SEMINAR

RAW MATERIALS

The history of raw material developments in our industry is quite long and complicated, but has been set forth in great detail by Mattiello and Von Fischer. As each of the new chemists has been provided with a copy of Von Fischer's treatise, it will be unnecessary to go into any great detail on this point. However, for purposes of a brief review, I want to point out that the ancients used vegetable oils first for preservative purposes, and later mixed these oils with materials that we now consider as mineral pigments to obtain colored effects. As time progressed, various other colored materials were used as pigments. Certain of the fossil gums where blended with the oils to improve their drying characteristics; later, these combinations were cooked to prepare a crude varnish for use as a clear finish or as a vehicle for the crude pigments. The art of finish making progressed through the stages of utilizing various gums, including Congo, Kauri, Manila, Damar and East India fossil gums, the various grades of rosin, and finally the first gum that might be termed a synthetic-Ester Gum - the reaction product of esterifying rosin with glycerol.

Probably the next synthetic gum was one such as now represented by the Amberol type, wherein the rosin is modified with a phenolic material or with maleic anhydride. All of the changes were designed to improve the properties of the finish from the standpoint of drying time, appearance, or resistance properties. Then, synthetic resins were prepared by condensing phenol with formaldehyde, enabling us to obtain a new level of resistance properties. The next large step was taken when polymers were prepared from oil, glycerol, and phthalic anhydride to give the familiar "Dulux", glycerol phthalate or alkyd type resins. The differences in properties between these various types of vehicles will be discussed in later talks in this series. Another type of development occurred during the later stages of this progress - the preparation of finishes with highly polymeric materials that dried only by solvent evaporation. The outstanding example of these is the nitrocellulose type finish, and further developments have produced such polymers as ethyl-cellulose, chlorinated rubber, methacrylates and the vinyl type resins. A recent vehicle is based upon the building of resinous polymeric materials from compounds based upon the silicon-oxygen linkage, the silicone resins as we know them today.

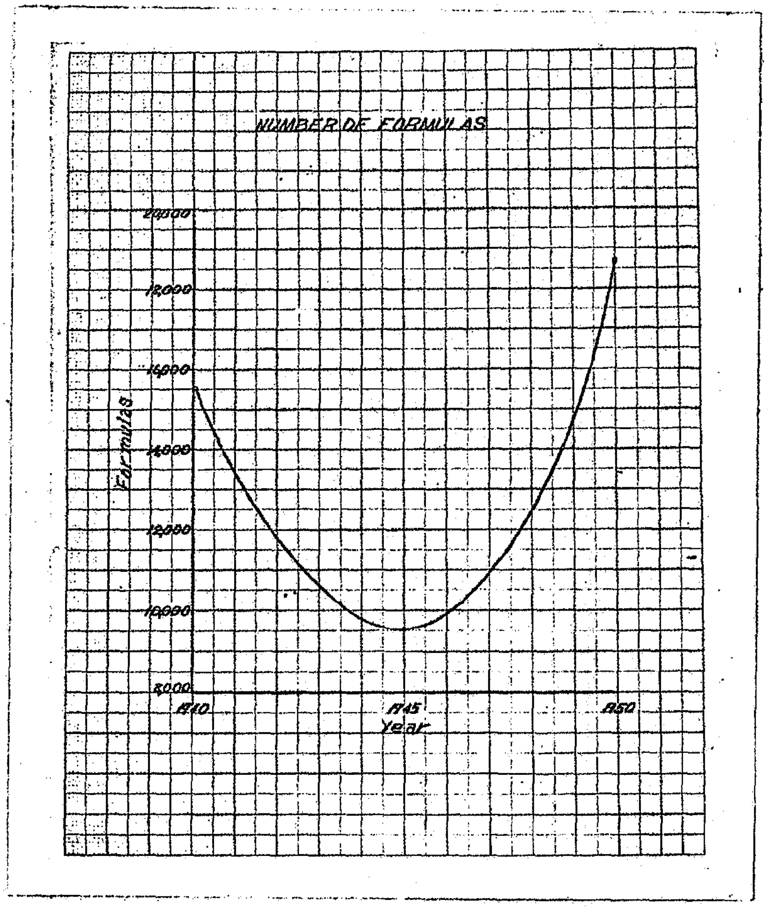
Another field of rapid development comprises the heat polymerizing resins, generally of the nitrogen type, including the urea-formaldehyde resins, melamine-formaldehyde resins and a recent development in guanamine-formaldehyde resins.

A number of these vehicles, such as the nitrocellulose and the nitrogen resins, produce films that are too brittle for normal use without modification and require the use of plasticizers to produce practical film properties.

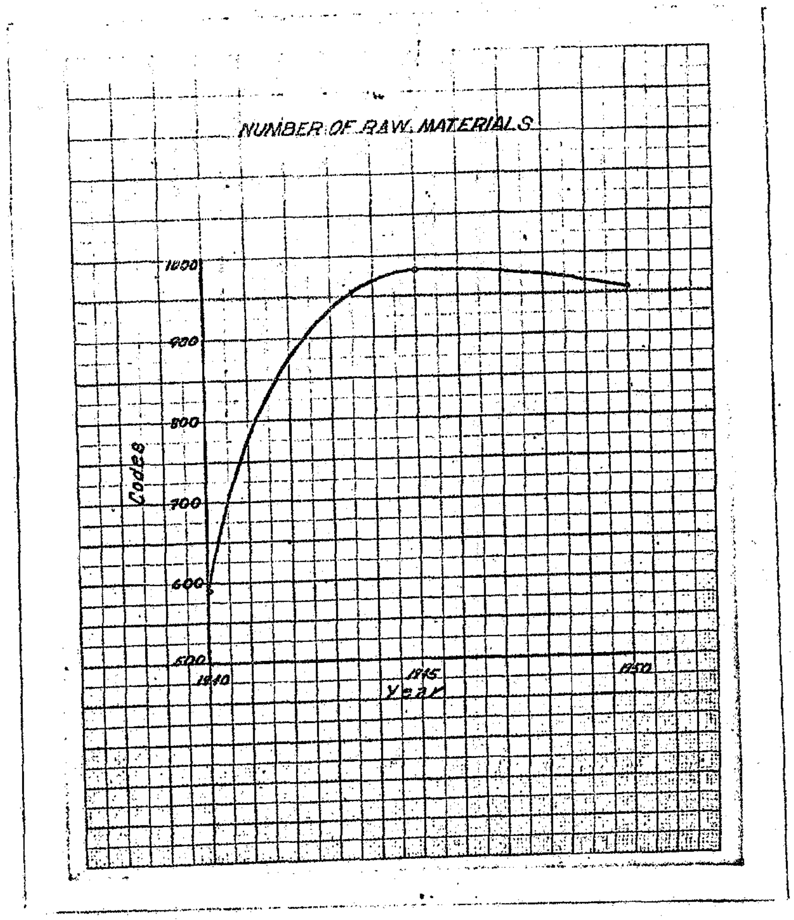
<u>CODING SYSTEM:</u>

As you came into the DuPont Finishes Organization, you were undoubtedly amazed at the magnitude and complexity of our coding systems. These systems are used for accuracy, simplicity and secrecy. By using a code number to designate a raw material, or finished product, we can specify easily and simply, a material meeting certain detailed requirements that will be satisfactory for our use. For example, it is very much easier to say or write G-78 than "a melamine formaldehyde resin from Rohm and Haas designated as Uformite MM-55, at 50% solids in 80% butanol and 20% xylol, having an acid number of 2 maximum on the solids, a color of one maximum, a viscosity of G to M by the Gardiner-Holt syste, and a specific gravity of .971 to .985". Actually, the code G-78 includes all of these specifications. When a raw material is received in the Plant, it must be tested against the appropriate specification before it can be consumed as the material represented by that code.

Also, by using a coding system, we are able to restrict confidential information. The laboratory manuals have indices to the coding systems that we use, but they do not give any idea of the magnitude of this system.



If you stop to realize that we have more than eighteen thousand active formulas in our files, you will see why it is impossible for any one individual to keep up-to-date in all our fields.

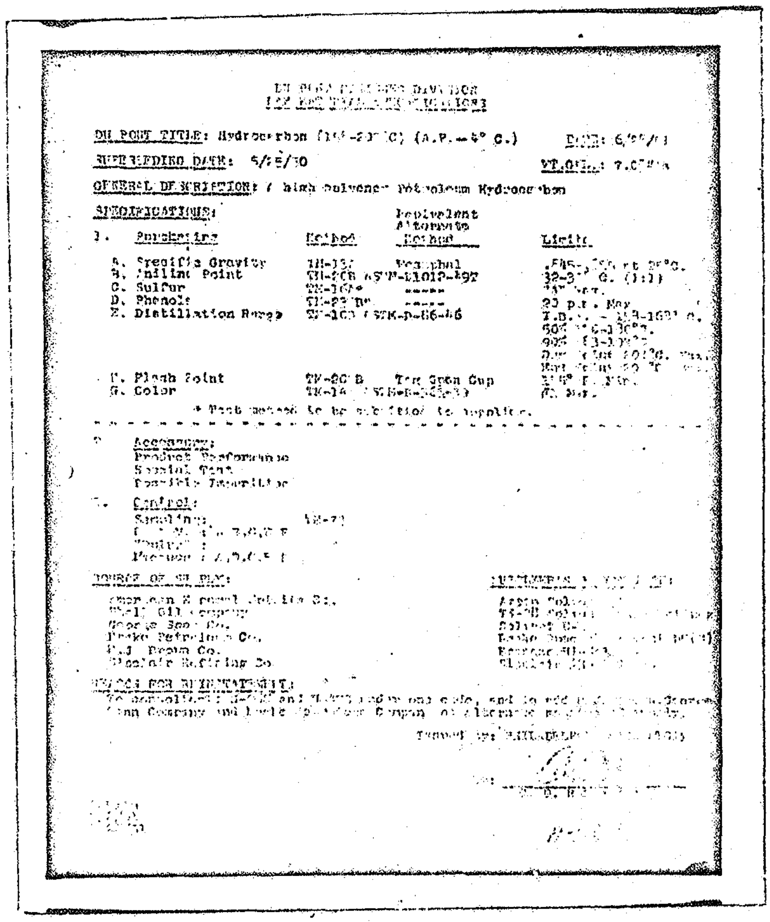


RAW MATERIAL SPECIFICATIONS:

When a new raw material comes on the market, it may come to our attention in any of several ways. Mr. H. G. Stauffer maintains contacts with raw material suppliers to keep abreast of new developments, and examine some of these materials for potential uses in our business. On the other hand, the Plant Chemical Groups have the responsibility of examining and evaluating materials that are of interest as alternate sources of supply for materials that we now use.

We have a system for keeping track of raw material samples that has been very useful. When a raw material sample is received in the laboratory, it is given a code number consisting of the letters DS followed by a serial number. A cross-index system is maintained to facilitate future reference to the specific sample or to related samples. It is important to see that each raw material sample is properly coded when it first comes into the laboratory.

Once a raw material is evaluated and found to be of interest, it is usually assigned a temporary raw material code consisting of the letter K and the proper G, H, or W code followed by a serial number. For example, a new pigment would be coded KW and the proper serial number. Tentative raw material specifications are prepared for this material to enable the Purchasing Department to obtain supplies for Plant Alignment tests or experimental work in a plant. As soon as the material is adopted, it is given a permanent G, H, or W code, as the case may be, and permanent specifications are prepared. We have the responsibility of setting-up and maintaining adequate raw material control tests to insure the receipt of uniform material. We also have the responsibility for testing and approving the sources of supply from which this material may be purchased. Our Purchasing Department works from the raw material specifications in obtaining supplies for the plants and are required to operate within the establishes specifications and sources of supply. One of our large problems is the establishment of alternate sources for the various raw materials. The attached sample a typical raw material specification and you may see the code number, our designation a general description of the material, the control tests, the st pulation as to which tests must be run as routine control, the designation and source of the standard, and the approved sources of supply, with those suppliers designations.



[illegible]

TITLE: Hydrocarbon [illegible] (A.P. [illegible]) DATE: [illegible]

DATE: 5/[illegible]/30 [illegible]

GENERAL DESCRIPTION: [illegible] high solvency Petroleum Hydrocarbon

SPECIFICATIONS:

1. [illegible]

	Method	Equivalent Alternate Method	Limits
A. Specific Gravity	[illegible]	[illegible]	[illegible]
B. Aniline Point	[illegible]	[illegible]	[illegible]
C. Sulfur	[illegible]	-----	[illegible]
D. Phenols	[illegible]	-----	[illegible]
E. Distillation Range	[illegible]	[illegible]	[illegible]
F. Flash Point	[illegible]	Tag Open Cup	[illegible]
G. Color	[illegible]	[illegible]	[illegible]

[illegible]

2. Acceptance:
Product Performance
Special Test
[illegible]

3. Control:
Sampling: [illegible]
[illegible]

SOURCE OF SUPPLY: [illegible]

Shell Oil Company
[illegible]
[illegible] Co.

REASON FOR [illegible]: [illegible]

[illegible]

OILS:

Chemically, the oils we use are fatty acids esterified with glycerol. The fatty acid chains usually contain double bonds (unsaturation) which are responsible for the bodying and drying reactions that convert the oil from a soluble liquid to an insoluble solid. We use a wide variety of types of oils.

