Du Pont de Nemours, E. I. & Co.
F & F Dep artment. R & D Division.
Marshall Laboratory.
Proposed pub. Organic coatings, by Seymore Hochberg. August 9, 1974. (Prepared for limited distribution to participants in a proposed short course - introduction to Organic Coatings - s the ACS.

FF-3310 REV. 7-66

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FABRICS & FINISHES DEPARTMENT

Marshall R&D Laboratory
August 9, 1974

PROPOSED PUBLICATION FROM THE FABRICS & FINISHES DEPARTMENT

ORGANIC COATINGS

BY: SEYMORE HOCHBERG

We submit for your information and comment a proposed publication on Organic Coatings.

This has been prepared for limited distribution to participants in a proposed Short Course - Introduction to Organic Coatings - to be sponsored by the American Chemical Society.

No patent applications have been filed and no patentable information is presented to our knowledge.

The Short Course will include two days of lectures and demonstrations explaining the ideas in the proposed publication.

We will be pleased to have any comments or suggestions on this paper that you care to make. Unless we hear from you by August 25th we will assume you have no objections.

R&D Manager

ORGANIC COATINGS

CHAPTER 1

1-1 PURPOSE OF THE COURSE

The course is designed for (1) people now in the Organic Coatings business who have become highly specialized and want to learn something about other developed areas of the technology, (2) people who want to understand some of the latter advances in the science and technology for their guidance in further study and (3) beginners in the field who want a quick survey of the subject.

An advanced specialist in a particular discipline, e.g. rheology or emulsion polymerization, will learn new things only about disciplines other than his specialty. The course will be concentrated on the qualitative understanding of the ideas. Little knowledge of mathematics will be needed. Literature references to more advanced study will be given.

1-2 OTHER SOURCES OF INFORMATION ON ORGANIC COATINGS

1-2-1 Books And Periodicals

Several books on the broad subject of the chemistry and technology of organic coatings can be particularly helpful for a survey of the subject.

H. F. Payne - Organic Coating Technology, Vol. I (1954) and II (1961) John Wiley, New York.

D. H. Parker - Principles of Surface Coatings Technology. Interscience, New York (1965)

Elias Singer - Fundamentals of Paint, Varnish and Lacquer Technology. American Paint Journal Co., St. Louis, Mo. (1957)

P. Nylen, E. Sunderland - Modern Surface Coatings. Interscience, New York (1965).

Journals dealing with current development reviews of pertinent topics are:

J. Paint Technology - Published by the Federation of Societies for Paint Technology, comprising twenty-five local constituent Societies, 121 South Broad Street, Phila., Pa. 19107.

J. Oil and Colour Chemists Assn. - Oil and Colour Assn., Wax Chandler's Hall, Gresham Street, London E.C. 2V7AB

Industrial Finishing - Hitchcock Publishing Company, Wheaton, Ill. 60187.

Products Finishing - Gardner Publications, Inc., 600 Main Street Cincinnati, Ohio 45202

The subject of organic coatings comprises several disciplines (for example, the chemistry and physics of polymerization or the unit process of grinding), each of which has its own literature. References to such literature will be supplied as the subjects are covered.

1-2-2 Study Courses

Courses of Study for the training of chemists in organic coatings research and development have been outlined by the Education Committee of the Federation of Societies for Paint Technology. Organic Chemistry I involves a 40 hour lecture course extending to 60 hours by laboratory study. Organic Chemistry II represents approximately 40 hours more of lectures.

Regular courses in organic coatings are given in various colleges, for example, University of Connecticut, North Dakota State University and Brooklyn Polytechnic Institute. A two-semester course was recently announced by St. Joseph's College.

CLASSIFICATION OF COATINGS

CHAPTER 2

2-1 CLASSIFICATION BY FUNCTION

Organic coatings are applied most commonly for purposes of protection and decoration. Long-term protection of steel and aluminum against corrosion, protection of wood against decay and disintegration, and protection of food products by coated film packaging materials are common examples of the protective function of organic coatings.

Coatings are commonly used to satisfy aesthetic requirements of appearance, to provide color, gloss and other optical effects.

Outside the field of protection and decoration, organic coatings are applied for imparting soundproofing, fire retardance, abrasion resistance, low friction coefficient, magnetic memory storage, electrical conductivity and electrical insulation.

2-2 CLASSIFICATION BY CHEMICAL TYPE

2-2-1 Inorganic Coatings

a) Metallic

Metals are coated on other metals and on plastics by a variety of processes but mainly by electrochemical reduction processes. Copper, nickel, cadmium, and chromium coatings for protection and decoration of steel are usually electroplated. Zinc is often electroplated on steel, but is also applied from a melt. Some metals are applied by explosive bonding. Aluminum is evaporated on plastics for decoration.

b) Conversion Coatings

Metals, particularly steel, aluminum, and zinc, are often treated with chemicals, chiefly chromic and phosphoric acid, to clean them and then to deposit adherent, relatively tough, inorganic oxidation products of the metal. These deposits are of slight protective value themselves, but they usually produce surfaces to which organic coatings adhere more readily than they do to untreated metal, and they enhance the protective value of the subsequent coatings. These are called conversion coatings.

The chemicals dissolve some of the metal and deposit insoluble basic salts and oxides. The reactions can be performed with chemicals alone, hot or cold, or with the aid of electric currents. Most often, proprietary mixtures of chemicals are used which are claimed to increase speed or details of effectiveness.

c) Siliceous Coatings

Ceramic coatings are silicate-based products applied from aqueous suspensions of oxides and siliceous materials. On drying off the water a porous powder results which is melted and then cooled to a glass. The coatings require high temperatures for application and are brittle in service. Although they tend to have excellent protective qualities when undamaged, they are easily damaged mechanically, and can be repaired only with difficulty. Their decorative quality is relatively limited.

