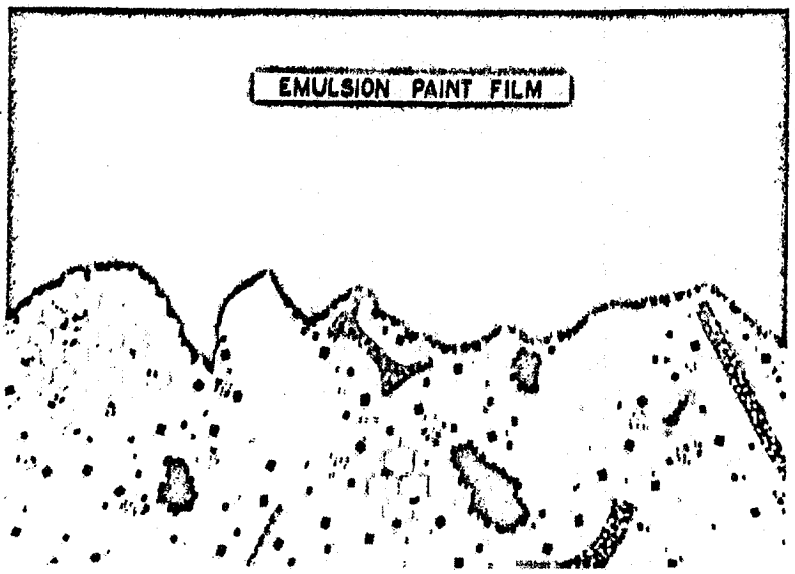
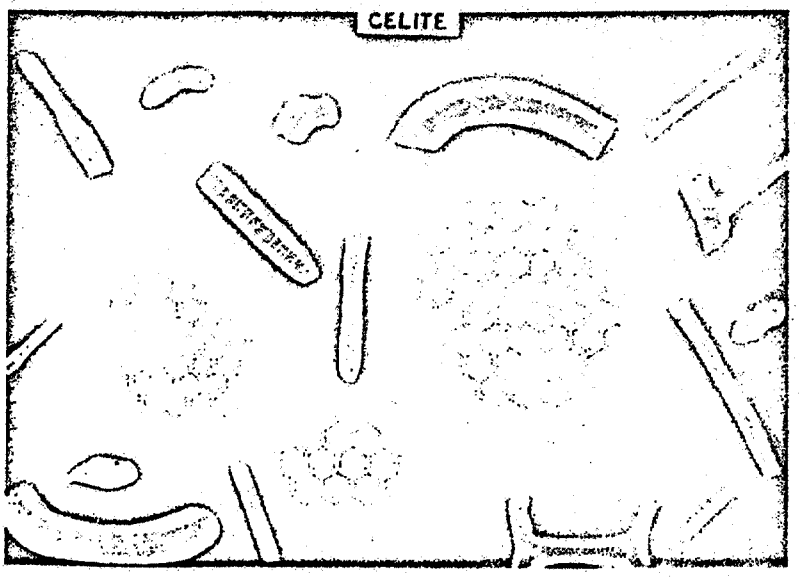


Figure 12—Common paint components in a dried paint film

EXHIBIT NO. IV



Celite is a registered trademark of Johns Manville Corp.

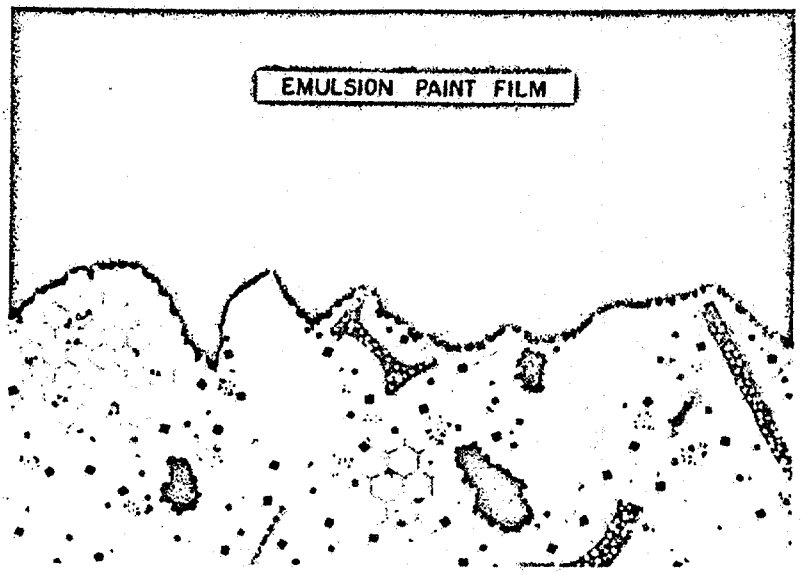


Figure 12—Common paint components in a dried paint film

EXHIBIT NO. IV

EXHIBIT NO. V

FIGURE 4—TYPES OF SURFACTANTS

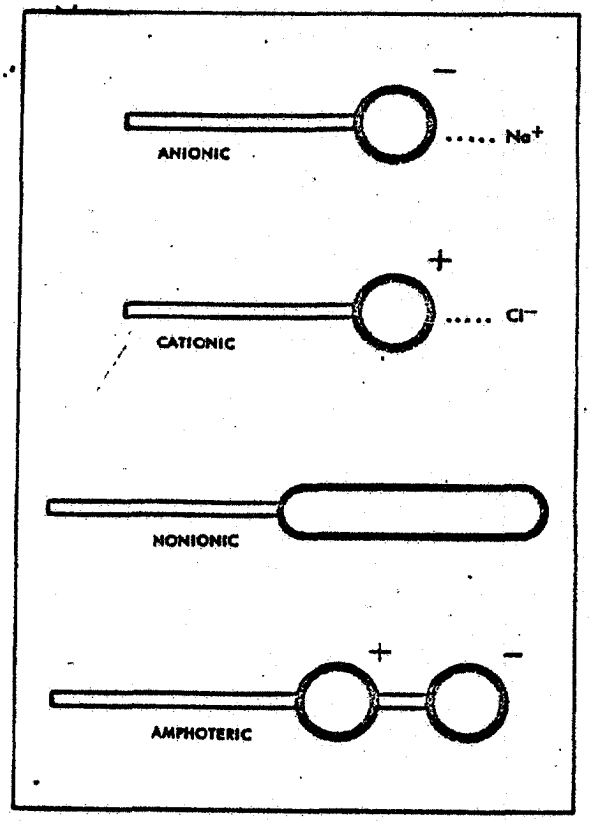


EXHIBIT NO. VI

389 / 406	NAME "FLOWKOTE" 1406 ROMAN WHITE		DATE 102667
COS	VISC. ST 86-90 KU	FCIE.	
.25/1.00 INT TIN/PHENOLIC	GAL.WT. 1084.00	Icc. Info.	+150U

INGREDIENTS / MANUFACTURING

CAUTION THIS IS A WATER PAINT. DO NOT CONTAMINATE WITH OILS RESINS OR SODIUM COMPOUNDS. FOLLOW THIS ORDER OF ADDITION AVOID UNNECESSARY AGITATION.