Chinawood oil, H-7, is extracted from the nuts of a tree that grows mainly in China, but domestic plantings are now producing a small portion of oil requirements. This oil is outstanding in speed of bodying and dry, and yields hard, water resistant films that tend to discolor on exposure to light and dark. Wood oil must be properly cured to prevent frosting or crowsfooting of the film.

Creosole, H-505, is used extensively for this purpose. Chemical ASA is less effective since it evaporates from the tank too readily. For very large dip tanks, where a high degree of stability is required and where high baking temperatures are used, other inhibitors may be used. These generally have a strong effect on dry and are limited to those finishes using a high baking schedule. Those in use are G-424, Beta Naphthol; G-498, Hydroquinone; and G-500, Phenyl-Alpha-Naphthylamine.

DOPING AGENTS

This group includes a number of materials for certain specific uses. They are generally used in relatively small amounts to impart a specific property. Larger quantities will effect other properties so that substitutions or alterations should not be made without the approval of the Control Laboratory. Some of them have been mentioned in the discussion of driers and inhibitors. Of the balance, the following are of interest.

(1) Anti-settling and Anti-sag Agents - Many of our pigments even when finely ground will settle in the container. Although excessive grinding might reduce this tendency, it is more practical to incorporate anti-settling agents. The agents generally used include G-12, Soya Lecithin as VM-7790; H-226, Coconut Oil Fatty Acids; H-522, Turkey Red Oil; H-526, Rubber Solution;and VM-1592 Aluminum Stearate Jell. Except for the H-526, these materials are also used to control sagging, particularly brushing products. In this case flow is to be retarded, at times to the point where brush marks may show, in order to obtain freedom from sagging on vertical surfaces.

(2) Fungicides - In order to reduce or eliminate the growth of mildew, dry rot or barnacles certain chemicals are used specifically for this purpose. G-231, Shirlan, is very effective in mill whites to retard mildew growth such as may be encountered in areas of high moisture such as dairies, etc. It is also non-toxic, a big advantage. G-263, Dowicide, and H-454, Phenyl Mercury Oleate, are used in Wood Sealers to retard dry rot. W-416, Cuprous Oxide, is used in ship paints to retard barnacle growth. Most fungicides are toxic and formula card instructions for handling should be followed carefully.

(3) Waxes - For uses, such as office furniture, refrigerators, washing machines, etc., the finish must possess a high degree of mar or scratch resistance. The inclusion of this property not only produces a finish having better wear resistance but reduces rejects during assembly. To impart this property waxes are employed. Small percentages are used and since they have an adverse effect on dry, are generally used in baking products. Among the waxes used are G-4, Candelilla as 732-912 for 700 Line finishes and G-95, Paraffine.

(4) Bodying Agents - At times it may be necessary to introduce bodying agents to impart a "false" body or "buttery" consistency for better brushing properties. G-217, Aluminum Stearate or 348-18323, Ammonium Stearate may be used. Fatty acids such as linseed H-255 has the opposite effect. That is, it reduces viscosity. This property is utilized to reclaim dip tanks that have bodied excessively and in our resin operation to salvage jelled resins.

CHART 1

WHY WE USE SOLVENTS

1. To reduce to a workable consistency
   a) In our plant for pumping, grinding, straining
   b) For our customers - for application
2. To reduce cost.

CHART 2

TYPES OF SOLVENTS

1. Petroleum
2. Coal Tar
3. High-Solvency Petroleum Naphthas
4. Turpentine
5. Alcohols

CHART 3

PETROLEUM SOLVENTS

		Distillation Range
H-257	V. M. & P. Naphtha	100° - 167° C.
H-287	Mineral Spirits	145° - 210° C.
H-265	Kerosene	163° - 292° C.

CHART 4

ONE TON OF COAL GIVES

1400 - 1500 lbs. Coke

10,000 - 11,000 cu. ft. Coal Gas

18 30 gals. Ammonia

2.7 gals. Motor Fuel (Chiefly Benzol)

10 GALS. COAL TAR

SOLVENTS, DRIERS, INHIBITORS AND DOPING AGENTS

SOLVENTS

Solvents represent probably the largest item in our business on a gallonage basis. On the average considerably more than half of the volume of a drum of paint is solvent, the rest being pigment and binder.

All of us realize that solvents or thinners evaporate from the film and therefore contribute little to the protection or decoration of the surface being coated. We frequently lose sight of the fact that in one sense the use of solvents is an economic waste of considerable magnitude. The greater the solids or "guts" in this drum of paint, the more square feet of surface can be coated at a lower cost.

Since solvents simply evaporate from the film leaving nothing behind, why do we use them? Our present knowledge and "know how" of formulating is inadequate to make, except in a few isolated cases, finishes approaching even 100% solids. Our solid vehicles such as "DULUX", varnishes and "DUCO" when formulated to have the proper balance of dry, hardness, gloss, etc.,are entirely too heavy in body to be useable and it is necessary to "thin" them so that they can be handled (1) in production from the viewpoint of pumping, grinding and straining, and (2) by our customers from the viewpoint of application. To illustrate, these three bottles show one of our common resins, RC103, at 100%, 75%, and 50% solids. You will note that the 100% solid material is so heavy it could not be pumped or strained. You as a customer would have considerable difficulty brushing it on your floor or furniture. (Chart 1)

Another reason for using solvents, and one which may appear contradictory to what I have just said, is to reduce cost. In this case it is cost per gallon - not cost per square foot of surface being coated. Some of our trade, particularly Trade Sales, is competitive and cost per gallon is of considerable importance. This industry has not been educated to the fact that what they are buying in a gallon of paint is solids. On the other hand, in Industrial Sales, where Sales and laboratory are frequently in direct contact with the buyer, we have been able to sell our products on the basis of cost per square foot in the face of higher gallonage selling price because we gave a higher volume of solids than our competitors. It may be mentioned that one of the 1947 selling tools of Industrial Sales will be a greater use of this principle.

Since we must use solvents, and you all know there are many, many different solvents called for in our formulas, what are the reasons or why do we select one solvent for this product or another for that finish. You might also ask why do you formulators make our lives miserable by calling for not one but two, three or as many as half a dozen solvents in an enamel. Before answering that question we must know something about the characteristics of the various solvents available.

There are many classes of solvents available today. For the purposes of our discussion we will limit them to five since these represent the bulk used at Philadelphia (Chart 2). The rest are important solvents too but are used primarily in nitrocellulose, vinyl or other specialty compositions not manufactured, or if manufactured only in limited quantities, at Philadelphia. There are at least three grades of solvents in each of these groups and each group possesses certain characteristics of value to the formulator.

Petroleum Solvents

The petroleum solvents, frequently called aliphatic solvents, as the name implies, are derived from petroleum. Crude petroleum contains products ranging from the highly volatile gasolines to heavy lubricating oils. (Chart 3)

After distilling and refining, the solvents we are mainly concerned with are H-257, V.M. & P. Naphtha; H-287, Mineral Spirits; and H-265, Kerosene. These solvents vary in distillation range and rapidity of evaporation from the binder. They have a relatively low order of solvent power, mild odor and about the lowest cost of any solvent we purchase.

Coal Tar Solvents

Again, as the name implies, these solvents are derived from coal. As indicated in Chart 4, one ton of coal produces by distillation ten gallons of coal tar, 1400-1500 pounds of coke, the balance being coal gas, ammonia and a small amount of benzol motor fuel. Of these products the portion of our interest is the ten gallons of coal tar. However, only a small portion(2½ gallons) of these ten gallons is the source of the solvents we are discussing (Chart 5)

It is evident that a coal strike can seriously affect our supplies of coal tar solvents and phthalic anhydride.

As in the case of the petroleum solvents, the coal tar solvents, frequently referred to as aromatic hydrocarbons, vary in distillation range and rapidity of evaporation from the binder. The advantage they possess over the petroleum derivatives is mainly one of solvent power. That is they are better solvents for some of our less soluble binders such as the "DULUX" and 700 line resins. These two solvent reductions of RC-350 illustrate this advantage. One is reduced with Toluol, a coal tar solvent, the other V.M. & P. Naphtha, a petroleum solvent. Because of their better solvent power, the lower boiling fractions are frequently used in paint and varnish removers. In general the coal tar solvents are more expensive than petroleum solvents.

From the 2½ gallons of light oil are obtained the five solvents of interest to us(Chart 6). Benzol is not used extensively in our business because of its toxicity. Toluol, Xylol and Solvent Naphtha are used in our spraying "DULUX" lines such as

93, 84, 700, etc. because of their fast-evaporating characteristics. High Flash Solvent Naphtha has been used in brushing lines because of its slower evaporating characteristics but since it has been available only in limited quantities in the past few years, it has been replaced by other solvents.

High-Solvency Petroleum Naphthas

These solvents are petroleum derivatives specially treated to increase their solvent power. This has been an important group of thinners since they could be produced in volume from petroleum and the increased solvent power permitted them to be substituted for the scarce coal tar solvents.

These naphthas are obtained from petroleum by several methods. One is to take certain crude oils, normally richer than others in the percentage of higher solvency components and extract the high solvency portions. Another is to subject the petroleum oil to a cracking process whereby the chemical structure of the thinner is altered.

These solvents are between the petroleum solvents and the coal tar solvents in solvent power. This group also is composed of various members differing primarily in distillation range. The most common are those listed in Chart 7.

The H-51 is a fast-evaporating solvent used extensively in our "DULUX" lines where spray application is involved. It is a good solvent for "DULUX". The H-200 thinner is also a good solvent for "DULUX" but, because of its slow evaporation and high distillation range, is used primarily in brushing lines such as 88, 87, and in some products applied by dip application. The H-202 is intermediate in evaporation and distillation and is used in our intermediates to a considerable extent.

Turpentine Types

Turpentine is one of the oldest solvents we have. It was known to the ancient Egyptians and its production was encouraged by King James at the time of the colonization of Virginia.

Fundamentally turpentine comes from Sothern long leaf yellow pine. If the trees are slashed and the sap allowed to flow into cups which are later collected and the sap distilled, a product known as "Gum Spirits" is obtained. The residue left in the still is our well known gum rosin. If, however, stumps from the pine forests are collected, charged into stills and the volatile material removed by steam, "Steam Distilled Wood Turpentine" as well as Dipentine and Pine Oil are obtained. The residue is known as "Wood Rosin". (Chart 8)

The turpentine group is relatively high boiling and slow evaporating and its use is generally limited to brushing or baking products. There is no fast-evaporating section such as present in the petroleum and coal tar types. The odor is characteristic and preferred by many painters. For this reason a few products contain a small percentage of "Turps". Solvent power is good. Pine Oil, because it is very slow evaporating and a good solvent, is used in small percentages to ease brushing and in larger quantities in baking products where good flow is required such as our 751 line, Venetian Blind Finishes.

Alcohols

Of the large number of alcohols, there are four of main concern to us. They are Ethyl, Isopropyl, Butyl and Isobutyl Alcohols (Chart 9).

The alcohols are good solvents for a limited number of the natural gums and synthetic resins. Shellac, for example, dissolves readily in ethyl alcohol. Urea-formaldehyde resins such as our RC-718 require the presence of an alcohol such as butyl for stable solutions.

There are many other solvents in addition to those enumerated. Times does not permit discussion of the balance. However, those listed constitute the bulk consumed at Philadelphia.

To return to the previous question regarding the choice of solvents, it must be remembered that we are dealing with numerous varnishes, gums, oils, alkyd resins and 700 type finishes. Each must be dissolved in a solvent. In this case the solvent is referred to as an active solvent. This solvent may be considered as a carrier for the binder resin or varnish (Chart 10). Since an active solvent for one class of finishes may be a non-solvent for another type of finish, it is impossible to classify them as active or inactive(diluent). Our orthodox varnishes, for example, are soluble in the petroleum solvents. However, these petroleum hydrocarbons are poor solvents for some of our "DULUX" resins and cannot be considered active for this group. The coal tar solvents and the high-solvency petroleum naphthas are, however, good solvents for these resins. Since these solvents are more expensive than the petroleum type, the latter are frequently blended to reduce cost. In this case the petroleum solvents function as a diluent which gives us our second reason, namely, to reduce cost. Under these conditions the active solvent should be one having a slower evaporating rate than the diluent in order to keep the binder in solution during the entire drying stage. If it is faster - a kick-out or precipitation of the binder might take place giving a film low in gloss or hazy.

Because some solvents, such as the coal tar and high-solvency types, are stronger than necessary they are blended with diluents such as the petroleum thinners to reduce cost. This is one of the reasons why we have blended thinners. For example, T-3810 or T-4628 may be made from either H-51 or from a blend of H-47 and H-257. Both give equal solvency. Because of this flexibility we can change from one to the other depending on availability or cost considerations.

It is sometimes necessary, particularly with specification products, to meet certain viscosity and minimum solids requirements. Although special resin or varnish cooks can be made to return the desired results, standard materials may be employed and the specification met by proper choice of active solvents and diluents. This gives us the third reason - to obtain desired solids-viscosity relationship.

Probably the most important reason for the choice of solvents is for application properties which may be by spray, brush, dip or roller coat.