Ceramic deposits are also applied as rough, discontinuous coatings on aluminum pots and pans before the deposit of a polytetrafluorethylene finish. The ceramic deposits improve the perceived resistance of the polytetrafluoroethylene to damage by scratching. In such cases, because the ceramics are discontinuous, the metal can be formed, even after the ceramics have been fused and cooled, without substantial damage.

Related to the ceramic coatings are coatings based on sodium silicate solutions which are hardened and made insoluble by the action of acids (even CO_2). Most prominent are the zinc-rich coatings containing sufficient metallic zinc powder to make the coatings electrically conductive. Applied to steel, they are hard, chemically resistant, and protective to the steel surface much as a galvanized steel coating.

Of lesser importance are other inorganic coatings like whitewash (lime) or portland-cement finishes applied from water.

2-2-2 Organic Coatings

a) Definitions, Binder, Pigment, Vehicle

Organic coatings are usually supplied as liquids which are converted on the substrate to solids. In order to have the required strength, the solid coating must comprise a continuous phase, the binder, consisting mainly of large molecules, which generally adheres to the substrate, and in which pigment particles may be dispersed. Organic coatings have organic binders. A pigment is a finely divided (0.01-25 microns) insoluble solid. Pigments provide, among other benefits, opacity, color, and durability, but they affect the flow properties during application and the mechanical properties later. Additives are used in minor amounts to provide special functions.

It is important that the organic binder have high molecular weight in its solid form in order to provide a strong film. The minimum molecular weight required will vary somewhat with the chemical characteristics of the binder. Low molecular-weight organic solids are, however, volatile, fluid, or weak. They will either smear or powder easily.

The binder in some cases may be of low molecular weight during application, but, in those cases, chemical reactions must be used to raise the molecular weight before the coating is put to practical use.

The term "vehicle" is applied to the ingredients of the coating before application exclusive of pigment. The vehicle will include solvents, water, organic polymers (either in high molecular weight form or in the temporary low molecular weight form) and various additives which remain dissolved or dispersed in the binder. Occassionally, organic coatings are applied in powder form. In such cases they are melted to a flowable liquid form before solidification. If the binder is of low molecular weight in the powder form it must be converted to high molecular weight after application.

b) Sales Classifications

1. Trade Sales Coatings - These are usually liquid coating compositions marketed to relatively unskilled users through paint dealers, hardware stores, and department stores. They are usually formulated to be applied with simple techniques - brushes, rollers, aerosol bomb containers and to require no ovens, or other machinery for converting a liquid film to a solid one or for dealing with solvent vapors.

2. Industrial Coatings - These are usually sold to factories where specialized application and drying equipment can be justified economically.

c) Classification by Chemical Reactivity

1. Non-Reactive - The binder usually solidifies as the solvent or water evaporates, and no further reaction is necessary to achieve strength or adhesion. Molecular weight of the binder is usually greater than 50,000. Nitrocellulose, polyvinyl acetate, polymethyl methacrylate are examples of such binders and the coatings of such binders are called lacquers.

2. Reactive - The binder consists of small molecules (molecular wt. $<$ 10,000) which react after application to yield the larger molecules required for strength and other properties. The coatings comprising these binders are called enamels. (The term enamel is also used to describe any hard glossy coating. Usually the context will help one to understand the meaning).

d) By State of Dispersion of the Binder Just Before Application

1. Solution - Sometimes the binder is molecularly dispersed as a solution in a suitable solvent or water.

2. Particulate Suspension - The binder is in the form of polymer particles dispersed in water or an organic solvent. In latex paints the binder is largely in the form of an aqueous dispersion. As a special case, the binder of the newer powder finishes can be considered as dispersions of polymer in air.

Dispersions of particulate polyvinyl chloride in mixtures of organic solvents and plasticizers are useful for coating cloth. Dispersions comprising methyl methacrylate polymer in solvents are useful in painting of automobiles.

2-3 ECONOMICS OF ORGANIC COATINGS

Regular reports on the status of the organic coatings business are provided by the U.S. Bureau of the Census, by Trade Associations, and private organizations on a subscription basis.

In 1971 total sales of organic coatings in the U.S. were reported as 950 million gallons. Trade Sales finishes accounted for 431 million gallons (1.56 billion dollars). Industrial Finishes accounted for 443 million gallons (1.27 billion dollars).

The organic coatings business is included in Chemical and Allied Sales but does not include manufacture of pigments or other paint ingredients. It constitutes about 5.5% of all Chemical and Allied Sales and employs about 71,000 people of whom 4,300 are chemists and chemical engineers.

2-4 REFERENCES FOR FURTHER STUDY

2-4-1 Conversion Coatings Steel, Aluminum, Magnesium, Zinc etc.

1. Metals Handbook - American Society for Metals 8th Ed. Vol. 2 (1964) Heat Treating, Cleaning & Finishing.

2. Aluminum Vol. III Fabrication and Finishing - Amercian Society for Metals, Metals Park, Ohio (1967).

3. A. G. Roberts - Organic Coatings - National Bureau of Standards BSS7, U.S. Dept. of Commerce, Superintendent of Documents, U. S. Govt. Printing Office, pp. 115-125.

4. Payne - Organic Coating Technology Vol. II p. 1028-1030 John Wiley, New York (1954).

5. Trade Literature of Alcoa, Dow, Parker Rustproof, Oakite Products.

2-4-2 Ceramic Coatings

1. Metals Handbook - American Society for Metals 8th Ed. Vol. 2 (1964) Heat Treating, Cleaning and Finishing.

2. Aluminum - Vol. III Fabrication and Finishing American Society for Metals, Metals Park, Ohio (1967).

2-4-3 References on the Economics of the Organic Coatings Industry

1. Census of Manufacturers - U.S. Dept. of Commerce - Bureau of the Census - is a collection of economic data published in book form every 5 years. The Census Bureau Industry Division, Washington D.C. 20233 publishes monthly reports (3 months late).