INGREDIENT				ALT #1
RC		11008		162.87

ADD WITH MIXER OFF + WITHOUT FREEFALL

INGREDIENT				ALT #1
G		747	*	3.00
H		506	*	2.00

*PREMIX AND ADD WHILE MIXING

INGREDIENT				ALT #1
	548	966		658.09
H		506	*	100.00
VM		5751		6.00

ADD IN ORDER WHILE MIXING //

AMOUNTS / DIRECTIONS

MIX 20 MINS. AFTER LAST ADD // *USE THIS ADD OF H-506 FOR WASHING DOWN "48 MIXER" //

MARSHALL LABORATORY
FILE COPY

INGREDIENT				ALT #1
	547	5630	*	2.64
W		728	*	0.06
W		247	*	-TRACE-

SHADE TO STD // *AGITATE SHADING BASES BEFORE USE // DO NOT USE LUMPY BASES // ALLOW 60 MINS. AGITATION AFTER EACH SHADING ADJUSTMENT //

INGREDIENT				ALT #1
H		506	*	149.34

ADD WHILE MIXING // MIX 20 MINS. AFTER LAST ADD // *DO NOT ADD BEFORE SHADING TO STD. HAS BEEN COMPLETED //

INGREDIENT				ALT #1
H		284	X55	---- ---
VM		5751	Y	---- ---
H		506	Z	---- ---

"X" CHECK PH AND ADJUST ALLOW 15 MINS. AGITATION AFTER EACH PH ADJUSTMENT SAMPLE MUST BE THOROUGHLY MIXED WITH MECHANICAL MIXER BEFORE CHECKING VISC. "Y" IF LOW ADD 1 LB. VM-5751 FOR EACH 2 KU RISE NEEDED PER 100 GALS. DO NOT ADD OVER 6 LBS. PER 100 GALS. MIX BEFORE USING. DO NOT DUMP. ADD SLOWLY WITH AGITATION "Z" IF VISC. IS HIGH ADD H-506. DO NOT ADD OVER 30 LBS. PER 100 GALS. ALLOW 30 MINS. AGITATION AFTER EACH VISC. ADJUSTMENT CHECK PH PRIOR TO FILLING.

TOTAL 1084.00

NOTICE KEEP FROM FREEZING IN PLANT. STENCIL KITS + CTNS. "KEEP FROM FREEZING"

EXHIBIT NO. VII

		5481	966	NAME	WHITE DISPERSION			DATE	5	3
230	PAT. MAR.				VISC.			FINE	2GA 2.5 MILS MAX	
231	CONT.				GAL. WT.	13.22 ±0.		SCC. DEPTH	+150	

		INGREDIENT		QT	SG	ALT. #1	ALT. #2	
632	MANUFACTURING INSTRUCTIONS AND	"48 PROCESS" RESINS OR SODIUM	// CAUTION DO NOT CONTAMINATE WITH OILS COMPOUNDS. FOLLOW THIS ORDER OF ADDITION.					
633								
635		W	165		S1	7 61	7 61	
736		G	1111	*		0 95	---- ----	
737		G	22	*		---- ----	0 95	
638								-ADD DRY BLEND 10 MINS.
639		STOP MIXER. WEIGH ACCURATELY. DISCONNECT DUST COLLECTOR						
640		WHEN LOADING G-22-G-1111						
742		H	506			26 49	26 49	
643								-ADD TURN ON COOLING
644		WATER. MIX [illegible] MINS.						
746		H	506			4 00	4 00	
747		H	658			0 42	0 42	
648								-STOP MIXER. USE H-506
649		TO WASH DOWN MIXER. ADD H-658. MIX 30 MINS.						
750		H	657		S2	0 65	0 65	
751		G	796		S4	0 04	0 04	
752		W	1011		S1	5 01	5 01	
753		H	514			2 95	2 95	
754		VM	5648		S3	1 82	1 82	
755		G	12			1 59	1 59	

756		W	1002		S1	10 21	10 21	
757		W	129			16 92	16 92	
[illegible]		W	1004			16 83	16 83	
659								-ADD IN ORDER WHILE
660		MIXING. MIX 30 MINS. AFTER LAST ADD.						
762		H	506			4 32	4 32	
763		H	284		S5	0 19	0 19	
664								-STOP MIXER USE H-506
665		TO WASH DOWN MIXER. ADD H-284. MIX 15 MINS. CHECK FINENESS						
666		+ STREAKING DRAIN						
667								
768			TOTAL			100 00	100 00	

EXHIBIT NO. VIII

MARSHALL DEVELOPMENT LABORATORY

TECHNICAL TRAINING SEMINAR

FORMULATING SOLUTION FINISHES

D. K. OGG

INTRODUCTION:

The three main ingredients of paints, varnishes and lacquers are the binder, the solvents and the pigments. In addition to these prime components, modifiers often are included in formulations to provide specific application or physical property improvements.

This paper will cover some general information on the formulation of solution finishes:

(I) Paint properties of importance to the paint formulator

(II) Binders

(III) Solvents

(IV) Additives

(V) Examples of how these ingredients are put together to formulate good paints.

Pigments and pigment dispersions have been thoroughly covered in other discussions and, accordingly, have been omitted here.

I. PROPERTIES

A. Application

The application properties of a paint must be ranked high on the list of its important functions. The ease of problem-free application and the good appearance of dry films are major selling points of finishes. The application of liquid paint to substrate being coated and the subsequent conversion to the dry film involves energy. Thus the rheological properties under the conditions of application, and under the dryingor baking conditions are of extreme importance.

1. Brushability

During the application of paint by brushing very high shearing rates are involved. Thus the flow properties at high shear are important functions of the brushability of paints. After application, the degree of leveling and sagging is dependent upon the yield value and viscosity at low shear or at rest. Low viscosity oils or resins, slow evaporating solvents, low pigment volume concentration, freedom from pigment flocculation contribute to good flow and leveling.

2. Spraying

Here again the application of paint by spray involves large amounts of energy. Factors which are of utmost significance in the spray properties of paints are the viscosity of paint, the volatility of the liquids, the surface tension of the system and the stability of the paint droplets.