For spray application, fast thinners consistent with good flow are desired. In many cases fairly heavy films are to be applied and the thinners should flash off quickly in order to set up the film so that sagging does not result. Fast and medium evaporating solvents are used for this purpose. Generally speaking:

(a) Orthodox finishes use H-257 and H-287

(b) "DULUX" finishes use H-51, H-202, H-47, H-15, H-257 & H-287

(c) 700 Line finishes use H-18, H-202, H-51, H-257, H-287 & H-278

Dry and sag resistance are not the only reasons for using these thinners. Solvent popping and poor adhesion can be obtained if a fast-drying finish such as 93 line or 700 line is accidentally contaminated with a very slow thinner. In this case, the film sets up or becomes rigid before all of the slow thinner has evaporated. In the case of baking finishes, this solvent will break thru the set-up film causing popping or in the case of air-dry finishes will remain between the metal and the film causing poor adhesion. Solvent popping may also be obtained in 700 line finishes if a poor balance of active and inactive solvents is used. The use of a fast-evaporating petroleum solvent substituted for a similar coal tar solvent, for example, will frequently result in this condition.

For brush application combinations of medium and slow-evaporating solvents are used. In this case solvent evaporation is retarded in order to keep the film fluid long enough to brush and lap in areas and to allow sufficient time for after flow to eliminate brush marks. The solubility and fluidity characteristics of the binder also have a bearing and the slowest thinner is not always required. For example, shellac has good brushing properties when cut in a relatively fast thinner such as ethyl alcohol. Mineral spirits is generally sufficient for orthodox products whereas "DULUX" finishes, because they set up faster and become insoluble quicker, require slower thinner such as H-200. Generally speaking:

(a) Orthodox products use H-287

(b) "DULUX" products use H-200, H-287, H-202 and in some cases Pine Oil.

Dip application is more complicated in that many sizes, shapes and conditions may be encountered. For small objects in small tanks some of our standard spray or brush products are satisfactory. However, most applications require special formulations. The first consideration is that the solvent be strong enough so that in combination with inhibitors, the finish will be stable under the severe conditions of agitation and aeration encountered. The second is that the solvent combination be balanced so that a reasonably uniform film is obtained on objects as long as 10-12 feet. If fast thinners are used, the film thickness at the top of the flow will be satisfactory but considerable build-up resulting in a soft, uneven film will be present on the lower portion. In addition solvent loss from the tank will be excessive, requiring frequent additions of thinner to maintain viscosity.

If the thinners are too slow, the film remains fluid too long giving low film thickness and poor hiding and build at the top of the object. It will also drain for an excessively long time dripping paint in the first stages of the baking oven.

The proper balance is a combination of fast, medium and slow thinners so that a satisfactory film from the viewpoint of hiding and appearance is obtained at the top of the object and no excessive build-up at the bottom.

Roller coat application consists of transferring the finish from a roller to a flat sheet. It is used extensively for the application of finishes to signs, containers, venetian blinds and metal or composition building sheets. It is an economical method since there is very little waste and film thickness can be controlled by machine settings. The main requirement from the viewpoint of solvent selection is good flow. This is particularly true in the container field such as tin cans where film thickness of as low as several tenths of a mil are applied. Solvents such as H-200, Pine Oil, and higher alcohols such as octyl are used.

DRIERS

Oils, varnishes and synthetic resins containing drying or semi-drying oils will dry to a tack-free and hard stage simply by the absorption of oxygen from the air or by polymerization. However, this process is too slow for normal purposes and some other means must be used to hasten the process. Drying at elevated temperatures is frequently used where this is feasible. In other cases the use of metallic compounds and oxygen-bearing materials is employed.

Compounds of lead, manganese or cobalt have been found to be most effective as accelerators for drying. It is felt that these materials hasten the oxygen adsorption producing the same effect as is obtained by longer drying periods with the drier-free varnish or resin. In some cases non-metallic materials such as oxygen-containing solvents are used. Tetralin or Cellosolve Acetate blown with air or aged turpentine, increases in oxygen content and when used as a thinner speeds drying because of its readily available supply of oxygen. G-434, Diphenyl Guanidine, has a specific drying action on "DULUX" resins having a high acid number such as RC-103 and therefore may be considered as a drier. However, it impairs adhesion and should not be used except where specified.

These metallic compounds may be introduced in vehicles in several ways. Years ago litharge, manganese borate, or umber were incorporated by grinding with the pigment. Litharge is still used on occasions. Some compounds, such as cobalt or lead acetate, litharge and lime, may be cooked with the varnish at the time of manufacture. However, the most satisfactory and the most universally used method involves solutions of compounds of these metals.

The three most important metals - lead, manganese and cobalt -can be combined with numerous products to form resinates, linoleates, linoresinates or naphthenates. Of these compounds, the naphthenates are most frequently used because they are more soluble, more stable, and have a higher concentration of metal.

Although these three metallic compounds hasten the dry and hardness, each metal has to a considerable extent a specific action. Considerable research work has been undertaken to determine the mechanism of their effect on drying. It is generally assumed that cobalt functions as a top drier, with manganese somewhat poorer. That is, they are most effective as a means for hastening the tack-free stage. Lead functions as a through drier to develop ultimate hardness. For this reason our air-dry products generally contain cobalt and lead or manganese or all three.

Since cobalt is a top drier, it is frequently the cause for wrinkling if excessive amounts are used. Temperature also plays a part in drying so that a combination of elevated temperature and high cobalt content may result in wrinkling. High cobalt also induces skin drying, delaying ultimate hardness and at times showing up as poor adhesion due to entrapped solvent. Lead and manganese are frequently used in baking finishes since they are less prone to cause wrinkling, and small quantities give a pronounced boost in baking potential.

All three driers impart a certain amount of discoloration particularly to whites. For this reason it is more difficult to "dope" whites for drying than colors. Baking also causes the driers to discolor. Of the three metals, lead has the least effect on color.

It should be mentioned that other metallic compounds are sometimes used. Iron compounds, for example, are used in some specialized fields as wire enamels and can coatings, either for the golden color they impart or to secure maximum adhesion.

INHIBITORS

If we consider driers as accelerators or positive catalysts for drying compositions, inhibitors may be called anti-oxidants or negative catalysts. Obviously we do not use them to deliberately slow the drying, except insofar as this is necessary to achieve the desired results. The three main reasons for using inhibitors are (1) as anti-skinning agents, (2) as anti-wrinkling agents, and (3) as stabilizers.

Of the agents used to retard skinning, H-505 Creosole, and its solutions VH-7551(1%) and VH-7552(10%); Thymol as VH-1833; and Chemical ASA, H-580, are most generally used. Creosole is very effective and has a pronounced effect on dry if used in excessive amounts. It also has a pronounced odor which is considered by many to be objectionable, particularly if the finish is applied in confined areas. When using Creosole a careful balance between it and driers must be maintained. Since it is volatile, larger quantities may be used in baking products. Thymol is less effective than Creosole but is more desirable for certain uses because of its better odor characteristics. Chemical ASA, a relatively new inhibitor, is being used also because of its better odor and because it has less effect on drying.

Since inhibitors have an effect on oxidation, they are also used as anti-wrinkling agents. Although Creosole, Thymol and Chemical ASA are effective to a limited degree, other materials are generally used because of their increased effectiveness. VC-1000, a short oil phenolic varnish, is used in air dry "DULUX". For baking "DULUX" products RK-1701, a solution of urea-formaldehyde or melamine resin, is very effective, particularly in the presence of considerable amounts of drier. Although RK 1701 is an anti-wrinkling agent, it has little adverse effect on the air drying of resins. In fact in baking products it also acts as a drier in that the rate of dry and hardening is accelerated. Among inhibitors RK-1701 is unique in this respect.

This property of inhibitors to retard oxidation is utilized to control the stability of intermediates such as mill bases and particularly finished products subject to aeration. Finishes applied by dip or flowcoat are constantly agitated either to keep pigment in suspension or by the repeated immersion and withdrawal of the objects being finished. This introduces air which tends to oxidize the paint. "DULUX" or varnish enamels, without inhibitors, would soon under this treatment body to the point where excessive thinning would reduce solids and ultimately jell. By the use of inhibitors this bodying can be reduced so that under normal operating conditions no trouble is encountered.

Oiticia oil H-553, is obtained from the nuts of a tree that grows in Brazil. It resembles Chinawood oil except that oiticia becomes more brittle on aging and can cause more difficulty in processing into vehicles. Linseed oil, H-253, is extracted from flax seed and most of our requirements are produced in this country, although appreciable amounts have been imported from Argentine. Linseed oil dries fairly well and retains flexibility well, but is not outstanding in color retention characteristics. Soya oil, H-59, is obtained from soy beans, which are grown extensively in this country. A major use for this oil is in edible products such as vegetable shortening and margarine, but we use large quantities in finishes. Soya oil is slower drying than linseed but has better color retention characteristics.

Castor oil, H-22, is a non-dryint oil obtained from castor beans which grow wild in Brazil. It has not been grown extensively in this country because the press cake, left after extraction of the oil, is toxic and cannot be used for cattle feed or fertilizer. Castor oil is used without modification or as an ingredient of alkyd resins for plasticizing the brittle resins such as nitrocellulose or the nitrogen resins. Dehydration of castor oil, under conditions of high temperature in the presence of acid, produces a drying oil which we use as H-156. Its bodying and drying characteristics are somewhat like linseed or soya oil, but it has better color characteristics than soya. Fish oil, has found little use in our products, so far. The odor is removed by careful refinement and the oil has flow and drying characteristics that make it interesting, but the supply is not dependable and the price fluctuates extensively.

Other non-drying or semi-drying oils such as cotton seed, corn, and coconut find specialized uses in our business.

Tall oil is a by-product of the paper industry and consists of acidic resinous materials similar to rosin oil acids.

Many of the oils may be treated before use in finishes. The raw oils may be refined by treatment with acid or alkali, or by solvent extraction, and they may be heat bodied or blown with air, or both, to provide materials suitable for specific uses.

VARNISH GUMS AND SYNTHETIC RESINS:

With the exception of rosin, the natural gums are imported and vary considerably in quality. In general, these natural gums are of fossil character. They are used only in limited places today such as rubbing varnishes and in gum cuts where solvent release is important. Shellac is derived from the secretion of the lac insect prevalent in India. It finds considerable use in finishing floors and as an undercoater for sealing surfaces that would otherwise bleed.

Rosin is derived from pine trees either by tapping the trees to yield the gum or by steam distillation of the wood.

Rosin is modified by esterifying with glycerol, or by reacting with lime, phenolic materials or maleic anhydride to improve the softening point or melting point, reduce reactivity, and improve color characteristics and durability.

The condensation of phenol, or a phenol derivative, with formaldehyde gives resins that speed the bodying rate of varnish oils, improve the durability characteristics and give increased resistance to moisture and alkalis. In spite of poor resistance to yellowing, they find rather extensive use where their resistance properties are a real advantage.

The heat-polymerizing type of resins opened up new fields of finishing and gave us performance that we had not been able to obtain in any other way. Urea-formaldehyde resins are the most economical of this type and heat-polymerize readily to give hard, brittle, water white films. These resins are modified with plasticizing materials, usually alkyd resins, to give films of required flexibility levels that are outstanding for speed of cure, chemical resistance, and resistance to yellowing. The next development in this field was the melamine formaldehyde resins, which, in spite of their higher cost, find considerable use where their speed of cure and resistance properties fit specific means.

As previously mentioned, the introduction of nitrocellulose provided a new working tool to give finishes that dried solely by solvent evaporation and greatly speeded drying schedules. Nitrocellulose, like the urea-resins, gives a film that is too brittle for most uses and must be plasticized. Of course, a very wide variety of plasticizing agents have been and are being used for this purpose. Later, there came into the picture the vinly resins which dry essentially by solvent evaporation, but will heat cure power to finishes are generally referred to as prime pigments. These may be further classified by color. One of the early white pigments was the basic carbonate of lead; later developemmts' included Lithopone (zinc sulfide/barium sulfate combination) and, currently, titanium dioxide. These developments each represented an improvement in hiding power and color characteristics.

Many of the pigments we use carry special surface treatments that affect their chalking resistance, color retention, dispersion characteristics or durability, as needed for the specific products. Titanium dioxide extended with calcium sulfate is used to give special application and film characteristics and to reduce costs in some Trade Sales items. Certain other chemical compounds are used as white pigments because of their chemical or physical action within a finish, in addition to any hiding power they may have. These include zinc oxide, white lead and antimony oxide. The zinc oxides and the white leads act as acid acceptors for reaction products formed in the degradation of films and as mildew inhivitors due to their toxicity towards certain organisms. Antimony oxide tends to retard the chalking of titanium dioxide pigments and is used for this purpose.

COLORED PIGMENTS:

Some pigments may be colored but are used primarily for other purposes, such as Red Lead, W-307, and Zinc Chromate, W-609, in metal protective primers. However, the greatest use of colored pigments is to impart color to the finish as desired by the customer.

The red pigments may be based on iron oxide, cadmium sulfide/cadmium selenide, or on organic dyestuffs. In general, the iron oxides are the cheapest and poorest in color but give good durability, while the cadmium pigments are highest in cost (per unit hiding) and fair in durability. The organic pigments are outstanding for color characteristics but are generally rather poor in durability and color retention characteristics. Also, many of these pigments are soluble to some extent in the paint thinners and will bleed into succeeding coats of paint applied over them. This later characteristic limits their use in many cases.