2. The Paint Industry - An Economics, Marketing, and Financial Investigation. Morton Research Corporation, 1666 Newbridge Road, Bellevue New York, 11710 (Oct. 1972).

3. Coatings - A Multiple Client Study - Skeist Laboratories, Inc., Newark, New York, (Feb. 1967). A private confidential report.

4. Annual Sales Survey for the Year 1970 (National Paint Varnish and Lacquer Association - Old Name) - National Paint and Coatings Association, 1500 Rhode Island Avenue, N.W., Washington D.C. 20005.

5. Marketing Guide to the Paint Industry - Charles H. Kline and Co., Inc., 389 Passaic Avenue, Fairfield, New Jersey 07006, Industrial Marketing Guide IMG 1-69.

THE BINDER - PHYSICAL AND MECHANICAL PROPERTIES

CHAPTER 3

3-1 THE BINDER

The binder includes all the materials constituting the medium including polymers, in which the pigments are dispersed when the coating is dry. Certain physical properties of the coating depend mainly on the nature of the polymeric portion of the binder.

3-2 PHYSICAL MODEL OF AN AMORPHOUS BINDER

The binder, when the coating is solid and in its useful form, consists largely - in some cases, entirely - of large molecules. Each of these molecules will generally contain thousands of carbon atoms linked together as a chain by covalent chemical bonds. In some binders the large molecules will contain in their chains also oxygen or other atoms, also linked with strong covalent bonds. Segments of the molecules are in constant vibrational, rotational, and translational motions which increase in violence with their temperature.

The chains of atoms in a polymer molecule are not straight. Each atom is linked to its neighbors by bonds which occur at typical valence angles For singly bonded carbon, most common in polymers, all its attachments will be at 109° from each other, arranged as the corners of a tetrahedron around its center. At each carbon atom the chain is bent at 109° (instead of the 180° representing a straight line). The distance between centers of two singly bonded carbon atoms is 1.54Å (1 Å = 10^{-8} cm.).

There is, for an isolated small molecule, approximately free rotation around each bond, but occasionally, and particularly as chain length is increased, there is substantial mechanical interference (attractions and repulsions) of one part of a molecular chain with another. When molecules are present in high concentration, as in a binder, there is considerable intermolecular and intramolecular interference with rotation or other motion in a bond, but there is nevertheless some constant vibrational, rotational and translational motion. While distances between successive atoms in a polymer chain are fixed fairly rigidly, the freedom of rotation about the many bonds results in rather easy distortion of a molecule. Rotation is prevented about double bonds and about conjugated systems of double bonds. Ring structures and bulky attachments also restrict rotation about bonds and make for stiff molecules. Consider a polymer molecule of 1000 carbon atoms linked by single bonds in a chain. Each carbon is separated from the next by 1.54 Å (1 Å = 10^{-8} cm.). The molecule would be 1540Å long if the distance between centers of chain atoms were added or if all the bonds were distorted to 180°. If the molecule were extended to its greatest length without disturbing the 109° bond angle the distance between its ends would be only 1250Å. If the molecule were allowed to assume all its allowed configurations the largest dimension could, for a small fraction of the time, be 1250Å, but on the average it would be much shorter.

Neighboring molecules approach the polymer to an equilibrium distance of about 4Å. Because the molecules are much longer and flexible and their distance apart short, it is obvious that there must be strong mutual interference with the free rotations and vibrations.

The picture of the high molecular weight portion of a binder is that of a mass of cooked, relatively strong spaghetti, each strand well lubricated with rather weak attraction to or repulsion from other strands, but in constant squirming motion. (Perhaps a mass of wet earthworms might be more descriptive).

Small amounts of tension applied to a mass of molecules tends to straighten kinked molecules and make them slip past each other. The more the attractive forces between parts of adjacent molecules and the longer the molecules, the more force must be applied to make the molecules slip. If the molecules are large enough and the intermolecular forces strong enough, molecules will break instead of slipping, and chemical changes will occur at the broken ends.

In certain binders - particularly those used in enamels - there are crosslinks or strong chemical attachments between chains. In such molecules the amount of translational motion of one molecule past another before breakage of chemical bonds occurs is smaller.

A good solvent for a polymer penetrates between the polymer molecules and separates them. The polymer is swollen by the solvent; a coiled polymer tends to become extended. When sufficiently swollen the polymer molecules slide past each other readily and the polymer is regarded as fluid and dissolved. If the polymer is crosslinked, the crosslinks prevent unlimited solution and while the translational motion before chain breakage is easier (the polymer mass is softer) the translational distance before breakage may not change much.

The usual binders are non-crystalline. They usually do not have a sharp melt temperature with a latent heat of fusion as common crystalline compounds do. Their chains of atoms are arranged more or less in haphazard disorder. Their density is less than it would be if all the molecules were neatly packed like uncooked spaghetti in a box.

3-3 PICTURES OF ORIENTATION AND CRYSTALLINITY

Some binders have forces between molecules strong enough to produce higher density and order between molecules or even between parts of chains of a single molecule. Such binders are crystalline. Crystalline polymers have a substantial fraction of their mass in the form of parallel, closely packed molecules. They show X-ray diffraction and have sharp melting points. As with smaller molecules, crystallization is favored by symmetrical arrangements of atoms, by high interatomic forces and by purity of composition.