3. Dipcoating

In this application, paints must exhibit low viscosity and extremely good viscosity stability, freedom from flooding, floating, silking, bubbling and pigment settling.

4. Flowcoating

Similar to dip coating in physical property requirements.

5. Curtain Coating

This is a special kind of flow coating.

6. Roller Coating

There are many kinds of roller coating equipment ranging from hand rollers to complicated industrial types. Each has its own specific requirements but in general the rheology at both high and low shear is significant.

7. Leveling

After application of paint to the substrate the degree of leveling effects appearance and gloss. The primary factors effecting leveling are viscosity, volatility of solvents, surface tension, yield value, and degree of flocculation of pigments.

B. Performance Properties

There are many performance properties of paints which must be considered by the formulator. Below is a list of some of these along with suggestions regarding ingredient affects on properties.

1. Skinning – This is a problem in paints or varnishes which dry by oxidation as well as some lacquers and dispersion type paints. The most effective way to prevent skinning is to exclude air but since this is not always possible, anti-skinning agents frequently are used. These will be discussed later.

2. Drying – The drying time, or baking time and temperature of paints is controlled by the binder, the solvents and to some extent by additives. In air dry products the dust-dry, the tack-free and through dry stages all are important.

3. Hardness – The hardness requirements of paint films vary with the end use. An applicance finish or automotive finish must be considerably harder than house paint. The hardness is controlled by the vehicle or binder and to a lesser extent the pigment volume concentration.

4. Flexibility – The degree to which paint conforms to movement or deformation of its substrate depends to a large extent on the binder but also, to some degree on the PVC, the degree of flocculation of the pigments and on the presence of plasticizers.

5. Adhesion – Knowledge of this important property primarily has been an art and not a science until very recently. Much has been learned about the chemical compositional effects on adhesion contributed by vehicles. Two kinds of adhesion are involved; (1) mechanical entanglement of the film in rough uneven substrate such as pores, cracks and fissures and (2) specific adhesion due to Van der Waals forces and hydrogen bonds. Polar groups such as a carboxyl group in a polymer contribute to adhesion. Epoxide compounds are noted for their excellent adhesion to a variety of substrates. Some experiments have shown methylol groups to be effective adhesion promoters while methyl groups have no effect. Some extender pigments promote apparent adhesion.

6. Abrasion Resistance – Good abrasion resistance is a requisite of many paints including floor finishes, chemical resistant finishes for laboratory furniture and traffic marking paints. Binders having a high order of toughness, such as vinyl chloride-vinyl acetate copolymers have good abrasion resistance due in part to the visco-elastic properties as well as good adhesion.

7. Exterior Durability – The resistance of paint films to degredation by sunlight, rain and winds depends upon the combination of binder durability and pigment. Since both have been discussed in previous papers these will be discussed only briefly. For years the durability of paints was limited by the binder. To state it another way, good pigments were more durable than

the best available vehicles or binder. However, in recent years, with the advent of fluoropolymer finishes, the binder durability here is greater than that of many supposedly good pigments which indicates an entirely new concept in binder/pigment relationship for durable paints.

8. Impact Resistance – Like flexibility, impact resistance of paint films is dependent upon binder type, PVC and degree of flocculation of pigments. Impact resistance differs somewhat from flexibility in that the rate of deformation is quite rapid. For good impact resistance paint films must have good cohesive and good adhesive strength.

9. Chemical Resistance – This term is quite broad since it covers a wide variety of chemicals. No single binder is best for resistance to all types of chemicals. Thus there are many binders used in chemical resistant coatings, some of which are Hypalon® (chlorosulphonated polyethylene), chlorinated rubber, polyurethane, Neoprene (chloroprene) vinyls, epoxy-polyamide, phenolics, fluoropolymers, some styrene copolymers and butadiene/acrylonitrile rubber. Pigmentation is important because some pigments react with acids, some with alkalis and some with oxidizing agents to cause color changes or film deterioration.

10. Resistance to Micro-organisms – The micro-organisms often found on paint films and organic coatings are bacteria, algae and molds or fungi. Their presence is harmful from the standpoint of appearance as well as chemical degredation of paint films. The presence of water or moisture is necessary for mold growth so this is not a problem in containers of organic solvent type paints, but is a problem in many latex paints, Dry paint films however, are subject to mold growth, especially in binders of the oil or alkyd types. Additives to minimize the problems are discussed later in this paper.

11. Corrosion Resistance – This is an important property requirement for many paint end uses. This subject to be handled properly would require much more time than is available now. In general, corrosion of iron or steel substrates is the result of an electrochemical action. This can be suppressed by the use of impermeable paint vehicles and by the use of corrosion inhibiting pigments such as red lead (tetravalent oxide PbO_2), calcium plumbate, zinc chromate, zinc dust, basic lead silicate and many others.

12. Miscellaneous – There are many other important properties of paint films which must not be neglected. Some of these have been discussed under pigments and/or polymers so here we will list them without further comment.

a. Gloss
b. Hiding
c. Color development and stability
d. Cold crack
e. Cold check
f. Water resistance
g. Electrical properties
h. Print or Mottle resistance

II. BINDERS

Binders or vehicles provide the cohesive and adhesive forces required to hold paint films together. Successful formulations demand the use of binders tailored to the end-use requirements of the finish. Polymers, or binders used in paints, has been the subject of a comprehensive presentation by P. Heiberger so no details will be given here.

Frequently paint vehicles consist of a blend of two or more binders or polymers to obtain cross-linking or a balance of properties not attainable in a single, available polymer. For example, soft and hard resins are blended to obtain desired hardness/flexibility balance, or modifying resins or binders may be used to alter physical properties such as solubility, viscosity, solids content, adhesion, durability, cost, etc.

For best results, usually, these blends should be compatible both in solution and in the dry state. Too often, such blends are observed only in the pigmented state where some incompatibility is masked by the opacity from the pigments. Better formulations could be developed if more time and effort were devoted to examination of binders before and after pigmentation, especially for compatability in the wet, initially and after aging, and dry film compatability.

III. SOLVENTS

Organic liquids used to dissolve binders have considerable effect on application properties as well as dry film properties of finishes. Frequently binders are so high in molecular weight that so-called solutions really are colloids. The rate of change in consistency or rheology as paints dry in air or in ovens primarily is a function of the type of solvent, the solvent power and the volatility. Improper solvents can cause popping, blistering, stresses in the film which may cause alligatoring or mud-cracking and other weaknesses.

Solvent systems for most paints consist of mixtures of two or many more liquids classified as true solvents, latent solvents, dispersants, and diluents. The proper combination of these liquids is necessary for good formulations.