The yellow and orange pigments are also of three general types: the iron oxides, either mined or manufactured from iron salts, inorganic chemicals (with a lead chromate base) and the organic dyestuff type such as Hansa Yellow, W-614. Again, the organic type is subject to bleeding and is limited in its use.

We use three types of blue pigments, the iron blues made from potassium ferrocyanide, Ultramarine Blue (W-514), a calcined mixture of various minerals, and the Monastral or phthalocyanine types. The iron blue pigments are used in making chrome green blends and in medium and dark blue tints but are rather poor in color retention characteristics in the light blue colors. Ultramarine blue is used primarily for tinting whites and is not satisfactory as a solid color. The Monastral Blues are expensive, but have good color and a reasonable durability level.

The violet pigments we use are Mineral Violet, W-501, and Purple Toner, W-518. The Mineral Violet is used solely for its red toning properties in tinting whites, and the Purple Toner is now prohibited by government order to conserve platinum.

Most of our green enamels are formulated with chromate type yellow and iron blue, but these combinations are not fully satisfactory in color retention characteristics. Stable green pigments can be made from chromium oxide; they give good green finishes but they are rather expensive. Monastral Green W-785 is expensive on a pound basis but economical on a tinting strength basis. This makes good clean colors that are light fast.

The brown pigments we use are of the iron oxide type obtained either from mineral deposits or made synthetically from iron oxide.

We use a wide variety of black pigments including those from all three sources, animal, vegetable and mineral. The mineral blacks include our old friend iron oxide (W-215), as well as those derived from graphite and from coal. The animal type of black pigment is W-284 Bone Black, made by calcining the bones of cattle and sheep. This pigment gives finishes that are relatively free from floating or flooding and have good durability. The carbon blackd are of the vegetable origin; being produced by burning natural gas or coal under conditions that give incomplete combustion and soot or carbon black in the flame. The carbon blacks cover a wide range of particle size, surface treatment, and performance in finishes. Most of the black pigments that we use now are supplied in a beaded form to facilitate their handling in the plant.

A few of the pigments for finishes are metal powders. Zinc dust, W-36, is used in the primer for galvanized metal to give satisfactory adhesion to this substrate. Aluminum powders, usually supplied to us in the paste form, are used as a sole pigment in the aluminum paints, but also are used to give the metallic sparkle to the poly-chromatic type of finishes such as those used on automobiles.

SOLVENTS:

The liquid raw materials we use as solvents to thinners can be generally classified into three types, the resinous, oxygenated, and the hydrocarbons. The resinous solvents are derived from pine trees and include, as well as the lesser known Dipentene, H-152, and Pine Oil, H-502. Relatively small amounts of these materials are used, generally for the peculiar wetting characteristics they may have, their odor characteristics, or as a denaturant where necessary to comply with some state regulations.

The oxygenated solvents, a term used to include alcohols, esters, ketones, and ethers, are used primarily in lacquer type finishes. We use most of the alcohols that are liquid at room temperature, starting with ethyl alcohol and progressing on up the series to octyl alcohol. As would be expected, progression through the increasing number of carbon atoms in the chain reduces evaproation rate and slightly reduces solvent strength. Selection of the proper alcohol is based largely upon the evaporation rate desired to give the proper flow characteristics in the finished product. Likewise, the esters are used in lacquer type products where their high solvency and rapid evaporation characteristics, together with excellent solvent strength, are real assets. The ketone solvents are relatively new in large volume supply, but have provided satisfactory application characteristics of finishes at appreciable cost savings from the level obtained with the alcohols and esters. In general, all of the oxygenated solvents are higher in price than the resinous and hydrocarbon types.

The hydrocarbon solvents consist of three types, the straight aliphatic, the straight aromatic (or ring type compounds) and the hybrid high-solvency petroleum naphthas which are in between the other two. In the aliphatic group, we have H-28, H-29, H-257, H-287, H-265 in a series decreasing in evaporation rate and, slightly, in solvent strength. In general, the aliphatic solvents are lower in solvent strength than any other type of solvent we use. The aromatic hydrocarbons are derived from coal tar or from petroleum and comprise Toluol H-49, Xylol H-583, and the higher boiling aromatic naphthas, H-596 and H-601. The greater solvent strength in these materials (as compared with the aliphatic solvents) is required for the newer type resins to hold them into solution. In addition to cutting faster than the aliphatics, the aromatics are higher in price per pound than the alophatics; this combination will noticeably increase the cost of the finishes.

In the hybrid group of high solvency naphthas, we have a similar range of increasing evaporation rate from H-51 through H-202 to H-200. As would be expected, these are intermediate between the aliphatics and aromatics and are generally used as diluents for lacquer solvents or as solvents for the alkyd resins. Another solvent that has come into fairly widespread use recently is H-506. I don't know yet how many of you may have been sent to the storeroom or various other places for a supply of this solvent, but, sooner or later, you are bound to learn that this is city water. The emulsion paints, as well as the old cassin-liphopone types, are reduced for application with water. The casein-lithopone type is a combination dispersion and solution, but the emulsion types are emulsions of organic coating materials, in a colloidal state in water.

MISCELLANEOUS MATERIALS:

We use a number of miscellaneous raw materials in the manufacture of finishes. The organic salts of polyvalent metals act as driers in oxidizing finishes. The naphthenates of cobalt, lead, and maganese have been used for many years and recent developments have centered around replacing the naphthenic radical for reasons of cost and supply. In varnish making, occasionally we cook in certain chemicals such as litharge, maganese oxahydrate, or calcium hydrate to form driers in the varnish itself.

Since air-drying finishes tend to surface dry, or skin, in partially filled containers, it is necessary to use inhibitors. Inhibitors are also used to stabilize dip tank material against oxidation, caused by aeration, in the dip tank. Phenol derivatives such as creosol, thymol, hydroquinone are frequently used. Recently, some newer materials have appeared on the market and weeuse the chemical ASA, H-580 (n-butyraldoxime).

Weeuse a number of surface active compounds for their effect on inhibiting settling of the pigments inaa paint and as controls for the flow properties to prevent sagging. These include soya-lecithin (obtained from the refining of soya oil) sulfonated castor oil, coconut oil fatty acids, and a number of the newer chemicals which have been generally termed surface-active agents, Also to be considered in this group are the bodying agents such as Bentone, W-1003, and China Clay, W-1, used to increase the body of finishes at a given soldis content.

Certain chemical compounds are toxic towards undesirable organisms such as marine growths on ships, mildews and bacteria. In this category are cuprous oxide, Shirlan Extra, Dowicide G and Phenyl-Mercury Oleate.

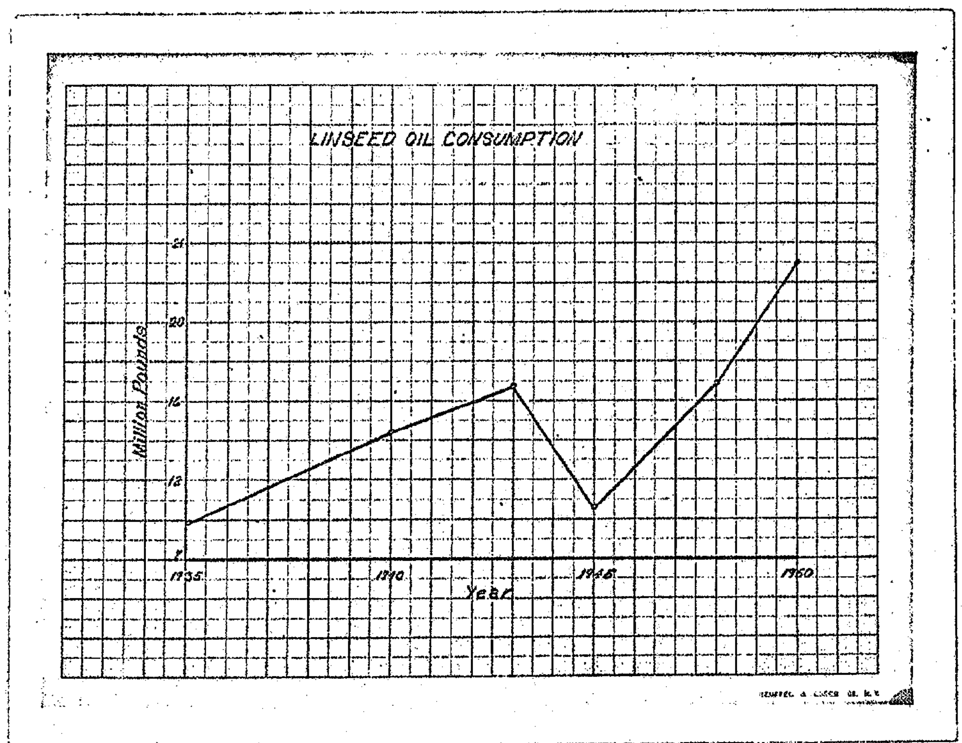
In addition to the chemical discussed above, we use a wide variety of specialty items as catalyst in the resin cooking operation, as mar resistant or abrasion resistant agents, and as corrosion inhibitors or abraiding materials in the Chemical Specialty Lines.

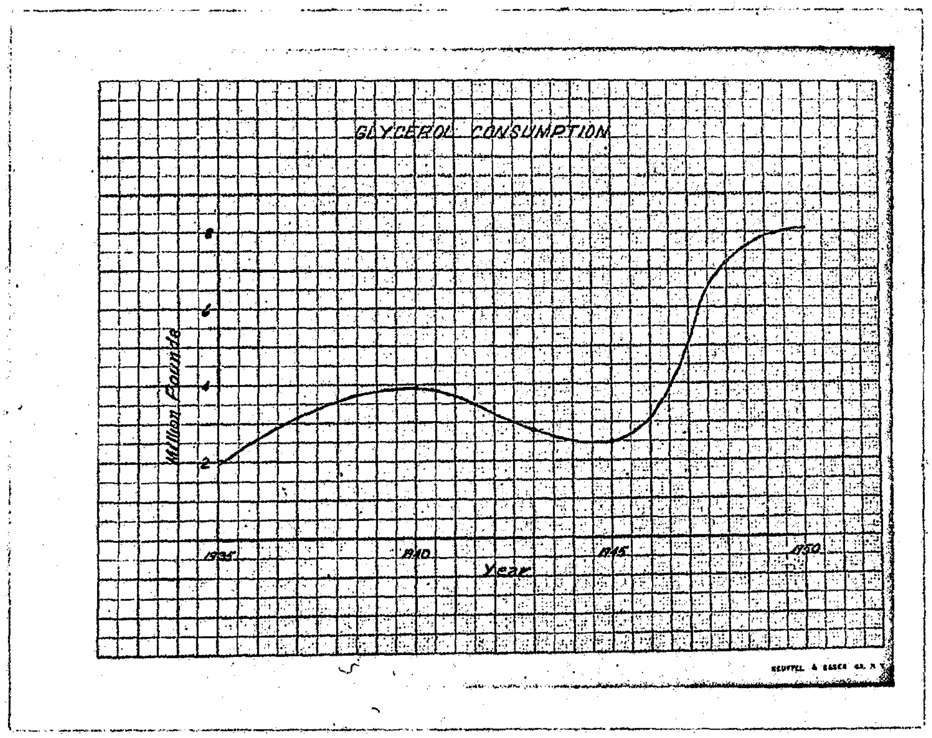
ECONOMICS:

We circulate to each chemist in the laboratory at periodic intervals a tabulation of the cost per pound of our important raw materials. The purpose of this bulletin is to facilitate the formulation of finishes atmminimum cost to put us in a better competitive position in the finishes business. There are several factors that need to be applied to these costs as they are submitted to you, since the price per pound is frequently not the controlling factor in the cost of the use of a material. Obviously, a material that costs $2.00 per pound and that requires 10 pounds to fill one gallon (thereby costing $20.00 per gallon) would be cheaper than a material costing $1.50 per pound and requiring 20 pounds to fill a gallon (thereby costing $30.00 per gallon). I realize that this example may be a bit exaggerated but we frequently encounter circumstances that are even more surprising than this. Actually, the whole subject of formulation to minimum cost could be the subject of many seminars and I cannot hope to do it justice here. However, I do want to point out two additional factors that should be considered, including the affect on final body-solids relationships of finished products by changes in oil absorption characteristics of the pigments, and the cost differentials of purchasing in large versus small quantities. A decrease in oil absorption of the pigment may increase the solids of the finished product sufficiently to cancel out a fairly appreciable cost differential in the raw materials involved. Also, the price of raw materials can vary considerably with the amount purchased, and the taking of material in small quantity adds appreciably to the cost per pound.

MARKET CONDITIONS:

Believe it or not, the paint business is big business. The quantities of raw materials that we consume in our division each month reaches a staggering total. Each of you have had an experience in college of going to the storeroom and withdrawing a gew c. c. or even a few hundred c.c. of a chemical for an experiment. Take for an example, Toluol, where you would draw the required amount from the storeroom and run your experiment, giving no further consideration to the source of the material. We buy Toluol in tank-car quantities at a really remarkable purity level, and there are certainly many more problems in furnishing material in quantities such as this than there are in manufacturing a few c.c.