If a binder is subjected to tension in one direction and stretched, its molecules slip past each other and will tend to align themselves parallel to the stretch. Such a structure, uniaxially oriented, will be stronger along the stretch lines than perpendicular to the stretch lines. It will tend to be easily fibrillated or broken into fibers.

If a binder is stretched two ways the molecules tend to arrange themselves in layers parallel to the plane including both stretch directions and there will be fewer molecules crossing the plane. Such binders will be stronger in the plane of stretching and correspondingly weak in the perpendicular direction. Thus a binder which is biaxially-oriented will tend to delaminate. Orientation tends to favor crystallization.

3-4 FORCES BETWEEN MOLECULES OF THE BINDER

The molecules of the binder, in spite of the fact that they do not touch each other, and that they are in constant vibrational and rotational motion, do not fly apart spontaneously. The forces that hold them to each other are of the same type as hold molecules of common chemicals together to form simple solids. These forces between molecules are a function of their distance apart. The forces are of several types. Their net effect is attractive at long distances and repulsive at short ones. Without the the disturbing effects of vibration, the parts of molecules tend to approach each other to the point where the net force of attraction and repulsion is zero. A sufficient amplitude of vibration would separate the atoms far enough so that their attraction would be negligible compared with other competing attractions and they might not return. A solid would melt and eventually evaporate. In polymers, such amplitudes are restricted by the relatively strong attachments of one atom in a chain to the next, so that vibrations of one tend to cancel the vibrations of the next. Furthermore, any large separation of the atoms of one large molecule from the atoms of another large molecule will involve simultaneous separations of substantially all the atoms of one chain from the others. Because the vibrations are random, such simultaneous separations of many atoms in a cooperative direction are rare.

The forces between molecules are of several types:

London Dispersion Forces: These are a result of interaction of fluctuating dipoles produced by motions of the valence electrons of the atoms in one molecule with the polarization they produce in a neighboring molecule. An attractive force is produced which diminishes with the sixth power of the distance. At very close approach, there is a repulsion of electron clouds of the atoms which varies inversely with the twelfth power of the distance. As a result, molecules are held at 3-5 A apart and the energy of total separation is 1 to 2 k cal/mol. This is an important source of binding between molecules - the only one present in hydrocarbons.

Dipole - Induced Dipoles - Permanent dipoles in molecules induce opposite dipoles in neighboring molecules. The resulting attraction is usually of unimportant magnitude.

Permanent Dipoles - Neighboring atoms of different electronegativity have permanent electric dipoles. The dipole moment is a measure of the charge separation and the distance. Strongly polar molecules have strong attraction for each other by this mechanism.

Hydrogen Bonds - Special attractive forces occur between atoms attached to hydrogen and electronegative atoms containing unshared electrons (e.g. the oxygen atom of a hydroxyl radical or the nitrogen atom of an amine radical). The hydrogen is shared to some extent between the electronegative

atom and the other atom attached to hydrogen. The stronger the electronegativity of the electronegative atom, the stronger is the hydrogen bond. In simple compounds, (e.g. water, acetic acid, and methanol) hydrogen bonds tend to reduce volatility and increase viscosity. In polymers, hydrogen bonds restrict motion.

Alcoholic hydroxyls or water tend to form dimers and large aggregates, molecules of a sort. Carboxylic acids tend to form dimers.

Ionic Bonds - Ionized carboxylate groups in polymers are held together by the counterions which are attracted to more than one carboxylate group. Such bonds are made labile with temperature, by strongly polar solvents, and by sufficient added low-molecular-weight electrolyte.

3-5 MOLECULAR RESPONSE OF THE BINDER TO FORCE

The molecules of a binder are most often associated together as a liquid at some time before hardening. The molecules usually form intertwining threads, much like a tangle of short lengths of string. Unlike the situation of a tangle of string, the molecules, not really touching each other and in constant small scale vibration and rotation, are free to respond to a consistent tension on one molecule by pulling slowly out of the mass. Real knots cannot occur in masses of linear or branched molecules. The rate of movement of a molecule out from a mass of molecules will naturally depend on the forces of attraction between the molecules, on the amplitudes of vibration and rotation (temperature), and the force applied. Pulling a strand of cooked spaghetti from the mass responds similarly to rate of application of force. For rapid applications of force there will not be sufficient time to displace all the intertwining strands and the mass will behave as though it had knots. The force will be great and the strands will break.

The response of a binder molecule to mechanical forces involves the motion of the molecule through a mass of molecules. Usually the forces are applied simultaneously to many molecules and the actual resultant motions are therefore somewhat complicated.

At temperatures where the binder is considered stiff, the application of small forces causes distortions of the molecules and small scale molecular motions with relatively little motion of slippage of one chain past another. The molecules will return more or less to their original positions by thermal vibration and intermolecular forces on removal of the force. The binder will act, for small distortions or rapid vibrations, in an elastic manner. Larger scale deformations (which may be possible only at higher temperatures without fracture) cause slippage of molecules past each other and the original shape does not return.

At higher temperatures, molecules move more, and the spaces between them are larger. Accordingly, at sufficiently high temperatures they slide past each other as in common liquids and there is no restoring force in molecules without cross-links. The force exerted to slide the molecules past each other is dissipated as heat. The mechanical response is largely viscous with a negligible elastic component. Crosslinking introduces restoring forces and therefore elasticity.

At practical use temperatures the response of the binder is said to be viscoelastic.

3-6 FUNCTIONS DESIRED OF BINDER IN ORGANIC COATINGS AND THE ASSOCIATED PHYSICAL PROPERTIES

3-6-1 Strength

The binder must be sufficiently elastic to withstand the dimentional changes of the substrate during use without the formation of cracks. It must be hard enough to withstand in tolerable fashion the effects of abrasion and indentation usually met in shipping, handling and normal use.