A. Solvent Types

1. Terpenes –

   Turpentine, dipentene, pine oil

2. Hydrocarbons (non-polar)

   a. Aliphatic - straight or open chain - saturated
   b. Naphthenes - saturated cyclic having benzene ring

3. Oxygenated (polar)

   a. Alcohols
   b. Esters
   c. Ketones
   d. Ether alcohols

4. Chlorinated compounds

5. Nitroparaffins

B. Solvent Properties

1. Solvent Power – This is quite complicated and for that reason many systems or tests have been devised to characterize solvents. The most fundamental of these is the solubility parameter concept which is applicable to polymer as well as solvents. Polymers having similar solubility parameters frequently (but not always) are compatible. Likewise, solvents which have solubility parameters similar to that of polymer usually are good solvents for that polymer. One useful application of this concept is the blending of two non-solvents mathematically to yield an average solubility parameter close to that of a polymer thereby obtaining a mixture which is a solvent for the polymer.

   Other measures of solvent power are:

   a. Dilution ratio
   b. Kauri-butanol value
   c. Aniline point
   d. Viscosity of polymer solutions
   e. Hydrogen bonding

2. Volatility – This property has an important effect on drying time, flow, leveling, sagging and many other performance characteristics. Boiling range often is used as a rough indication of volatility but this can be misleading. Vapor pressure multiplied by molecular weight correlates better with volatility. The solvent release properties of polymers also influence evaporation of solvents from films.

3. Flash Point – This is important in many paint applications where low flash point cannot be tolerated because of fire hazard. Generally, the faster the evaporation rate the lower the flash point, but there are exceptions, for example the chlorinated solvents.

4. Color – Most solvents used in the paint industry are water white in the pure state but commercial grades may contain impurities causing discoloration.

5. Odor – Odor arises from the volatility of solvents, or of binders containing volatile components. This property is of special importance in paints used indoors in areas where ventilation is limited. The so-called odorless solvents are aliphatic hydrocarbons substantially free of aromatics.

6. Toxicity – The need for non-toxic solvents in many paint applications is obvious. Some liquids such as isophorone, chlorinated hydrocarbons and nitroparaffins are excellent solvents for many applications but their use is restricted by the high order of toxicity.

7. Corrosion and Acidity – Solvents used in paints should be free of acidic materials and sulfur compounds which are corrosive to metals or which may react with pigments or binders.

IV. ADDITIVES

Frequently modifying ingredients are added to paints in small percentages to improve application or performance properties. These additives often are beneficial in specific formulations but have no effect or are even detrimental in other formulations. Many such materials are available. A list of approximately 160 additives in current use by F. & F. was issued October 24, 1968 by W. P. Colio. Philadelphia Plant Technical Report No. 29 also contains information about additives. This should be used as a reference when searching for additives to modify properties of formulations. However, since additives which are used to improve one specific property may have an adverse effect on some other property, they should be used only after a thorough evaluation of all properties of the paint.

A. Plasticizers – These materials could be considered a part of the binder, or as relatively non-volatile solvents. Binders, or film formers can be adjusted for flexibility by internal plasticization or use of flexible monomers in copolymers. An easier, but often less desirable means of doing this is the addition of external plasticizers. They act like solvents, penetrate polymer chains, permit uncoiling and lower T_g (glass transition temperature). Literally there are many hundreds on the market and selection of the best one for any specific use requiresa large amount of evaluation.

They can be classified in the following manner:

1. Monomers
2. Non-drying fatty oil
3. Esters (both monomeric and polymeric)

Examples of several of the commonly used plasticizers are phthalates (dioctyl phthalate, dibutyl phthalate) phosphates (tricresyl phosphate), polyethylene glycol di 2-ethyl-hexoate, and epoxidized soya oil.

B. Driers – These additives are used to accelerate the conversion of liquid to dry film mostly in the oxidizing air dry coatings but also to some extent in baking type finishes. The precise mechanism of the drier reaction in many instances is not well known but it is thought that natural drying oils contain anti-oxidants which must be oxidized by driers before oxidation of the oil can take place.

Some of the common driers are the heavy metal soaps of organic acids i.e. lead, cobalt, manganese soaps of linseed fatty acids or rosin acids. (See driers in the additive list by Colio.)

C. Skinning Inhibitors – Inhibitors generally are volatile anti-oxidants which retard oxidation in paint containers but which volatilize after paint application. Typical examples are oximes and substituted phenols.

1. Butyraldoxime
2. Methyl ethyl ketoxime
3. Cyclohexanone oxime
4. Hydroquinone
5. o-methoxy phenol
6. o-isopropyl phenol

D. Fungicides – Preservatives – Below are a typical few of the many preservatives currently available. Each has certain disadvantages such as dark color, reactivity, with sulfur, toxicity, odor, or drying inhibition.

1. Organo-mercurial compounds
   a. Phenyl mercury salicylate
   b. Phenyl mercury oleate

2. Copper compounds
   a. Cuprous oxide
   b. Copper naphthenate
   c. Copper quinolinolate

3. Chlorinated phenols
   a. Pentachlorophenol

4. Miscellaneous
   a. Salicylanilide
   b. Zinc oxide
   c. Calcium carbonate

E. Flow Control – Several of the major factors influencing flow are evaporation rate the surface tension of paint systems, degree of pigment wetting and flocculation, and viscosity. Additives to increase flow and leveling consist of silicon oils and resins to reduce surface tension, plasticizers to hold film open longer, surface active agents to provide pigment wetting and/or to alter surface rheology. Too much flow also is a problem in some applications where sagging or thin coats on high spots of rough substrates are critical. Additives to reduce flow by increasing viscosity and thixotropy include soya lecithin, aluminum stearate gel, calcium linoleate and many proprietary products.

F. Flooding and Floating – The problem of flooding, floating and vortex cells, or Benard cell formation is a complex one which can be discussed only very briefly here. Currents in drying films carry pigments along and deposit them at different locations in the film which cause color and appearance problems. Additives to minimize these problems include:

1. Silicone oils (reduce surface tension)
2. Thickening agents
3. Surface active agents

G. Miscellaneous – There are many other additives used in paints i.e. dispersing agents, UV screening agents, anti-foams, anti-static agents, mar-proof agents, etc. Many examples of these are found in the additive tables issued by Colio.

V. COMBINING THE INGREDIENTS

The manner in which the individual ingredients are combined has significant effect on the quality of the finished paint. The order of addition and mixing cycles should be established to develop maximum utilization of pigments and obtain utmost compatability of vehicles or binders. The most common order of pigmented products is as follows:

A. Resins – Mix thoroughly before adding pigmented dispersions.

B. Aluminum dispersions of Pigments.

C. Other pigment dispersions – Larger amounts than 2.0lbs./100 gals.

D. Driers, inhibitors – other additives.

E. Pigment dispersions – less than 2.0 lbs./100 gals.

F. Solvents.

G. Shading dispersions.

This suggested order of addition may be changed, if necessary, for best quality, freedom of seed, freedom of dimpling, etc. See formulating practice FP-05 for a further discussion at order of addition.