A sudden cessation of use of a raw material that we have been buying in large quantities can leave the plants with tremendous stocks on hand for which they have no use. Conversely, greatly expanded demands for any of our raw materials can put us in a position where these are not obtainable. After all, the old laws of supply and demand are still in effect and any sudden move, either in large volume by one consumer or in smaller volume by a number of consumers, puts quite a strain on the supply of that material. When a raw material suddenly becomes unavailable, all the paint manufacturers begin a frantic search for substitutes or replace ments and most of them tend to move in the same direction. Consequently, it is easy to evaluate and approve a raw materia as a substituteaand then find that all available supplies have already been absorbed from the market.

We wish to stress the importance of careful consideration of raw material supply problems that may be involved in any new development in your field. Before you chase too far down a road that may turn into a blind alley, please have the price and availability information developed for you. Of course, it will be necessary to have a reasonable idea of the volume of raw material involved. Mr. Reinecker has contacts with the Works Supply and Purchasing Departments in Wilmington that will expedite this for you.

<u>DISCUSSION:</u>

<u>Question</u>

How should we get the availability of a raw material?

<u>Answer</u>

Determining the availability of new raw materials should be initiated by written request to Works Supply. Standard raw materials frequently may be checked by phone and the information received promptly. On a new raw material where market information has to be developed and new plant installation explored, the request certainly should be in writing.

Question

In cases where we try out a new material perhaps being pushed by a particular consumer, what is the policy on how much information we can divulge to the particular salesman who comes into the lab?

Answer

We do not tell him what specific use we make of a material. We usually advise him of the general type of production involved, so he may be able to offer valuable suggestions. We also report shortcomings and plus values revealed in our evaluations in order that their technical department can be of further help to us. We are not permitted to divulge our consumption figures.

PHILADELPHIA PLANT LABORATORY

I. L. MC GINNIS

RAW MATERIALS FOR MAKING OUR PRODUCTS

According to the program plans, this is to be a general survey of the things we use to make our products. Selected experts are to discuss each class of materials at later sessions of this series and they will have time to cover each item in more detail.

If I were to limit this review to those materials that are readily available at the present time, there would be little to discuss. We thought we had shortages and substitutions during the war, but the peace has not been settled yet and the supply of many materials is worse than ever. For instance, linseed and castor oils are short, titanium oxide and organic red pigments are limited in supply, glycerol and phthalic anhydride to make "DULUX" resins are both tight and so it goes. Furthermore, we need increased supplies of these materials all at one time, because an overabundance of one item would simply make the need for another one to go with it even more critical.

Now let's take a look at the great variety of materials we use in making our products According to the plan suggested by the committee on arrangements, this is to survey briefly the different types of materials, some of their outstanding properties and uses, and a few pointers regarding economics. When you count up the total number of materials or permanent codes that we use here at Philadelphia and arrive at a number in the neighborhood of 280, you can realize what a problem we have had in boiling the data down to keep within the time limitation.

A. PIGMENTS - W CODES

First we will look at our pigments, which are designated by W codes. We will consider white pigments and extenders, then colored pigments and blacks, in that order. We will leave the details to Stuart Grayes and Pete Evans, who will discuss these materials more fully later on.

1. High Opacity White Pigments

Perhaps the most important characteristic of white pigments is hiding power, which they derive from a high index of refraction, viz. the ratio of the velocity or speed of light in air to that in the medium through which the light passes. The original white pigment, white lead, was replaced by lithopone and then titanium oxide superseded lithopone in view of increased hiding power. More recently, a further increase in hiding power of white pigments was developed in the rutile type titanium oxide.

In the high opacity group of white pigments, we have the new rutile type titanium oxides at the top of the list. The denser structure of the rutile type provides a higher index of refraction and, hence, greater hiding power. These pigments carry special surface treatments, in some cases, which affect their chalking resistance, color retention, dispersion characteristics, etc., for use in different types of products. Hence, they are not readily interchangeable.

A variety of anatase type titanium oxides were used previously. We still use, W-16 and W-5, the untreated grades in outside house paints, tank whites, etc , to provide better cleanliness because they chalk more freely than the other pigments of this class.

For some uses, the great hiding power of the titanium oxide pigment permits the use of extender to give them special application or film characteristics and reduce cost The "Ti-Cal" types are extended with 70% of a specially prepared calcium sulphate, which provides high bulking value, good color, and relatively low cost. The "R" type Ti-Cals W-49, W-51 and W-54 are based on the rutile type titanium oxide. You will note that they vary in consistency characteristics and the R-60 type, W-51, is treated to provide a measure of durability on exterior exposure which explains its use in Brush "DUCO" Enamels, since these products are used for both interior and exterior surfaces.

Since barium sulphate is less soluble in water, the analogous "Ti-Bar" type pigment, W-57, is used in exterior products and in primers due to its inherent moisture resistance. However, we carry a special restriction on water soluble salt content and a quantitative sodium specification on W-57 to be sure that it will not blister under extreme humidity conditions in refrigerator primers. Recent attempts to blend titanium oxide and blanc fixe in the mill base to match "Ti-Bar" met with initial failure because the W-30, blanc fixe, ran too high in water soluble salt content, showing the importance of this specification.

Next in order come the zinc sulfide pigments and lithopones, the latter being extended with barium sulphate. The zinc sulfide pigments as a class are less durable and more reactive than titanium oxide types We are using them currently to extend our supplies of the titanium pigments. The different types vary in surface treatment and consistency characteristics. W-33 is the enamel grade of lithopone with normal consistency. W-13 carries the "J" treatment for ease of dispersion and is high in consistency. The same grade untreated is W-113. At the present time we are trying to eliminate the "J" treatment to increase production capacity for white pigment at the Pigments Department. The HC grade, W-40, with high consistency has been used in flat wall paints because of its high flat hiding.

2. Reactive White Pigments

Some white pigments are used because of their chemical or physical action within a finish rather than their hiding power. In this class we have zinc oxides, white leads, and antimony oxide. Except for the last-mentioned, the value of these pigments depends upon their acid acceptance or soap-forming characteristics.

Zinc oxides are widely used: (a) as acid acceptors by forming reaction products in the film, (b) as mildew inhibitors due to their toxicity to certain organisms, (c) as chalking retarders due to their high ultra-violet opacity, and (d) as yellowing retarders for titanium oxide pigmented finishes.

There are generally two classes, viz., the French Process, W-20, made directly from metallic zinc and the American Process, W-8, W-19, and W-41, made from zinc-containing ores which vary in lead content and may yield leaded zinc oxides, W-18, as well as the fairly pure grades of zinc oxide. Their properties seem to depend on particle size to a great extent which governs their reactivity. The "Kadox" types, W-78 and W-154, are used for rubber compounding as well as finishes. They are so fine that they have low hiding power. Small proportions are used with titanium oxide to reduce yellowing tendencies with a maximum of gloss retention which is generally adversely affected by zinc oxides. The leaded zinc oxides are used in outside paints. The cofumed types are preferred because they carry less fines than the blended varieties and are, therefore, more durable

We have found electron microscope photographs to serve as an excellent guide in selecting zinc oxides and we may want to set up such a specification sometime when the instruments are generally available.

Only two white lead pigments are of interest for paint products, i.e., basic carbonate white lead and basic sulphate white lead. Basic carbonate white lead, W-2 and W-68, is used in exterior paint primarily for sales policy reasons and as an acid acceptor in some primers and undercoats. Because these lead pigments are toxic we follow the policy of having them supplied in paste form. Due precaution should still be exercised to prevent contamination of food products by exercising extreme cleanliness.

Antimony Oxide, W-52, was used with titanium pigments to retard chalking, but the special treatments on some of the newer types of titanium have generally resulted in replacement of this pigment. It is used in dark shades because it is more chalk resistant than any of the titanium oxides, but it causes checking in lighter shades where a greater quantity is needed. this pigment is also a stabilizer for vinyl resins, which tend to decompose in contact with iron surfaces under the influence of heat and/or light so that special stabilizing agents are required for high bake finishes and for exterior exposure.

3. Extenders and Their Uses

Extender or inert pigments do not possess the properties of hiding or pleasing color, but they greatly influence the physical, chemical and optical properties of the paint in which they are used. Thus the terms "extender" and "inert" are both misnomers, since these pigments do not merely adulterate or cheapen paints nor are they unreactive. These pigments lack hiding and opacity due to their refractive index being about the same as the dried vehicles or binders containing them and lower than the high opacity type white pigments.

Extenders as a class occur abundantly in nature and are generally mined or quarried at relatively low prices. The deposits are natural rock, rock decomposed by weathering, and fossil deposits of certain organisms. Some extenders are manufactured as by-products from some process or as deliberate attempts to improve upon the natural product.

In general, solvents are the only other paint making materials that are cheaper than extender pigments. They range in price from 1/2 to 8 cents per pound. The importance of these pigments can be gathered from the fact that about 35% of the total pigments handled by the Division in 1941 were extenders. High quality house paints carry 35 to 75% of extender in the pigmentation. In lower quality types, e.g., the Chivo Line, the extender content may go up to 75% of the pigment. Primers and surfacers use as much as 85% extender pigments.

Extender pigments vary in specific area according to type, shape and structure of the particles as follows:

1. High specific area due to dimorphous nature and porous structure, e.g., Diatomaceous Earth, W-44, and Chalk Whiting, W-90.

2. High specific area due to irregular surfaces, composed of clusters of needle-shaped particles or having many indentations, e.g. Precipitated Calcium Carbonate, W-73.

3. High specific area from fibrous, elongated or plate-like particles, e.g., Asbestine, W-4, Talc, W-132, and Mica, W-71.

4. Relatively low specific area due to solid particles with regular shape and few indentations and little porosity, e.g., Blanc Fixe, W-30, Barytes, W-34, and Silica, W-31 and W-62.

Whereas the white pigments are used to furnish hiding, a pleasing appearance, and to protect the final film from too rapid deterioration due to light rays, etc., the extender pigments by contrast are used primarily for the following purposes:

1. To strengthen and toughen the films to prevent cracking and flaking.

2. To provide abrasion resistance.

3. To reduce film shrinkage and thereby promote adherence to the substrate.

4. To increase consistency so thicker films can be applied without sags or runs.

5. To lower gloss in semi-gloss or dull finishes with velvety appearance.

6. To improve moisture resistance and mildew resistance.

7. To reduce settling of other pigments in the package.

8. To impart good sanding properties to undercoats and rubbing varnishes.

9. To improve hiding at higher pigment volumes and in emulsion paints.

10. To lower cost.

4. Colored Pigments

Now let us review briefly some of the colored pigments that we use in our business of making finishes. You are all familiar with the fact that white light may be broken up into all colors of the rainbow. So color results when light waves strike an object and some of the rays are absorbed and others reflected. The color varies according to the wave length of the reflected light in decreasing order as follows where a milli-micron is the unit of measure for wave length amounting to about 39 billionths of an inch.

Red	-	610-700	milli-microns
Orange	-	590-610	"
Yellow	-	570-590	"
Green	-	500-570	"
Blue	-	460-500	"
Violet	-	400-460	"

With the addition of brown and black pigments this will form the outline for our consideration of the colors we use.

Some pigments may be colored but are used primarily for other purposes, e.g., Red Lead, W-307 and W-316, and Zinc Chromate, W-609, are used for metal protective primers. These are generally quite reactive, like zinc oxides, and care in handling and use must accordingly be exercised. For purposes of this discussion, we will restrict ourselves pretty much to those pigments used chiefly for their color characteristics.

(a) Red Pigments

Iron oxides are amongst the oldest known colors. They occur naturally as ore deposits in admixture with limestone and siliceous matter or are precipitated by chemical means and possibly blended to yield special types. The most brilliant iron oxide we normally use is W-372, Persian Gulf. It contains 65-70% iron oxide and requires no calcination. Spanish Oxide, W-369, contains 80 to 85% iron oxide but is contaminated with lime making it reactive. The domestic oxides, W-371 and W-878, vary considerably in iron oxide content, viz., 35% to 80%, and in tone and tinting strength. The synthetic oxides are made (a) by heating copperas $FeSO_4 \cdot 7H_2O$, for Indian Reds like W-303, or (b) reacting copperas with lime or whiting in a furnace to make Venetian Reds like W-306, or (c) by precipitation from copperas with an alkali followed by controlled oxidation for relatively pure iron oxides like Mapico Red, W-895. These generally vary in masstone and tinting strength and cost according to iron oxide content which ranges from 40% to 98%.

The next class of red pigments are the organic reds and maroons, a highly specialized group of dyestuffs. They are complicated organic compounds used alone or precipitated on some base to form a so-called "lake". Essentially, they comprise azo pigments and azo salts plus a miscellaneous group of vat dyes and alizarine dyestuffs.

The azo pigments are represented by W-865, Toluidine Red, and W-880, Fire Toner, which are bright colors with good lightfastness in masstone, but fade in tints. Otherwise, they have good durability and vary in bleeding tendencies from slight to bad. In this class also may be put the Para Toners, W-317, W-864, and W-874, which are soluble azo dyes made at relatively low cost but are poor in durability and fugitive in the light due to the presence of reactive groupings.

Some azo pigments are precipitated as metallic salts which generally vary in characteristics according to the metal iron used as follows:

<u>Barium & Calcium Salts</u> - Brightest, but poor in stability and durability. Typical pigments are W-331 and W-339, the lithol toners, which do not bleed in most vehicles but darken on exposure, fade in tints and are otherwise poor in durability.