The strength properties are measured in a variety of ways. One obvious way is to subject the coating on its substrate to the service conditions and for the lifetime expected, and to observe cracks and other evidence of insufficient strength. Although this is the ultimate test, it is often time-consuming and expensive. Other tests are therefore used that yield indications of final performance of the coating.

Tensile strength, elongation, modulus of elongation, and creep describe properties of coatings which are pertinent to mechanical integrity of the films in service.

A film of the coating is formed on a plane substrate to which it does not adhere. The film is peeled from the substrate and test specimens are cut from it. The test specimens (which might be three inches long, one inch wide and two thousandths of an inch thick, for example) are mounted in the jaws of a machine which stretches the specimen parallel to its length at a controlled rate and measures the force applied. The data of force applied per sq. in. cross-section, the "stress", are plotted against fractional elongation, called "strain". Various kinds of curves are obtained depending on the nature of the film, the rate of elongation and the temperature. The "initial modulus" represents the stiffness of the film in response to small forces and is the slope of the stress/strain curve at low values of strain. For small forces and extensions, much of the strain is recovered when the stress is removed.

While the film is being stretched there is generally some viscous flow within it - the molecules do not return exactly to their original positions when the stress is relieved. When a force is applied to stretch a film and the dimensions are then held constant there will always be a gradual decay of stress as molecules gradually move (Fig. 3 - 2). If the molecules are constrained by cross-links and "knots" so they cannot easily move relative to each other, there is correspondingly less stress-relaxation. Creep refers to the gradual change of dimensions on application of a steady force. (Fig. 3 - 3).

Beyond a certain strain the film breaks. The tensile strength and the degree of elongation are less than would be predicted from a uniform material of the internal constitution on the basis of intermolecular and intramolecular forces. The breaks are therefore presumed to be initiated at flaws in the specimen, readily introduced in sample preparation or as impurities.

The more brittle the film, the harder it is to avoid accidental damage during the test of elongation. When figures are given of elongations as small as 1 to 5 percent, they should be regarded with extra suspicion. Because the molecules of a binder may not return to their previous positions when stress is relaxed, repeated stress may cause gradual drifts of molecules away from certain portions of a film and result in weakness and eventual breakage.

The elongation required of a finish before rupture depends on the dimensional changes required of the substrate at service temperatures. Thus, finishes for steel will require only the elongation and compression experienced during temperature changes, while those for wood require the elongation experienced during swelling of wood and coating by water, and finishes for rubbery plastics require the still higher elongations required of the rubbery plastics themselves.

Wood expands differently on immersion in water depending on grain direction and the plane of the annual rings. Boards are cut roughly parallel to the annual rings. Measurements of swelling of wood in water showed an expansion of only 0.1% - 0.4% in length and 2 - 4% in width. A paint film attached to wood must be capable of withstanding much larger elongations and shear between adjacent fibers.

Linear elongation for a finish for automobiles might be of the order of 5-10%, for formable finishes about 70%, for rubbery plastics about 200%.

The actual elongations experienced by surface films are usually two-dimensional, and the one-dimensional values obtained in the usual tensile tests are only approximations. Forming machines, which test the elongation of a film attached to steel or aluminum by pressing a dimple in the coated metal, actually measure the response to a two-dimensional strain under conditions more nearly approximating service conditions.

The measurement of a detached film is likely not to yield the same results as the measurement of an attached film - particularly if the film is attached by a strong bond to a metal. Thin films of brittle paint films on steel appear to be more flexible in bending and "bumping" tests than thick films. Apparently the stiff strong metal resists the localized expansion preparatory to crack formation.

Recent experiments with multiple layers of plastics by W. J. Schrenk and T. Alfrey, Jr., Polymer Eng. and Sci. 9 393 (1969), (See Fig. 3-4) are in accord with this idea. They made films of thin alternate layers of two plastics differing in elongation characteristics. They demonstrated that the elongation of a hard brittle plastic can be increased many-fold by sandwiching it between two layers of a strong high elongation plastic to which it has good adhesion.

The extrapolation of free film data to thin films on metals should be cautious.

The usual lacquer is applied to a solid substrate from solution in a solvent. At some point during evaporation of the solvent the motion of polymer molecules becomes restricted, even as the solvent molecules diffuse between the binder molecules and evaporate. The adhesion to the substrate prevents motion parallel to it during the shrinkage process and all the shrinkage occurs perpendicular to the substrate. The effect is the same as though the binder were allowed to dry as a free body away from the substrate and then stretched to the dimensions of the substrate.

As a result attached lacquer films are under tension and are oriented to some degree.

Orientation can also be introduced by stretching a coating on its substrate by compressing it, or by blowing bubbles in it while in a sufficiently viscous condition.

3-6-2 ADHESION TO SUBSTRATE

Usually, except in the case of strippable coatings, it is hoped that the coating will adhere to the substrate with forces that do not permit its clean detachment by application of tension or shear. An adhesive strength larger than the cohesive strength of the coating is desired. To obtain the desired adhesion, one (usually unsatisfactory) way is to soften the coating sufficiently.

Much effort has been spent to relate molecular structure to cohesive and adhesive behavior. However, cohesive strength, and adhesive force too, are not related easily to any practical mechanical test. The force required to rupture a specimen depends on the way the bonds are broken - whether they are broken one at a time or almost simultaneously. The energy required to rupture a specimen, another criterion of strength, is divided between the energy used in distorting the entire specimen and that required to merely rupture molecular bonds at the breaking place.

For many years people have been looking with no avail for some fundamental measurement of adhesion in terms of force or energy per unit area which could be correlated with practical observations of adhesion and detachment. Instead, there are a series of different laboratory tests each of which measures "adhesion" in terms of the particular mixture of adhesion, distortion, flaws, etc. that affect the test.