Attached are some examples of finished paint formulations typical of products currently being handled by the Marshall Development Laboratory.

D. K. OGG

DKO/emv
10/15/69

REFERENCES

1. Organic Coating Technology - Vol. I - Payne
2. Organic Coating Technology - Vol. II - Payne
3. Principles of Surface Coating Technology - W. H. Parker
4. Modern Surface Coatings - Paul Nylen/Edward Sunderland
5. The Technology of Solvents and Plasticizers - Doolittle
6. Paint and Varnish Technology - Von Fischer
7. FP - 05
8. Philadelphia Plants Technical Report #29 Characterization and Simplification of Additives.

724-66325 LUCITE® AP-5 HB ENAMEL-REFRIGERATOR

910-1123	White Base	493.33	White Base W-123 ground in RC-6028 and RC-731 with G-44 (MPA) as anti-settling agent
RC-6028	Acrylic Resin	270.21	Styrene/AA/Cardura E (61/11/28) in H-583 H-596 and H-12
RC-731	Melamine Resin	197.89	Cross-link with acrylic
32-5979	Wax Dispersion	12.58	G-820 Polymekon wax - mar resistance and slip
910-1021	Flatting Dispersion	11.74	W-1021 Super Fine Super Floss - Gloss adjustment
VH-1260	Silicon Solution	1.99	H-427 Silicone fluid - imparts "orange peel" and sag resistance
H-143	Solvent	12.58	Butyl carbitol - Slow solvent - popping resistance and flow.
H-514	Solvent	14.67	Ethylene glycol - increase conductivity
732-514	Pigment Dispersion	0.10	Shading base W-514 and RC-718
732-630	Pigment Dispersion	0.21	Shading base W-630 in RC-718 - Soya Lecithin added for anti-settling
910-5224	Pigment Dispersion	0.42	Shading base - W-224 ground in RC-6028 Cresole as anti-skin
H-601	Aromatic Hydrocarbon	32.28	Diluent
	Bake =	30 min. at 325°F	
	Gloss =	82 to 87 at 60°	
	Substrate	Primed CR Steel	

876-5440 LUCITE® ACRYLIC ENAMEL WHITE

RC-11104	Acrylic Resin	121.00	S/MMA/EA/AAM/AA thermosetting acrylamide resin with good durability hardness/flex.
H-601	Solvesso 150	4.54	Aromatic hydrocarbon diluent-low cost and low volatility
H-224	Butyl Cellosolve	22.08	Good solvent for RC-11104 & G359
H-44	MIBK	22.08	Ketone solvent Add/Mix 15 min.
G-768	Syloid 404	36.02	Amorphous silica flatting agent - good adhesion and formability. Add slowly while mixing - mix 3 hours.
331-5001	White dispersion	514.40	W-185 and W-135 (Talc). Extender - good slip Add while mixing-mix until uniform
RC-11104	Acrylic Resin	171.12	Resin
331-5004	Wax dispersion	61.04	Polyethylene - slip, pressure mottle resistance.
G-359	Epoxy soln.	16.82	Epon resin for improved adhesion on bends
H-79	Cellosolve Acetate	44.15	Good solvent for both resins - proper volatility
H-596	Solvesso 100	25.70	Aromatic hydrocarbon diluent - proper volatility
	Bake	60 sec. at 530°F. to metal temperature of 440°F.	
	Coverage	601 sq. ft./gal./mil	

Key	Explanations
1	Nitrocellulose is basic film former of this finish. The blend listed is selected for proper formula viscosity, consistent with other required properties.
2	Alkyds generally impart additional properties such as adhesion, hardness, processing, lower cost. The blend listed was selected for hardness, print resistance, apparent build, and processing.
3	This is the plasticizer of the finish. It imparts good retained flexibility. This is important for a finish for wood which swells and shrinks considerably over a period of time due to changes in atmospheric conditions.
4	This is a flatting pigment used to control gloss of the product. This % may vary depending upon gloss specifications of product. It will be eliminated if full gloss is desired.
5	Silicone oil is added for improved flow and elimination of "orange peel". It also imparts improved "feel" to finish.
6	This group of solvents has been selected and balanced after much experimentation in laboratory and field. This will vary considerably with the type lacquer and with conditions in each customer's plant. They can be broken down into: a. active solvents) b. latent solvents) As can be noted in the formula, they are further broken down into varying boiling ranges for proper dry under wide ranges of temperatures and humidities. c. diluent solvents)

15206 – DUCO® LACQUER FURNITURE FLAT

Ingredients	Identification	100% (Wt.)	Key (See Sheet 2)
PX-7400	1/4" – Isop wet nitrocellulose(70% solids)	7.2%	1
PX-7680	1/8" – Ethyl wet nitrocellulose (70% solids)	4.9	
RL-622	55% CNO-PE Alkyd (70% solids)	10.4	2
RL-623	55% Co/CNO/PE Alkyd (65% solids)	8.3	
HF-186	Di 2-Ethyl Hexyl Phthalate	10	3
G-1090	Syloid 978 (SiO_2)	18	4
VH-5379	2% Silicone Soln. (Xylol)	05	5
H-44	Methylisobutyl Ketone	99	
H-40	Methylisoamyl Ketone a-(active)	39	
H-145	Diisobutyl Ketone	21	
H-224	Ethylene glycol mono butyl ether	08	
H-41	Methanol	39	6
H-69	Isopropanol b (latent)	55	
H-12	Butanol	98	
T-8612	Toluene (or toluene substitute)	74	
H-583	Xylol c(diluent)	226	
		100 0%	

Formula Specifications

Solids – Wt. – 24%
Vol – 16.6%

Visc. – 7c/55-65"
(ready to spray)

Gal. Wt. – 7.56 lbs.