<u>Aluminum & Iron Salts</u> - Dark and dull in color. Intermediate in stability and durability. A typical pigment in this class is W-873, Infrex Maroon, which is dark, non-bleeding, darkens in masstone and fades in tints with fair durability, being better than lithols but inferior to the next class.

<u>Manganese Salts</u> - Intermediate in color characteristics and best in stability and durability. Hence, these are most suitable for high-grade products. A typical pigment is W-875, Victoria Maroon, which is non-bleeding, rather difficult to grind, has good durability but tends to darken in masstone and fade in tints.

The vat dyes are represented by our W-889 and W-311, Indo Maroons, which are thioindigoid types with bright masstone color and relatively good durability although they fade slightly in tints and darken and bronze in masstone. These pigments are reactive and their high cost limits their usefulness to special products. Among the alizarine types, we use W-308, Madder Lake, used for Tuscan Reds and to blend with mineral oxides, and W-380, Maroon Lake, used for toning dark maroons and for tinting whites. These pigments are "laked" to reduce the cost. They both have bright color but are relatively poor in light stability and in film integrity on exposure.

The third class of red pigments are the cadmium sulfo-seleindes, which are inorganic precipitates used alone or extended with barium sulfate to make so-called lithopone grades. They vary in color from light red to dark maroon. They are non-bleeding and have fair durability although they tend to chalk, check and fade in tints. They are quite expensive and hence limited in use. Our codes from the lightest to the darkest are W-383, Light, W-384, Medium Light, W-382, Medium, W-381, Deep, and W-843, Maroon. These find special use in washing machine finishes because they are alkali resistant and in products where bleeding is prohibited.

(b) Yellow and Orange Pigments

The yellows and oranges line up somewhat like the reds in type. First, we have the earth colors, such as W-602, French Ochre, and W-616, Domestic Ochre, which are cheap and used for making tints and browns and some oil colors They contain 20% to 60% iron oxide blended with alumina, siliceous matter and combined water of crystallization. These were used during the war as ferrite yellow substitutes, but are being replaced again with the better grade pigment which does not settle out so badly.

Ferrite Yellow, W-624 and W-630, synthetic grades of iron oxide, which vary in color according to the degree of hydration,is higher in hiding and tinting strength than ochres and used for shading buffs, ivories, grays, tans, browns, olive greens, etc. It is rather difficult to grind and some of the recent developments have been to provide low oil absorption grades with easier dispersion, e.g., Mapico LO and Reichard Coulston's ED types.

Then we have an organic dyestuff type, W-614, Hansa Yellow, which is one of the azo pigments characterized by poor hiding but good tinting strength. It has good lightfastness in masstone but fades in tints. It bleeds considerably and is therefore limited in use.

By far the most extensively used yellow and orange pigments are the inorganic chrome types W-679, W-676, W-677 and W-610, which vary in color according to chemical composition, lead sulfate being used for yellow and lead oxide for the red tone with the lead chromate base. These are relatively cheap pigments and provide good long term durability with good film integrity and some rust inhibition. They darken on exposure, especially in sulphide fumes. They are used in enamels and some grades W-697 are blended with iron blues to make chrome greens.

Finally, we have a special Molybdate Orange, W-622, which is made like a light chrome yellow but some of the lead sulfate is replaced by molybdate, making the pigment stronger and more opaque but also making it darken more on exposure. We are using it to extend less available lead chromates in Safety Color Code Alert Orange and Coal Marking Red Paints.

(c) Green, Blue and Violet Pigments

Most of our greens are formulated with Shading Yellow, W-697, and Milori Blue, W-582, but these combinations darken on exposure as solid colors, fade in light tints and are sensitive to alkali. Greater stability is obtained from the Chromium Oxide pigments, W-754 and W-789, which are almost pure Cr_2O_3 made by roasting sodium dichromate in a reducing atmosphere. They have good hiding lightfastness and chemical resistance; but they are fairly expensive. Guignets Green, W-701, is a hydrated chromium oxide made by fusing sodium bichromate with boric acid and hydrolyzing in water. It is a bright color with good lightfastness and chemical resistance but it is poor in hiding and relatively expensive.

The most recent development in green pigments is our W-785, Monastral Green, which is expensive at $4.00 a pound but the tinting strength is so good that it is economical to use in light tints which are clean and very lightfast. However, this pigment bronzes badly if used as a solid color.

The iron blue pigments are made from potassium ferro-cyanide and comprise three familiar types. Prussian Blue, W-580, is used in black enamels and solid blue colors. It has a dark, slightly brown masstone and a reddish tint. Chinese Blue, W-583, is a dark, jet blue masstone with a greenish tint. It bronzes badly in solid colors, fades in light tints and is poor in alkali resistance. Milori Blues, W-582 and W-586, have light plum color in masstone and a greenish tint. They are used in making chrome green blends and in medium and dark blue tints. These pigments also bronze badly on exposure in solid colors, fade in light tints and are sensitive to alkali.

Ultramarine Blue, W-514, is a calcined mixture of china clay, silica, soda ash, sodium sulfate and sulfide. It varies from a greenish to a reddish tint, is fugitive and relatively expensive. It is used primarily for tinting whites. Blue Lake, W-512, is a dyestuff precipitated with aluminum hydrate on blanc fixe. It is low in tinting strength and hiding power but is quite lightfast. Hence, it finds some use in relatively light-stable pale blue tints and for toning blues generally.

The Monastral or phthalocyamine blues are the latest addition to this group of pigments. They are quite reactive and we have had difficulty in dispersing them. W-505 has been found preferable to W-515 but both seem to have their uses due to difference in tone but W-515 is restricted by its poor color drift. They are expensive but are clean and green-toned. They bronze on exposure in solid colors.

The only violet pigments we use are W-501, Mineral Violet, and W-518, Purple Toner. Mineral Violet is a manganese ammonium phosphate used for tinting whites. The Purple Toner is a blue dyestuff precipitated with phospho-tungstic acid. It is not very lightfast hence limited in use to interior finishes.

(d) <u>Brown Pigments</u>

Many tan and brown colors are made by blending bone black with ferrite yellow and iron oxide, etc., but sometimes it is desirable to use a straight brown pigment. Some of the oldest known are the earth siennas and umbers, which are similar to the ochres mentioned previously under yellow pigments. They vary in iron oxide content and may contain some manganese dioxide to yield the browner colors which also makes them reactive. W-422 is a light raw Italian Sienna containing about 60% iron oxide and is the best of the siennas in color and tinting strength. W-450 is one of the domestic siennas which are usually not as bright as the Italian grades. This one contains about 50% Fe_2O_3. W-377 is a Burnt Sienna, which is lightened and brightened in color by heat treatment. These are all used for masstone, e.g., in oil colors, and as tinting pigments in tans, buffs and ivories.

The term "Turkey Umber" comes from the fact that the best umber came from the Island of Cyprus which once belonged to Turkey. W-420 is the raw umber type yielding a greenish-brown tone. W-719 is the burnt umber type which improves the brightness through the heat treatment. Both of these pigments are used in brown stains and for tinting purposes.

Domestic browns are both natural and synthetic like the iron oxide reds. W-401, Metallic Brown, is a natural earth pigment containing about 76% iron oxide. W-402, Van Dyke Brown, was originated by the Flemish painter and was imported from Germany originally. It contains about 60% organic matter. W-407, Prince's Metallic Brown, contains about 50% iron oxide and is rigidly controlled for specification requirements.

The synthetic types are either mechanical mixtures or co-precipitated black and red iron oxides. W-476, Mapico Brown, is one of these used principally in VZ specialties.

All of these pigments have good durability as far as checking resistance is concerned although they tend to chalk and lose gloss.

(e) Black Pigments

Black pigments are probably the oldest colors known. They are classified as follows: Mineral, Vegetable, Animal, Lamp and Carbon Blacks, with the latter being most important not only for finishes but for rubber tires and many other products.

The mineral blacks comprise W-318, Graphite, characterized by lead pencil streak, greasiness to touch and excellent resistance to chemicals and weather; W-214, W--221 and W-235, the Coal Blacks, having a brown tone, low oil absorption and good durability, used chiefly as extenders; and W-215, Mapico Black, iron oxide prepared synthetically and used in primers and as tinting pigment where rust inhibition and the property of chalking the same shade as the original are required.

We no longer use a vegetable black, but we use quantities of bone black, the animal type, produced by calcining the bones of cattle or sheep, ending up with a composition of about 10 to 20% carbon mixed with calcium phosphate and ground to proper fineness. We use W-284, Bone Black, for shading grays, tans and olive greens due to its relative freedom from "floating" or "flooding".

Some of the earliest documents of China, India and Egypt refer to the use of Lamp Black. W-205 is made by collecting the carbon smoke from burning coal by-products in a limited supply of air as a free flame. The size, shape, height, color and temperature of the flame are important factors in determining the quality of the lamp black produced. It is used as a tinting pigment to give blue-toned grays, etc. W-222, Molacco Black, is a hybrid type black pigment being a coarse particle size carbon black obtained from burning natural gas in a furnace as a free flame and collected like a lamp black. It has a bluish tone like lamp black in gray tints and has less tendency to flood than lamp or carbon blacks.

We use a number of carbon blacks which are obtained from the incomplete combustion of natural gas by impingement of the flame against metal surfaces and collected by scraping. Carbon black has the finest particle size, highest tinting power, and highest color values of all black pigments. The pigments we use may be classified roughly according to density of color:

The highest color black and most expensive are W-217 and W-230, Neospectra Beads and Mark II. The pigment is the same but the beaded black is specially compacted to improve ease of handling and reduce dusting tendencies. Due to its high oil absorption this type of black is difficult to formulate into finished products and great care must be used in handling the bases and enamels containing it to obtain maximum color without loss of dry on aging, bodying, gelation or seeding troubles.

The medium color blacks are typified by W-201 and W-223, Superba Beads and Powder, respectively, which have fairly good color, grinding qualities and stability with a medium price. Hence, Superba is widely used in our products.

The low color blacks comprise W-275, Excelsior, and W-224, Raven Beads, which are lower in price, oil absorption, masstone color and tinting strength. They are, therefore, used in cheap orthodox paints, primers, etc.

(f) Metal Powders and Pastes

Finally in the category of "W" codes, we have a few metal powders and pastes. Zinc Dust, W-36, is used for special primers, particularly where adhesion to galvanized surfaces is required. Then we have several aluminum pastes, W-64, W-72 and W-163, which comprise various particle sized aluminum powder wet with stearic acid to promote leafing and enough high flashing thinner to form a usable paste. The dry powders tend to ignite under certain conditions of dusting and exposure to air, hence for safety sake we use pastes. Even these must be handled with some caution and a standard practice has been set up recently for doing so. Besides their use in well-known aluminum paints, which give good metal protection, heat reflection and appearance, they are more recently being used to give the metallic "sparkle" to so-called metallized or polychromatic finishes.

B. VARNISH GUMS AND SYNTHETIC RESINS - G CODES

Now let us briefly survey the G codes designating the varnish gums and synthetic resins we use as binders for the pigments just reviewed. We start off with the natural gums including rosin, asphalt and pitches. Then we will discuss the rosin modified varnish gums and finally the synthetic resins, including phenolics, alkyds, urea and melamine resins and finally the vinyl resins.

1. Natural Gums

The imported natural gums we used before the war are still hard to obtain. When plentiful, some of them are used because they are usually cheaper than specially treated rosin and phenolic types. Manila gum is a copal type of alcohol-soluble resin available in various grades according to age. The MA grade G-346 is one of the softer types used in chemical specialties. The harder grades find general use in traffic paints. Congo, G-36, is a hard, fossil resin with limited solubility in oil and solvents until it is run, G-8, or esterified. It yields good rubbing and quick dry varnishes with good adhesion to metal surfaces. East India, G-29 and G-32, is a semi-fossil resin related to the dammars but readily soluble in hydrocarbon solvents. It yields varnishes with good alkali resistance and quick solvent release. It was used in VG-4295, Kwik-Lac, before the war with good success.

Shellac is derived from the secretion of the lac insect prevalent in India. Bleached Shellac, G-72, is the most popular type used because of pale color. We use it for venetian blind primers and it is popular for finishing floors. It is simply dissolved in alcohol but deteriorates on aging for long periods either solid or cut in solvent.

Rosin is derived by tapping pine trees to yield the gum variety or by extraction from pine stumps blasted out of the ground to yield the wood rosin grades. Rosin is sold on the basis of visible color the American grades being in the order of decreasing color - B, E, E, F (or FF for wood rosin which is slightly redder), G, H, I, K, M, N, WG, WW, and X. The price increases with paleness. We use the WG grade as G-40 and H grade as G-42, which is preferred for varnish work because of lower cost.

One of the useful characteristics of rosin is its acidity, mostly abietic acid, which permits esterification, as we shall mention later, and the formation of lime and lead soaps in VC-950 & VC-810, respectively. These varnish formulating vehicles thus have slightly better dry, hardness, water resistance and lower solids at a given body, resulting in low cost orthodox products.