For the laboratory measures of adhesion there are a variety of measures, peel tests, cross-hatch tests, knife scratch, etc. and they are suitable and reproducible enough to measure performance under conditions approximating the test.

Nevertheless, there exist measurements and theories related to the fundamentals of cohesion and adhesion that people are confident bear on the problems.

The bulk properties i.e. the cohesive properties of the sample are important, particularly for those cases where a good bond is formed, i.e. there are no weak impurities which concentrate at the interface.

However, to form a good bond, the molecules of the binder must reach the surface. The rheology must therefore be important. When the binder reaches the surface it must bond to the surface with sufficient force. Thus, adhesion is related to absorption of binder molecules. Surface energy and wetting are therefore also involved.

A good definition of the nature of a surface is hard to find except in rare instances. Practically all surfaces are contaminated with foreign material, the atomic arrangements are not homogeneous and dislocations and flaws exist even in zone-refined crystals. All the useful metals are coated with oxide, hydroxide, carbonates, etc.

Perhaps as a result of this complicated situation the art of adhesion was developed by formulators who developed a useful folklore about adhesion, some which may be true. Roughness, once thought very important, hardly appears to count, although in some cases grit-blasting, as used in coatings of polytetrafluoroethylene, and roughness as distinguished from cleanliness appear to be functionally useful. Undercutting of the surface by grit may be an effective mechanism. Softening of a surface by a solvent in preparation for coating with a resin is largely a fairy tale. The term usually used is "bite". However, casual wiping of a surface of a polymer is sometimes effective in making a subsequent coat of paint adhere to it usefully. A notable example exists in the recoating of certain alkyd/melamine enamels, where sanding is usually recommended to obtain adhesion of a subsequent coat of paint.

There are some chemical binders that manage to achieve the status of adhesives because they tend to adhere to many surfaces. As coatings they do the same. Notable examples are the epoxy resin group of binders and the thermosetting urethanes which are often used in small concentrations to improve adhesion. See Table 3 - 1.

Primers, or coats of paint applied to a surface in preparation for the attachment of a second coat of paint, can sometimes be formulated without pigment or with a low level of pigment. When little or no pigment is used, however, the primer will be useful only for a small range of topcoats. Paints formulated with enough pigment to yield rough surfaces have a larger range of suitable topcoats. Sanding them increases the range. It is probable that organic binders stick better to hard inorganic surfaces than to other organic binders.

Binders are often formulated with small amounts of special adhesion - promoting groups attached to the molecules. Notable among these are carboxyl, hydroxyl, amino, and the reaction product of carboxyl with ethylene or propylene imine. Notable examples are a copolymer of vinyl chloride with 2% maleic anhydride, copolymers of methyl methacrylate with 2% methacrylic acid. Adhesion to paper and wood seem to be favored by nitrogen containing resins.

TABLE 3 - 1

ADHERENCE TABLE

Adhesive resin	Adherence to				
	Paper	Wood	Metal	Ceramics	Rubber
Alkyd	6	7	5	6	7
Cellulose nitrate	5	3	1	5	5
Epoxide resin	10	10	8	8	8
Furane resin	8	7	1	8	7
Melamine resin	10	10	2	2	2
Phenolic resin	9	8	2	6	7
Polyester, unsat.	6	8	2	5	7
Poly(ethyl acrylate)	3	4	3	5	6
Poly(vinyl acetate)	8	7	7	7	3
Poly(vinyl chloride)	5	7	6	7	6
Polyvinylidene copolymer	4	7	6	7	7
Silicone, thermosetting	4	6	7	7	8
Urethane, thermosetting	8	10	10	9	10

[a] Rating: 1, poorest or lowest; 10, best or highest.

From Patrick - Treatise on Adhesion and Adhesives Vol II, p. 5 - Marcel DeKker Inc. New York (1969)

3-6-3 Barrier Properties

Generally in the coatings industry, it is desired to keep particular materials, e.g. water, air, carbon dioxide, or flavoring materials from penetrating a film. Polymers vary considerably in their ability to absorb and transmit liquids and vapors.

In general, small molecules can permeate through a film by a variety of mechanisms.

1. Pores - The film may consist of unevenly spaced molecules with many relatively large unobstructed paths through it. In this case the selectivity depends on molecular size and shape but little chemical selectivity.

2. Swelling - The polymer may absorb water (or other solvent) into its already dense structure and swell. In this case the water molecules solvate, or are associated with, polymer molecules. The water molecules diffuse through the swollen polymer by a process of small discrete displacements, so that a water molecule need move a short distance while displacing another water molecule which moves on to the next position.

The rate of permeation P' of a film by a gas is directly proportional to the concentration gradient $\frac{dc}{dt}$ and diffusion coefficient D of the gas, and to the area of the film A.

Accordingly: $$P' = \frac{DA dc}{dt}$$ Eq. 3-1

If the concentration gradient in the film is uniform the permeation is proportional to the difference in concentration on both sides of the film.

The permeability describes the rate of permeation at a fixed difference of concentration.

For a group of films laminated together, the overall permeability P is calculated from that of each of the layers:

$$\frac{t}{P} = \frac{t_1}{P_1} + \frac{t_2}{P_2} + \frac{t_3}{P_3} + \text{etc.}$$ Eq. 3-2

P = Permeability of composite
t = Thickness of composite
t_i = Thickness film i
P_i = Permeability of film i

Permeation rates for water through polymer films saturated with water vapor on one side and dry on the other support the idea that highly polar materials tend to transmit water. See Table 3-2.