Gloss – 60°/6-8

RF-5270 "Dulux" Furniture
Flat

Key	Explanations
1 and 2	The film former is a blend of a hard brittle urea formaldehyde resin and a more flexible alkyd resin. The blend employed represents optimum for desired properties, such as flexibility, print resistance, dry, processing. This product drys by polymerization and must be catalyzed and be given mild bake for proper curing. The catalyst is octyl acid phosphate (50% solids) and 2%(wt.) is required prior to application. Potlife is a minimum of 3 days. Typical baking schedule is 1 hour at 40°F.
3	Santocel 62 is a flatting agent which controls formula gloss. If full gloss is desired, this is eliminated.
4	Nylon Sol'n. is used to facilitate smooth flatting appearance from Santocel 62. If this is eliminated, "silking" or streaking occurs. This is eliminated in clears.
5	Silicone oil is added for improved flow and elimination of "orange peel". It also imparts improved "feel" to finish.
6	The inhibitor solution reduces "yellowing in dark" of applied finish by reducing oxidation of the DCO oil in the alkyd.
7	The 3 solvents employed are: Butanol – for the UF resin Xylol – for the alkyd resin Ethyl acetate – to improve compatibility (this is particularly important in clear versions of this product).

RF-5270 - "DULUX" FURNITURE FLAT

Ingredients		Identification	100% (Wt.)	Key	Formula Specifications
RC-718	Solid Ingredients	Urea Formaldehyde Resin (60% Solids)	27.3%	1	Solids - Wt. - 36.6%
RC-6000		25% Sty. - 35% DCO Alkyd (45% solids)	45.7	2	Visc. - 7C/45-55"
G-1035		Santocel 62 (SiO_2)	1.5	3	Gel Wt. - 7.89 lbs.
VG-332		Nylon Sol'n (5% in ethanol)	2.2	4	Gloss - 60°/31-35
VH-5379		Silicone Sol'n (2% in xylol)	0.5	5	
VH-965		Hydroquinone Sol'n (7.8% in butanol)	0.3	6	
H-12	Solvents	Butanol	12.5		
H-583		Xylol	8.8	7	
H-136		Ethyl Acetate	1.2		
			100.0		

VG-5735 EPON CAN COATING

BASE COAT UNDER VINYL TOPCOAT - INTERIOR COATING FOR BEER/BEVERAGE CANS

Cold Cut

H-39	Diacetone Alcohol	118.5	Good solvent for dye and resin - poor plate wetter
G-297	Luxol dye	3.0	Alcohol Soluble dye for gold color add in order with agitation - mix until clear
RC-718	Urea Formaldehyde	73.0	Cross-link with epoxy
H-583	Xylol	87.4	Low Coat diluent
H-44	MIBK	232.6	Good solvent for epoxy - good plate wetter add in order - mix 10 min.
G-1050	Epon 1007	293.5	Epoxy vehicle - good adhesion and resistance add over 1/2 hour period - mix for 3 hours before checking for solubility

Bake	12 min. at 420°F.
Solids	40%
Epoxy/UF	87/13

VC - 188 SANITARY ENAMEL

OLEORESINOUS VARNISH - ONE COAT SYSTEM USED ON CAN FOR ACID OR BLEND FOODS NOT SULFUR FOODS
F ENAMEL BY SM. CAN.

			Open Kettle Cook
G-113	Velsicol Resin	184.24	Gold color low cost petroleum hydrocarbon resin.
H-7	Tung Oil	79.48	Vehicle - flexible - good chemical resistance - rapid dry. Also known as chinawood oil
H-553	Oiticica Oil	159.79	Vehicle similar to tung oil in properties
			heat to 500°F. - blow with inert gas for 15 min. remove heat but retain blow - hold at 450°F.
H-596	Solvesso 100	341.17	Low cost aromatic - good plate wetter - good for high speed reverse roller application
			Thin in mixer
H-173	Manganese Naphthenate	1.15	Drier - through drier
H-583	Xylol	37.93	Low cost aromatic - more volatile than H-596
		Bake	12 min. at 420°F.

FUNCTIONAL USES OF COATINGS

by W. J. McConeghey

SLIDE I

FUNCTIONAL USES OF COATINGS

SLIDE I COMMENTS

I am going to talk to you about a system of classifying coatings - really a way of thinking about coatings - that I believe will be helpful to you in your work. It will help you whether you are in research, in development, in production or in sales.

There are many systems for classifying coatings and each system is useful in its own way.

Here are some commonly used classification systems:

SLIDE II

COATING CLASSIFICATION SYSTEMS

1) Binder type

2) End use

3) Substrate

4) Application method

5) Cure mechanism

6) Vehicle type

7) Physical Properties

SLIDE II COMMENTS

Each system is useful both as a means of defining the characteristics of the coatings and as a convenient designation when talking about them.

Binder type (vinyl, alkyd, acrylic) identifies the chemical composition, and defines in a general sense what the chemical and physical properties are.

End use (automotive, house siding, furniture) identifies a marketing field and gives some conception of what performance is expected.

Substrate (wood, aluminum, paper) indicates loosely a set of properties the coating must have.

Application methods (spray, dip, roller coating) implies certain levels of viscosity, flow, evaporation rate, etc.

Cure mechanism (solvent evaporation, oxidation, bake) indicates the limits on line speed, and states the requirements for ovens or other curing equipment.

Slide II Comments
(Continued)

Vehicle type (solution, emulsion, organosol) defines formulation techniques, and implies some of the characteristics of the coatings.

The physical properties such as color, gloss, durability, stain resistance, etc. are used to define the performance requirements of a coating.

Other classifications supply still other information.

Each of these systems describes one or more characteristics of a coating and defines to some degree what performance can be expected of it. They are useful and convenient classifications to use.

There is, however, another system of classification that is more fundamental: one that gives a clearer overall view of coating requirements and is more directly related to the purposes for which coatings are actually used.

SLIDE III

THE PURPOSE OF COATING A SURFACE
IS TO MODIFY THE FUNCTIONAL PROPERTIES
OF THE SURFACE

SLIDE III COMMENTS

The Purpose of Coating a Surface is to modify the functional properties of the surface.

- to change it so it will perform some function that it could not perform without the coating. This is the only reason for coating a surface.

It is these functional properties that I want to discuss. They are the fundamental basis for the coatings industry.

Thinking of coatings in terms of their functional use has a number of advantages.

SLIDE IV

ADVANTAGES OF CLASSIFICATION BY FUNCTION

1) It defines the real reason for using the coating

2) It clarifies technical objectives

3) It places performance specifications in perspective

4) It focusses attention on what we actually sell

5) It expands our thinking beyond paint

6) It leads to new markets

SLIDE IV COMMENTS

1) Knowing the function(s) that a coating must perform enables us to judge how well we have met our goals. The coating must function better to be better.

2) It clarifies technical objectives in that it defines them in terms of broad concepts rather than narrow specific properties. Changes in properties must be judged in relationship to their effect on functional performance.

3) Classification by function places performance specifications in perspective. Performance specifications not related to the functional requirements of the coating are of questionable value. Performance specifications that are related to functional requirements must not be overlooked.