The Penbro Resin, G-88, is a dark, partially polymerized rosin residue gum, which was used during the war as a substitute but it was found satisfactory in Freight Car Paints and is much cheaper than other grades of rosin so we continue to use it in these products where pale color is not important. Asphalts, pitches and tars have been used since ancient times as binders for preserving the dead, for waterproofing boats, etc. We still use these naturally occuring bitumens, G-61, or the still residues from distillation processes in the petroleum and vegetable oil and fat industries, G-65 and G-59, to make black varnishes, cheap black paints and roofing compounds. Blown Asphalts, G-381, have a higher penetration for a given softening point and are more viscosity stable with varying temperature. These materials vary in consistency from very soft and soluble to the hard, semi-fusible and less soluble grades. Hydrolene, G-57, is a still residue from cracking petroleum oil; Stearine Pitches, G-59 and G-323, are still residues from animal fat recovery processes and Cottonseed Pitch, G-314, is the soft carbonaceous residue left from refining cottonseed oil.

2. Rosin-Modified Varnish Gums

The simplest synthetic resin and the first to be used in the finishing business is ester gum, G-43 and G-608, which is rosin essentially abietic acid esterified with glycerol. This process raises the softening point and makes the gum less reactive chemically, thus improving the water and alkali resistance of varnishes made from it. This esterification process can also be modified by using some maleic anhydride to produce the original Amberol type gums, G-104 and G-105, which have still higher melting points, better color characteristics, faster bodying rates and better durability.

When phenol-formaldehyde resins were invented by Baekeland in 1909, they were used to modify ester gum and we now use F-7, K-12-A and BS-1 Amberols, G-327, G-17 and G-328, respectively, in varnish vehicles because they have improved water and alkali resistance compared to the original ester gum. Also, the phenolic constituent increases the melting point and bodying rate and helps to cure Chinawood oil which is generally used with these gums.

More recently, another polyhydric alcohol, pentaerythritol, has come into commercial use and this will esterify rosin to yield higher melting point, better color and faster bodying gums than the corresponding glycerol types. Although several grades have been used in the past, we have tried to do some simplification recently and we now use Pentalyn G, G-55, a maleic modified PE ester, where color is important and Amberol M-93, G-107, or Pentalyn M-802-A, a new one coded G-114, which are highly modified phenolic pentaerythritol rosin esters for use where chemical resistance, hardness and toughness are required.

Further experimental work is in progress in the Philadelphia Laboratory to determine the most advantageous varnish, gum and oil combinations to use from the standpoint of quality and cost, so some additional simplification and replacements will come along later.

These gums find their chief use in our varnish clears and formulating vehicles, such as VC-1329 and VC-805, which go into a wide variety of orthodox products for industrial use.

3. Synthetic Resins

The next class of synthetic resins that are important in our varnish business are the phenolic types based on the condensation of phenols with formaldehyde, which first became prominent commerically in 1928. Both acid and alkaline catalysts may be used for this reaction to yield two essentially different types of resins, non-heat reactive, oil soluble types such as G-15, G-18 and G-20, and the heat reactive types, which advance on heating to the infusible state. Various modifications of these essential types are made possible by using different phenolic compounds and methods of processing. In general, these resins speed the bodying rate of varnish oils, improve the durability characteristics and give increased resistance to moisture and alkalis. However, they are notoriously poor in yellowing resistance in spite of their pale initial color, so their use is limited to spar varnishes, floor and deck vehicles and solid color paints and enamels. The thermosetting or heat reactive types, G-5, G-60 and G-318, are particularly useful for baking enamels, can coatings, alkali resistant primers, and insulating varnishes.

During the war, the Bakelite Corporation exploited a phenolic dispersion resin which we know as G-39, Bakelite Gook. This is a gelled short oil, phenolic resin varnish treated with zinc oxide to reduce acidity for stability reasons and dispersed in a hydrocarbon diluent. It is characterized by speed of dry which occurs on evaporation of the solvent. This is one of the important constituents of zinc chromate primers used for aircraft.

I mention the well-known alkyd or "DULUX" resins only in passing because they are important intermediates based on the interaction of various oils with glycerol, H-2, and phthalic anhydride, G-243, but are not raw materials as we normally consume them. However, we are using some competitive alkyd resins from Reichhold nowadays to extend our supplies of oil, glycerine and phthalic so these then come into the category of raw materials. Leo Hubbuch will elaborate on alkyd resins on October 29.

In conjunction with the alkyd resins as plasticizers, we use for 700 Line products some urea-formaldehyde, RC-718, and melamine-formaldehyde, G078, resins, which are thermosetting or heat-reactive polymers yielding hard, chemically resistant finishes with good color retention characteristics. They are soluble in alcohols and are restricted in compatibility with other materials carrying lean thinners like mineral spirits. Hence, some care is necessary in using them and mixing directions should be followed more carefully than in the case of the more tolerant orthodox varnish and alkyd "DULUX" type products.

Just recently we have been working with vinyl resins based on copolymers of vinyl chloride with vinyl acetate and this development will undoubtedly become more important in coming days. These materials are generally thermoplastic, i.e, they soften under heat and pressure, require active solvents, such as ketones and aromatic hydrocarbons, and are limited in compatibility with other resin vehicles we use. Hence, extreme care is required in handling these relatively new materials. They produce finishes with exceptional chemical resistance and are finding use for kitchen appliances, tank linings, can coatings, etc. There is considerable competitive activity in this field so our work is being continued to exploit the possibilities of using vinyl resins, both in solution and as dispersions.

Finally, we have been using some hydrocarbon resins such as Velsicol AD-4 and AD-6-3, G-335 and G-113, respectively, for varnish type can coatings. Just recently, some of the rubber companies have started to exploit their compounds from synthetic rubber plants and we are looking at some interesting polymers based on styrene and butadiene, etc., which seem to have good color characteristics, speed of dry, etc., and may find a place in our business. Therefore, our use of hydrocarbon resins derived from coal tar or petroleum should expand in the near future as these new developments find their place on the market.

4. Waxes

Then we have uses for a number of waxes, both petroleum and natural types, which we should mention. They are important in chemical specialties and provide certain marproofness, blocking resistance and yellowing resistance in some products.

Carnauba Waxes, G-311, G-370 and G-390, are the hardest types with melting points in the range of 80-90° C. These are used principally in chemical specialty polishes but are hard to obtain these days since they are imported from South America.

Candelilla Wax, G-4 and G-392, is harder than beeswax but not as hard as Carnauba, having a melting point of about 65-70° C. It is used to provide marproofness to 700 Line baking enamels where it also seems to improve yellowing resistance as well. Some is also used to modify a special flooring wax.

You are all familiar with the paraffin waxes, especially those used for household canning. These are derived from petroleum and can be made in various grades of color, wetting point, solubility, etc. We use G-86, G-94 and G-95 in chemical specialties such as paint and varnish remover and in some special varnishes and wax polishes.

As representative of the synthetic waxes, G-690, is hydrogenated castor oil which is used in an alkyd plasticizer for lacquers. Halowax, G-233, is a chlorinated paraffin used in a furniture wax and polish.

C. OILS - H CODES

Chemically speaking, the oils we use are fatty acids esterified with glycerol. The fatty acid chains give flexibility to the dried film. The chains may contain double bonds indicating unsaturation, and these are responsible for the bodying and drying reactions that convert an oil from a soluble liquid to an insoluble solid. Now let us examine some of the oils used in our paints, varnishes and synthetic resins, their sources, treatment, important characteristics and general usefulness.

The first group are drying oils. Chinawood Oil, H-7, has been imported from China and more recently grown in the southern U.S. At the present time, it commands a premium price about 40¢ a pound, but it is still "tops" for quality as a drying oil. It is outstanding in speed of bodying and dry but must be properly cured to prevent frosting or crowsfooting. It yields hard, water-resistant films, but tends to discolor on exposure to light and dark. Oiticica Oil, H-553, comes from Brazil and is related to Chinawood oil in characteristics except it tends to become more brittle on aging. We would use some Perilla Oil, H-340, from Manchukuo or India, if we could get it. It bodies and dries rapidly being intermediate in this respect between Chinawood and linseed oils. Linseed Oil, H-19, comes from flaxseed and we can't get enough right now to go around because Argentina is not supplying the usual amounts. It is the old standard for paints and varnishes, alone or in combination with Chinawood oil. It dries fairly well, retains flexibility better but is less water-resistant than Chinawood oil. Soya-bean Oil, H-59, is becoming more popular since its slower drying characteristics can be improved by treatment with maleic anhydride or pentaerythritol. Its color retention characteristics are definitely better than linseed. Dehydrated Castor Oil, H-156, is chemically prepared from the non-drying type of castor oil so that it will body and dry somewhat like linseed and soya-bean oil and has color characteristics somewhat better than soya-bean oil. Fish Oil, H-106, has found little use in our products so far but it has properties of flow on application plus good drying characteristics that make it interesting for further development whenever the supply becomes adequate and the price is right. The odor is removed by careful refinement.

We have a few semi-drying oils. Cottonseed Oil, H-250, is used mostly for modifying alkyd resins to be used in "DUCO" lacquers, since it is durable, light in color and retains flexibility fairly well. Corn Oil, H 335, is used in a special varnish VC-837, for coating bus bar insulation in view of its inherent slip, flexibility and electrical resistance. Here also I might mention Tall Oil, H-453, which is a by-product of the kraft paper industry containing oil acids mixed with resinous acids like rosin. It is rather cheap. It is slow-drying as is but can be treated with maleic anhydride and pentaerythritol or sorbitol to make pretty good varnishes which may find some use later on.

Finally, we have a couple of non-drying oils. Castor Oil, H-22, familiar from childhood days, is pressed from beans imported from Brazil and India. It has good retained flexibility and color characteristics when used in lacquers or baking products. Coconut oil can be used as is or hydrogenated to form "Opalwax", our G-700, for making alkyd resin plasticizers for lacquers and 700 Line baking enamels where good durability, heat resistance, and retained flexibility are desired.

These raw or refined oils are used for paints and varnish cooking or they may be further treated to produce better dispersing, compatibility or drying characteristics by the following techniques:

(a) Boiled Oil, H-108, is heat-treated with driers present to form "in situ" driers for promoting dispersion and oxidation.

(b) Blown Oils, H-249 and H-141, are heat-treated while being blown with air, which forms peroxides to accelerate drying and increases the compatibility and wetting characteristics.

(c) Heat Bodied Oils, H-241 and H-410, are heat-treated, possibly under vacuum, without driers added for relatively long periods of time to develop a high degree of polymerization.

(d) Solvent Extracted Oil, H-571, is made by a special process whereby the faster drying fractions of linseed oil are separated from the slower drying portion.

(e) Chemically Treated Oils, H-557 and H-592, are oils or fatty acids modified by special chemical processes with maleic anhydride, pentaerythritol, styrene, dicyclopentadiene, sorbitol, etc., to improve drying, bodying rate, chemical resistance, color retention and other characteristics. These were developed during the war as substitutes for Chinawood oil but they have something to be desired and will probably only find specialty uses from now on.

(f) Catalyzed Oils are those treated with special chemical compounds which accelerate the bodying rate while maintaining the other essential characteristics of the oils. "Kellitol", KH-3437, produced by Spencer-Kellogg is one of the most promising of these specialties on the market so far. It bodies in one-third of the time as H-19. The chief advantage of these oils is the ultimate savings in fire time and kettle capacity involved in their use.

D. SOLVENTS AND THINNERS - H CODES

Now let us consider very briefly the liquid raw materials we use as solvents or thinners which comprise the volatile portion of the various products we make. We will consider three general classifications in order - resinous types, oxygenated types, and the hydrocarbons.

1. Resinous Solvents

The resinous solvents are derived from the distillation of pine sap or pine wood chips. They include Gum and Wood Turpentine, H-266 and H-58, Dipentene, H-152, Terpene Hydrocarbons, H-472, and Pine Oil, H-502. Turpentine has been replaced by petroleum hydrocarbons which are more plentiful and cheaper. Dipentene is higher boiling and expensive but is used in some specification products. The terpene hydrocarbons are derived from the synthetic camphor process and are similar to dipentene. Pine oil is a very high boiling fraction and slow evaporating. Small amounts are used for brushability, flow, and other application characteristics. It is also an active wetting agent for 700 Line products.

2. Oxygenated Solvents

The oxygénated solvents such as alcohols, esters, ketones and ethers find considerable use in lacquers. However, a few are used for special purposes in some of our products. Denatured Ethyl Alcohol, H-1, is low boiling, fast evaporating and used for stains and paint and varnish remover. Isopropyl Alcohol, H-84, is slightly higher boiling and used in a variety of our products. Butyl Alcohol, H-12, is still higher boiling and is the chief solvent in 700 Line products where a definite proportion must be used to maintain solubility and stability of these finishes. Methyl Isobutyl Carbinol, H-48, is a new product put out by Shell and is similar to butyl alcohol in solvency with slightly higher evaporation rate. Diacetone Alcohol, H-39, is rather high boiling and is an active solvent due to the ketone substitution. It is used in varnish stains. In this category belong Glycerine, H-2, and Pentaerythritol, G-419, which are polyhydric alcohols used for esterifying rosin and phthalic anhydride to make ester gums and "DULUX" resins, respectively, but could not strictly be classed as solvents for our purpose.