TABLE 3 - 2

Transmission Rate of Water Thru Polymers [Q in g mil/(m^2)(day)]

	Temp.	Q
Cellulose	35°C	1600
Polyvinyl Alcohol	39.5°C	1500
Polyethylene-low density	"	17
Polymethyl methacrylate	"	150
Polyacrylonitrile	"	180
Polyvinylidine chloride	"	4.8
Polytetrafluoroethylene	"	4.8

(Data from H. Yasuda - Polymer Handbook - Brandrup and Immergut, Interscience, New York 1966, p.V-13.)

Temperature increases permeability exponentially according to the relation:

$$P = P_o\, e^{-Ep/RT} \qquad \text{Eq. 3-3}$$

Where P is a constant, Ep is the activation energy of permeation; T is the absolute temperature; R is the molar gas constant.

Permeability is reduced by increasing the density of the binder (through crystallinity and orientation) and the use of fillers. Cross-linking of polymers tends to reduce permeability, particularly for larger molecules. Permeability is increased by use of most plasticizers (including water).

Density of polymers is affected by mechanical history and by the structure introduced during drying of a polymer film. Weak solvents evaporated from a film at low temperature tend to leave loose structures which are then more permeable than the structures left when stronger solvents are used.

Permeation of water through films is particularly important in connection with protection of water-sensitive substrates such as wood or steel from water. The coatings are never impervious to water, so that eventually water penetrates to the surface. The damage caused by the water depends on the adhesion of the surface coating to the substrate, the presence of salts or other water-soluble solutes of low permeation rate in the coating, and the modulus of elongation or stiffness of the coating.

Osmotic pressure is the result of higher concentration of water-soluble material in the film than in the water in contact with it. It results in blisters in the film provided that the osmotic pressure exceeds that which can be resisted by the modulus of the film. During penetration of the film by water there is also permeation of the soluble substances to the outside. If the soluble substances move slowly compared with water a large amount of water will penetrate and make a blister or bubble of aqueous solution inside the film or at an interface. Blistering can be reduced by increasing the rate of extraction of water-soluble components or by increasing hardness or stiffness of the film.

3-6-4 Pigment Dispersion

Pigment particles usually have greater attraction for each other than for solvents or most polymers. Surface-active agents are often added so that pigments can be held apart by the suspending medium or vehicle. These may be of various types, but the most convenient is often a polymer with polar substituents. This surface active agent is used in substantial quantity between 2-100% of the binder. It coats the pigment and makes it act as though the pigment particle were a large molecule of the surface active polymer.

3-6-5 Durability

The binder is often the limiting factor in the life of the coating. Various reactions occur with the environment to shorten the life of the binder. These will be discussed in Chapter 7.

3-6-6 Electrical Properties

Electrical components, particularly wires, are coated with electrical insulation to prevent the flow of electric current between contacting adjacent components.

The electrical conductivity of a binder for a unidirectional current depends largely on the presence of water or other conductive impurities in it. These ionic carriers conduct by movement of ions through the binder and these ions are discharged at the electrodes. The movement of these ions depends on the viscosity of the binder, which can be changed by plasticizers or by temperature.

For use in electric circuits at high potential, insulation must be resistant to the chemical effects of the corona or the ionized air which surrounds high potential gradients. Such air forms ozone, particularly reactive towards binders with unsaturation (like rubbers).

The flow of a strong electrical discharge as with a spark, through a binder will damage the binder by heat and by ionization and will develop a carbonized track along the path of conduction. Some do not develop a carbon track along the discharge path readily and are therefore sometimes more useful.

Electrical insulators become polarized in an electric field and this involves the motion of induced dipoles or permanent dipoles in the polymer. Such dipoles can be frozen into a polymer and form electrets, permanent electric dipoles corresponding to permanent magnets. The dielectric constant increases as the dipoles are more responsive.

The motion of the dipoles takes some energy from the electric field. The amount depends on the displacements, and on the attached atoms or the neighboring unattached atoms that are moved. In an alternating field there is a corresponding alternation of the dipoles and a constant drain of energy. In a unidirectional field the drain occurs only twice - on application and removal of the field. As a result, insulation for alternating current devices heats up by polarization effects. The amount of heat depends on the frequency, the magnitude of the electric potential

and the response of the atoms of the binder to the forces. If the binder is extremely rigid and has high resistivity, for example porcelain or mica, the response of the binder will be small and the energy losses low.

Because different segments of a polymer chain respond differently to mechanical and electrical forces by motions which absorb energy (polymers are generally poorly elastic) there will usually be a dependence of loss on electric frequency and temperature. If the main chain of a polymer carries the dipoles, the mechanical losses and the electrical losses will both be greatest near the glass transition temperature. If the side chains carry the dipoles, the loss maxima will occur at lower temperatures corresponding to immobilization of the side chains.

Sometimes an electrically conducting coating is desired. Since ionic conduction always results in oxidation at one electrode and reduction at the other, ionic conduction is not usually desirable. Instead, electronic conduction through conducting particles - metal, graphite, MnO_2, Fe_3O_4, must be used. To be useful, the particles of the electronic conductor must be in close proximity to each other, within a few angstrom units, to permit electrons to flow across the gaps. Since high concentrations of pigment and correspondingly low concentrations of vehicle must be used, the binder must be particularly elastic and strong if the film is to have practical strength.

Magnetic tapes have coatings containing dispersions of magnetic material in a binder applied to a strong flexible film. Although particle-to-particle contact is not particularly desired, it is most important to have a high concentration of magnetic particles to obtain high magnetic response. Again high elasticity and toughness are required.