SLIDE V

Organic Coatings perform many functions.
Most familiar are:

1) to decorate

   a. Color
   b. Pattern
   c. Texture

2) to protect

   a. Physical barrier
   b. Chemical activity

SLIDE V COMMENTS

Organic Coatings perform many functions.
Most familiar are:

1) to decorate

The color, pattern and texture of coatings appeal to our esthetic sense and influence our psychological moods.

With exactly the same set of walls we can manipulate the decorating scheme so that it can be described as restful or stimulating, complex or simple, dramatic or neutral. We can even alter the psychological response to the room's dimensions and temperature by our selection of coatings.

Slide V Comments
(Continued)

2) to protect

The type of protection required of a coating depends on the weaknesses of the substrate and on the harshness of the environment. Coatings may give protection against weather, ultraviolet light, sea water, oils, solvents, chemicals, industrial wastes, abrasive agents, extreme temperatures, mold, bacteria, insects, marine plants or animals, and many other harmful agents.

Some coatings simply place a barrier between the substrate and the harmful agent. Others protect by chemical activity. Examples of chemically active coatings are mildewcides to inhibit mold growth, poisons to kill marine growths, corrosion inhibiting materials to regard corrosion, etc.

But there are many other functions that coatings can perform:

SLIDE VI
FUNCTIONS

3) TO CONTROL HEAT

a) Reflection

b) Absorption

c) Radiation

d) Insulation

e) Ablation

f) Chemical Reaction

Slide VI - Comments

3) To Control Heat

Coatings may be designed to control heat. Light colors reflect heat and dark colors absorb heat. A white roof and a black roof may give as much as 20° F difference in interior temperature on a sunny day.

Colors that absorb heat readily are also good radiators of heat, while reflective coatings are poor radiators.

Thick or foamed coatings insulate.

The ablation coatings used on re-entry space vehicles dissipate heat by sloughing off as they reach high temperature.

An endothermic chemical reaction in the shatterproof coating on flash bulbs serves to absorb some of the heat emitted by the bulb. Conversely, exothermic reactions provide enough heat to accelerate the cure of some films.

Slide VI - Comments
(Continued)

Thus, the proper selection of coatings can make our homes more comfortable, cut evaporation losses in fuel storage tanks, make heating and cooling equipment more efficient, control the temperature of space vehicles and much more.

Heat control via coatings has even been used to speed the germination of seeds and the growth of plants. A dark colored mulch, which later bleaches white on weathering, first warms the soil for early germination, then reflects more light to the leaves of the growing plant and keeps the soil cool to cut down water evaporation.

The Coast Guard has experimented with melting ice bergs by spraying a dark coating on them.

SLIDE VII

4. TO CONTROL AND MODIFY LIGHT

a) Reflection

b) Absorption

c) Color

d) Texture

e) Opacity

f) Transparency

g) Fluorescence

4. To Control and Modify Light

Coatings have a profound effect on light. The reflection, absorption and transmission of various wavelengths of light, of course, determine the color of an object. The texture of a coating determines whether the reflection will be diffuse or specular (mirror like). The opacity or transparency of a coating determines whether or not light will be transmitted. Wavelengths of light outside the visible range (the infra-red and ultraviolet ranges) are also subject to control by coatings. By using fluorescent coatings we can change the wavelength of the incident light. With conductive coatings we can even manipulate waves in the radio spectrum.

We use these light regulating properties in many fields. A low reflectance coating reduces stray light on the interior of optical instruments. A beam of light can be "split" by reflecting part and transmitting part. High reflectance coatings increase the efficiency of lighting equipment. Textured surfaces diffuse light to give visual comfort. We make any color we want from white light by either reflecting it from a coating or by transmitting it through a coating. An example of the latter is the slide you are now viewing.

Slide VII Comments
(Continued)

Fluorescent coatings are used in sign finishes, high visibility aircraft markings and brighteners for fabrics.

With light reflecting and light absorbing coatings we can even translate light energy into mechanical energy with the radiometer.

SLIDE VIII

5) ELECTRICAL CONDUCTIVITY

6) ELECTRICAL INSULATION

7) ADHESION

8) RELEASE

9) WATER REPELLENCY

10) WETTABILITY

11) FLAMMABILITY

12) FIRE RETARDANCE

Slide VIII - Comments

5) Electrical Conductivity

Conductive coatings are used for printed circuits. By using a conductive primer coat we can topcoat non-conductive ware via electrostatic spray. Conductive coatings have potential as heating panels for walls or appliances.

6) Electrical Insulation

Insulation coatings protect printed circuits, wiring, and condenser coils. High temperature resistant insulation coatings permit construction of smaller, higher efficiency electric motors.

Slide VIII Comments
(Continued)

7) Adhesion

Coatings that provide adhesion may be actual adhesives, or they may be primers or sealers whose function is to promote adhesion between surfaces and coatings that do not themselves adhere. Postage stamps, fly-paper, contact cements, masking tape, heat sealable coatings and various types of primers are typical examples of adhesive coatings. Adhesives bind staples and nails into slugs for staplers and nailing machines. A rosin coating on nails melts from the heat of driving, binds the nail in place and retards corrosion.

8) Release

Release coatings are used on the backing of adhesive tapes and on the protective cover of pressure sensitive labels. They are also used on non-stick cookware, ice cube trays, and molds of many kinds. In some cases, the mold-release coating releases from the mold, but adheres to the article that is cast and serves as a coating for it. A strippable coating for temporary protection of a surface is another case where the coating itself releases from the substrate.

9) Water Repellency

A water repellent coating on rainwear improves its performance. It minimizes the staining of fabric or paper by water borne solids. A water repellent coating on highways reduces skidding.

10) Wettability

Wettable coatings on towels and diapers increase their absorbency. A wettable coating on windshields prevents formation of water droplets and stops fogging. Primers and other coatings that are to be re-coated must be wettable by the succeeding coat to prevent cissing or crawling.

Slide VIII Comments
(Continued)

11) Flammability

Charcoal briquets and matches are treated to give them controlled flammability. The coating on match heads ignites by friction and provides the initial oxygen and fuel to ignite the impregnated wood or paper. Another component of the impregnant inhibits the formation of glowing coal when the match is extinguished.

12) Fire Retardance

There are two kinds of fire retardant coatings. In one, the coating itself is simply non-flammable. In the other, the coating is not only non-flammable but foams into a heat insulating layer when exposed to flame. Heat reflective pigmentation also helps.