We use no esters except for special experimental products and for cleaning purposes, where their high solvency is an asset. Butyl Cellosolve, H-224, is an ether-alcohol with rather high evaporation rate which we use for 700 Line thinners and special products. The ether group increases its solvent power beyond that of an alcohol of the same boiling point.

The ketone solvents are quite active and are required for the newer vinyl resin formulations. Acetone, H-30, is the fastest in evaporation and is used in paint and varnish remover Methyl Ethyl Ketone, H-35, is a relatively low boiling ketone. Methyl Isobutyl Ketone(or Hexone), H-44, is next in boiling range and hence somewhat less active as a solvent. Cyclohexanone, H-66, is an aromatic type with the highest evaporation rate of this series of ketone solvents. Some higher boiling ketones are available and may be required later on for vinyl vinishes such as Methyl Amyl Ketone, Disobutyl Ketone and Isophorone.

Generally speaking the oxygenated solvents are higher in price than the resinous types and the hydrocarbons. Also in view of their solvent power, they should be handled more carefully to avoid dermatitis, burns and poisoning.

3. Hydrocarbon Solvents

The hydrocarbons are divided into two main types based on derivation, viz., coal tar or petroleum, and into two classifications according to chemical structure, viz., aliphatic for straight carbon chain types or aromatic for carbon ring types. The high solvency petroleum naphthas are hybrids being a cross between the aliphatic and aromatic types. The composition of the hydrocarbon solvents varies with the location of the differend crudes as follows:

Michigan - almost 100% paraffinic
Texas - high in naphthenic
California - high in aromatic.

Generally speaking, in each classification, solvent power decreases with increased evaporation rate or boiling range. Solvent power increases with aromaticity. Cost increases with solvent power.

Formerly, our aromatic hydrocarbons were derived only from coal tar but recently the petroleum industry has made improvements in their cracking and fractionation processes so that they are able to duplicate the coal tar products. We still use coal tar Toluol or Toluene, H-47, which is the fastest evaporating and best in solvency of this group but some petroleum grades are available on the market. In the case of Xylol or Xylene, H-583, we have swung over to the petroleum grade because it is lower in cost. It is somewhat higher boiling and slower evaporating than H-47. In the high flash naphtha class, we now use a petroleum hydrocarbon, Solvesso 100, H-596, since it is more active and more readily available than the coal tar variety, H-278. These aromatic hydrocarbons are chiefly used for 700 Line and vinyl resin finishes although some other varnish and "DULUX" products require them in lesser amounts. A rather high boiling coal tar fraction, Tetralin, H 550, is used in a special "Winter Thinner", where it is oxidized to speed up the drying of air dry "DULUX" enamels particularly under adverse conditions. Last in this class is Creosote Oil, H-264, which is very high boiling but has good wetting and impregnation properties, hence finds use in shingle stains.

In the hybrid group of high solvency naphthas, we have a similar range in evaporation rates increasing in the order named. H-51 is similar to Toluol in evaporation rate being quite fast. Next is H-202, which is in the evaporation range of Xylol. Then comes H-200, which is in the class of slower evaporating solvents like high flash naphtha. We have no really high boiling naphtha in this class but some of the petroleum companies are working on such a composition and we may have another one to add to this series later on.

In the aliphatic series we have a greater spread in evaporation rates. H-29 is somewhat like H-47 and H-51 but evaporates noticeably faster than either of these. Next comes H-257, V.M. & P. (standing for Varnish Makers and Painters)Naphtha, which is somewhat like H-202 but slightly faster in evaporation rate. Then we have H-287, the familiar Mineral Spirits, which is widely used in orthodox varnish and "DULUX" enamel formulations but is not so good in 700 Line or vinyl resin products. This is the accepted replacement for turpentine, except for odor characteristics. We are still looking for a mineral spirits with better odor but they have only been different so far. A still higher boiling type of aliphatic hydrocarbon is H-262, Heavy Mineral Spirits, used for paint products, where low cost and lots of time for brush lapping is needed. Next in line is H-265, Kerosene, which is familiar as a fuel, but also goes into some paint products to promote brushability by slowing down the evaporation of solvent. Finally, a hydrocarbon oil is used in some chemical specialties known as Neutral Oil, H-520, which is practically a lubricant and not strictly a solvent type.

In this category as thinner I mention in passing H-506, which many a greenhorn has been sent looking over the plant to find just as the storekeeper sends his new clerks for a bag or paper stretcher and the mechanic sends his new apprentice out to look for a left-handed monkey wrench. H-506, City Water, is getting to be a popular and usable diluent now for emulsion paints like "Speed-Easy" and we may see other types coming on the market soon. It is cheap and it has good odor characteristics provided it is cleaned up on coming from the Schuylkill or the Delaware.

E. MISCELLANEOUS AGENTS

We should mention briefly that variety of chemical agents we use as driers and catalysts, which speed the rate of drying, bodying or other chemical reaction, the inhibitors which retard drying, settling, etc. for practical reasons, certain surface-active compounds which serve as flatting and bodying agents, and a few fungicides which retard the growth of harmful organisms. Let's review them quickly in that order.

1. Driers and Catalysts

The common metallic driers we use are cobalt, lead and manganese soaps of naphthenic acids which are quite soluble, stable and relatively easy to disperse. H-172 is a 6% cobalt solution which we reduce to 2% metal content as VD-1450 to permit more accurate weighings. It acts generally as a top surface drier or oxidation promoter. H-171 is a 16% lead solution which we use at this concentration as VD-1428 since larger amounts of lead are used generally to promote thorough dry of heavy films. H-173 is a 6% manganese solution which we reduce to 3% metal content for use as VD-1846; it acts as a promoter for the cobalt and lead driers and is particularly good where wrinkling is often a problem. In this connection also, G-434, Diphenyl Guanidine, has been found useful to promote drying of air-dry products.

A few oxide type compounds are used for varnish making where they react with the oil and gums to form resinate driers "in situ". W-603, Litharge, is a lead oxide used as a catalyst for alkyd resins as well as a varnish drier. G-240, Manganese Oxyhydrate, is used for varnishes. G-212, Calcium Hydrate, or lime is used to body up and harden formulating varnishes based on rosin where low cost products are desired.

H-184, Zinc Naphthenate, is used as dispersing agent and hardener for special products. H-181, Iron Linoleate, and H-182, Iron Naphthenate, are used as hardening agents for can coatings and some paint products.

G-218, Caustic Soda, is used as catalyst in resin cooking operations.

2. Inhibitors

Chemical antioxidants are used as drying inhibitors and flocculating agents are used to suspend pigments so as to prevent settling on longtime storage. As inhibitors we use:

(a) Creosote solutions based on H-505 which is the cheapest one available.

(b) Thymol, G-495, which is relatively expensive but better smelling than creosole.

(c) Hydroquinone, G-498, and Triethanolamine, H-534, which are used as frosting inhibitors on baking 700 Line products.

(d) N-butyraldoxine, more familiar as chemical ASA, H-580, which is relatively new but works well as a skinning and bodying inhibitor without slowing up the dry so much due to its relative volatility.

The suspension agents are surface-active compounds varying in type and specific in their use as settling inhibitors and sag control agents. The following are typical ones we use:

(a) G-12, Soya Lecithin, a phosphatide derived from the refining of soya-bean oil.

(b) H-522, Turkey Red Oil, a sulphonated castor oil.

(c) H-526, Rubber Solution, a dispersion of milled crepe rubber in xylol.

(d) H-226, Coconut Oil Fatty Acids, which is derived from splitting glycerine away from coconut oil.

(e) H-555, Neofat #7, which is a specially segregated fatty acid fraction from coconut oil.

3. Flatting and Bodying Agents

In this group we use selected chemical compounds or solid, highly absorptive materials which are surface active and reduce gloss or cause an increase in body so as to provide desirable application characteristics or appearance or lower cost by permitting the use of more cheap thinner in certain products. Typical agents of this type are the following:

(a) G-217, Aluminum Stearate, used in flat varnishes principally.

(b) G-416, Powdered Bentonite, used in chemical specialties.

(c) W-1, China Clay, which is a cheap extender and bodying agent for stencil pastes.

4. Fungicides

These are selected chemical compounds with varying degrees of toxicity toward pestiferous organisms which are better known as mildew, mold, termites, barnacles and bacteria, which may cause trouble in certain paints or on the surface of finishes. In this class we make use of the following agents:

(a) W-416, Cuprous Oxide, specific for marine growths on ship paints.

(b) H-454, Phenyl Mercury Oleate, specific for wood sealer.

(c) G-276, Dowicide G, a chlorinated phenolic compound used to prevent putrefaction in protein-type water paints such as "Speed-Easy".

(d) G-231, Shirlan Extra, which is an organic derivative, salicylamide, used for mildew resisting mill whites, etc. and is relatively non-toxic.

F. SPECIFICATIONS

Finally, let me draw your attention to the procedure we use for establishing purchasing and control specifications to govern the type and quality of the raw materials we use here.

A facsimile of a raw material specification sheet is attached for reference. You will note that the specification sheet covers the following points:

a. Raw Material Code (G, H, W or K codes).

b. DuPont Title - may be same as supplier's designation if only one source of supply, but not general practice.

c. Date of Issuance and Superseding Date.

d. Gallon Weight

e. General Description - as technical as possible to provide for use by formulators.

f. Purchasing Specifications - these are provided the supplier and his material must meet these requirements in all respects. Any deviation is cause for rejection by the plant receiving shipment of the material. We show the title of the test, the TM number covering the test method and the limits established for each property, characteristic or measurement.

g. Some materials require Accessory Specifications, including an actual evaluation in a finished product where the material must perform equal to a given standard, previous satisfactory production or within certain stated limits. Sometimes a special test is required for only one or a few materials and a test method (TM) is not written to cover it, since they are restricted to general tests, but the test procedure is actually shown on the specification sheet. Certain precautions regarding possible impurities or contaminants, handling of toxic or hazardous materials (we have a number of these in use) and any other special notations are included.

h. The Control Specifications are generally a series of letters, A, B, C, etc., to refer to the Purchasing Specification tests, which the Plant Control Laboratory makes on arrival of the shipment of the material before it may be used in a designated class of finished products, viz., Paint & Varnish, "DULUX" enamels, or "DUCO" lacquers.

The Sampling Specification is generally designated as TM-73, which described the standard practice for obtaining a uniform, representative sample of any raw material shipment for testing and retain storage.

i. Then the list of acceptable sources of supply or names of suppliers (original or agents as the case may be) are given with each supplier's designation for the material which is used by the Purchasing Department to order the material.

j. Most of our materials are controlled by comparison with accepted standards and these must be maintained and renewed as occasion arises so we have a record on the specification sheet to show the source, designation, date of adoption and plant responsible for establishing each standard.

k. Finally the reason for issuing or revising each specification is given just as we do with our formulas, and the sheet is signed by the originator and the laboratory he represents.

That constitutes a raw material specification and sometimes the originator must endure many "birth pains" to get one properly born and then keep it growing by periodic revisions to add or modify tests for quality control, sources of supply, changes of reference standard, etc., but these specifications are a vital part of the manufacture of our products because any error at this point can cause considerable havoc in plant production or customer complaints. You might say that these raw material specifications are the "foundation stones" for building and maintaining the quality of our products. A considerable amount of research and development work is generally involved in establishing a new material and the writing of the specifications is the climax of this effort because permanent specifications are not written until a new material has been proven satisfactory in actual plant production.

CHART 5

ONE TON OF COAL

↓

TEN GALLONS OF COAL TAR

↓

2½ GALS. LIGHT OIL	1 GAL. CARBOLIC OIL	1 GAL. CREOSOTE OIL	5½ GALS. PITCH, CARBON, ETC.
(Benzol - H-503) (Toluol - H-47) (Xylol - H-15) (Coal Tar Naphthas - H-504 & H-278)	(Phthalic Anhydride)		

CHART 6

COAL TAR SOLVENTS

		Distillation Range
H-503	Benzol	79.1° - 81.1° C.
H-47	Toluol	109° - 111° C.
H-15	Xylol	132° - 145° C.
H-504	Solvent Naphtha	125° - 180° C.
H-278	High-Flash Solvent Naphtha	140° - 210° C.

CHART 7

HIGH-SOLVENCY PETROLEUM NAPHTHAS

		Distillation Range
H-51	Low-Boiling Naphtha	95° - 141° C.
H 202	High-Solvency Petroleum Naphtha	135° - 175° C.
H 200	Heavy Petroleum Naphtha	183° - 201° C.

CHART 8

TURPENTINE GROUP

		Distillation Range
H-266	Gum Spirit	150° - 170° C.
H-58	Wood	150° - 170° C.
H-158	Dipentine	170° - 182° C.
H-502	Pine Oil	185° - 225° C.

CHART 9

ALCOHOLS

		Distillation Range
H-1	Ethyl Alcohol (Denatured)	78.5° C.
H-84	Iso Propyl Alcohol	79° - 81° C.
H-12	Butyl Alcohol	113° - 118° C.
H-18	Iso Butyl Alcohol	106.3° - 108.3°C.

CHART 10

CHOICE OF SOLVENTS

1. Active carrier for the binder.
2. To reduce cost (diluent).
3. To obtain desired solids-viscosity relationship.
4. Application properties.
    a) Spray
    b) Brush
    c) Dip
    d) Roller Coat