SLIDE IX

13) TOXICITY

14) NON-TOXICITY

15) PERMEABILITY

16) IMPERMEABILITY

17) SOLUBILITY

18) INSOLUBILITY

19) SMOOTHNESS

20) ROUGHNESS

SLIDE IX - COMMENTS

13) Toxicity

Anti-fouling paints contain copper salts or other agents that are toxic or repellent to marine organisms. Creosote coatings protect wood from bacteria and mildew. Many paints contain bacteria and fungus control agents, as preservatives for the wet paint as well as for the dried film. Germicidal paints have been used in hospitals. Insecticides and insect repellents have been incorporated in coatings.

14) Non-Toxicity

Certain coatings are so non-toxic that they are approved by the FDA for contact with food. Other coatings are edible. The chocolate shell on Eskimo pies and the sugar coating on M&M chocolates are examples.

Slide IX - Comments
(Continued)

15) Permeability

The good blister resistance of acrylic latex house paints is, in part, a result of the permeability of the film to moisture. The comfort of leather and poromeric shoe uppers is maintained by using moisture permeable dressings and polishes.

16) Impermeability

The coating on glassine potato-chip bags retards the transmission of moisture and oxygen to keep the contents fresh and crisp. A wax coating on turnips and other food products prevents withering by loss of moisture. Staining of topcoats by knots, cedar oils, and bleeding pigments may be prevented by suitable sealer coats.

17) Solubility

A soluble coating of starch permits easy removal of soil from a painted surface .

The coating on medicinal pills may control the rate of solubility or the place where solution will occur; some in the stomach under acid conditions, and others in the alkaline environment of the lower intestines.

18) Insolubility

We think of insolubility as the norm for coatings but sometimes the coating must be resistant to specific solvents such as gasoline, Sky-drol hydraulic fluids, hot grease, acids, alkalies, etc.

19) Smoothness

Cement block fillers make rough porous dirt-catching surfaces into relatively smooth easily washed surfaces. Fillers for open pored woods also provide smooth surfaces free from dirt catching pores.

Slide IX - Comments
(Continued)

The basecoats used in silver-reduction metallizing and vacuum metallizing serve primarily to provide a mirror smooth surface.

20) Roughness

Non-skid deck paints, sandpaper, stipple paints, and textured paints are examples of coatings whose function is to provide some degree of roughness.

SLIDE X

21. MASK FLAVOR

22. PROVIDE FLAVOR

23. MASK ODOR

24. PROVIDE ODOR

25. LOW VISIBILITY

26. HIGH VISIBILITY

27. PROMOTE CHEMICAL REACTION

28. INHIBIT CHEMICAL REACTION

SLIDE X - COMMENTS

21) Mask Flavor

Bitter pills have sugar coatings. Can Coatings prevent the development of off-taste that foods develop on contact with metal.

22) Provide Flavor

Bitter pills have sugar coatings. Breakfast cereals are flavor coated.

23) Mask Odors

Low odor paints contain re-odorants to mask the smell of their own solvents and curing reaction by-products.

24) Provide Odors

Odorants are added to paints to give them a fresh clean smell. Perfumes, encapsulated and used in printing inks, can be released by rubbing the print to rupture the capsules.

25) Low Visibility

Camouflage paints are formulated to have not only the same visual color as the background, but also the same infra-red reflectance.

Industrial structures are painted to hide unsightly details. Rust colored paints on steel keep rust stains from showing.

26) High Visibility

We have mentioned that fluorescent paints are used for high visibility aircraft markings. Night time visibility of highway signs is enhanced with reflective glass beads. Moving parts of machinery are painted in contrast to stationary parts as a safety measure.

27) Promote Chemical Reaction

The strike panel for safety matches is one example.

28) To Inhibit Chemical Reaction

The inhibition of corrosion is the principal such function. The use of masking coatings or stop-off lacquers in chemical milling is another.

SLIDE XI

29) PREVENT EVAPORATION

30) IDENTIFICATION

31) CONTAIN EXPLOSIONS

32) LAY DUST

33) TRANSFER COLOR & PATTERN

34) PROTECT SEED

35) PROTECT FOOD

36) PROTECT WOUNDS

SLIDE XI
COMMENTS

29) Prevent Evaporation

A monomolecular layer of cetyl alcohol will decrease evaporation losses from a water reservoir.

30) Identification

Coatings are used as identification markers in many ways. Wiring in complex circuitry is color coded, striped etc. Piping, valves, switches, etc. are color coded. Safety and warning signs are coded by both color and shape.

31) Contain Explosions

Flash bulbs, glass aerosol containers, and safety glass use coatings to contain explosions and prevent the shattering of glass.

Slide XI - Comments (Continued)

32) Lay Dust

Dust-free landing pads for military helicopters are made by pouring quick setting coating material on the ground.

33) Transfer Color and Pattern

Decals, carbon paper, typewriter ribbon, and the encapsulated dye/acid combination used in National Cash Register's no-carbon-required Speedimemo paper are examples of coatings used to transfer patterns.

34) Protect Seed

Seed is treated with fungicide and fertilizer. Irregularly shaped seed is pelletized with coating material to adapt it to mechanical sowing.

35) Protect Food

We mentioned the wax coating on turnips to prevent withering. Cheeses are also wax coated. Eggs are dipped in sodium silicate to seal the shells for better preservation. The sugar coating on M & M chocolates melts in your mouth, not in your hand.

36) Protect Wounds

A coating of collodion protects minor wounds and is transparent to permit inspection.

SLIDE XII

37) TO DETECT AND RECORD

a) Magnetism

b) Temperature

c) Light

d) Atomic Radiation

e) X-Rays

f) Toxic Gas

g) Moisture

Slide XII - Comments

37) To Detect and Record

Coatings perform many detection and recording functions.

The shape of a magnetic field can be recorded in the pattern of magnetic flake in a coating. Unusual decorative effects can be achieved this way. Sight and sound can be recorded indirectly in the magnetic fluctuations of video and recording tape.

Coatings can record temperature by either reversible or irreversible color change.

Photographic film records light, atomic radiation and x-rays.

Special coatings have been developed for the detection of military gases.

Moisture indicating coatings change color with the weather.

There are, of course, many other functions that coatings perform, but we have shown enough to illustrate the point. Let's sum-up what we've covered.

SLIDE XIII

OUR BUSINESS

IS

SURFACE MODIFICATION

VIA

FUNCTIONAL PERFORMANCE

OF

COATINGS

Slide XIII Comments

The introduction to the concept of functional performance of coatings gives us an over-all view of the forest. Now we have a better idea of where we are going because we see the trees for what they are. Performance specifications, composition specifications, property requirements, control tests, market needs, etc. are just guide posts toward the goal of functional performance.

With this guidance we have a better understanding of why we use a coating, what our technical objectives really are, the relative importance of performance specifications, what the saleable features of our coatings are, what we can sell besides paints, and how to recognize new marketing fields.

Thank you.