3-7 EFFECT OF TEMPERATURE ON TECHNICAL PROPERTIES OF BINDERS

Increase of temperature increases the mobility of chain segments and the effective volume they occupy; the spaces between molecules increase on the average. An increase of temperature therefore reduces the resistance to flow of the polymeric materials used in binders. As the free volume increases larger and larger segments of the molecule are forced to move. If an amorphous, un-crosslinked polymer film is stretched, and the force required is measured as a function of elongation, curves are obtained as in Fig. 3 - 1. If the stiffness or modulus of elongation is measured as a function of temperature, a curve is obtained like that of Fig. 3 - 5.

In the glassy region of the curve the polymer is hard and brittle. It is primarily elastic until it breaks at low elongation. In the leathery and rubbery regions it is softer and strong. It has elastic and viscous properties. At significantly high temperatures it is liquid and has important viscous properties with little elasticity. In this region molecules slide readily past each other with negligible restoring force.

If the film has crosslinks in it the curve of molulus vs. temperature shows no sharp drop corresponding to the liquid flow region for the uncross-linked polymer. The rubbery region then extends until decomposition occurs.

For chains to move past each other at a perceptible rate in response to a mechanical stress the motions of large segments (say 10-40 atoms long) is needed. For these to occur there must be at least temporary openings of sufficient size. These occur by any processes which increase the space between the large molecules - e.g. heat, or plasticizers and the natural random vibrations associated with temperature.

3-7-1 Glass Transition

Many liquids, including many polymers used as binders, glycerine, and glass usually cool to hard yet non-crystalline substances. They are said to be glasses. While the liquids harden to practical solids, there is no latent heat of glass formation and no sharply defined transition temperature.

The glassy quality in polymers is a result of immobilization of segments of the molecules above a certain size (10-40 chain atoms), while some smaller segments can still move. The glass transition temperature is a strong function of chain stiffness because stiffness immobilizes the structure.

There is some variation of glass transition temperature of polymers with their molecular weight. In general, higher molecular weight results in higher glass-transition temperature. The chain ends, being free at one end, are higher in mobility than segments in the middle which are held at each end. Chain ends are more frequent, therefore more important, at low molecular weight. The glass trnasition temperature, usually abbreviated as Tg, is related to the molecular weight by an equation which is in accord with that idea.

Eq. 3-4 $$\frac{1}{Tg} = \frac{1}{T} + \frac{K}{\overline{Mn}}$$

Tg = Glass Transition Temperature

T = Glass Transition Temperature at high molecular weight.

$\overline{Mn}$ = Molecular Wt. - number average

Eq. 3-5 $$Tg = T + B/\overline{Mn}$$

B,K = Constants

Above a molecular weight of about 20,000 the Tg changes little with temperature.

Plasticizers - Low molecular weight, non-volatile solvents also reduce the glass transition temperature by increasing the segmental mobility.

Arrangements of atoms affect stiffness of the chains. Mere bulkiness of groups attached to a chain of atoms restricts their rotations. Large ring structures and ladder - like structures, particularly stiff aromatic nuclei, increase stiffness. Polar groups with strong relative attractions also increase stiffness. These stiffening influences therefore have the effect of increasing the Tg.

The degree of segment-mobility which is significant depends on details of the test applied, in particular the magnitude of the force applied or the rate of distortion of the polymer. The glass transition temperature therefore is actually a range of temperature of several degrees depending on many details, particularly rate of application of force.

The glass transition temperature depends mainly on chain flexibility, but like crystalline melting point, it depends on the forces between molecules and on free volume or mobility. Therefore, it is not surprising that glass transition temperature and melt temperature are related; When there is a crystalline melting point it usually is above the glass transition temperature.

At the crystalline melting point there are sharp changes in density, specific heat, modulus and solubility. At the glass transition temperature there are no such sharp changes in the values of specific heat, density or modulus but there are changes in the temperature variation of these. The measurement of the temperature coefficients yields values of Tg.

The glass transition temperature is associated with various practical properties of the binder.

a) Flexibility - Below the Tg polymers are brittle towards extension.

b) Cracking by Solvents - Below the Tg the polymers are strained. They are apt to crack on exposure to solvents before dissolving or swelling much.

c) Sticking of Polymer Powders - At some critical temperature near the Tg, powders will stick and lose their flow properties.

d) Coalescence of paints applied from suspensions or dispersions. The low temperature coalescence limit is called the critical film forming temperature. Below this temperature coatings applied from dispersion dry to powders rather than films.

3-7-2 Measurements of Transition Temperatures

a. Torsional Pendulum

If a sample of polymer is subjected to small alternating mechanical stress, for example by its use as the suspension in a torsional pendulum, it acts somewhat as an elastic structure, and the pendulum tends to return. At the same time energy is lost in the slippage of molecules past each other so that the polymer heats up. If the pendulum is free, the amplitude of the oscillations will diminish, and the rate of decrease is a measure of the mechanical loss at that temperature. The loss will be a function of temperature and will be a maximum at the glass transition temperature. Other maxima in loss will show up at temperatures corresponding to the immobilization of side chains or small segments.

The elastic modulus, which determines the frequency of oscillation of the pendulum (stiffer polymers yield higher frequencies), will undergo an inflection at the glass transition temperature and at other transition temperatures as well.

b. Temperature Coefficients of Density and Other Properties

The rate of change of density and of specific heat with temperature changes in the region of the Tg. Careful measurements therefore of density (or refractive index which is sensitive to density), or of specific heat as a function of temperature, show changes of slope at the Tg.

3-7-3 Time-Temperature Superposition

Motions that occur in samples of polymers are observed conveniently only over the relatively short time interval, from a second to 100 hours, for example. In any one plastic the internal motions may become too rapid at high temperatures and too slow at low temperatures for convenient measurement by the methods comtemplated.

Un-crosslinked polymers tend to behave similarly in the respect that their differences can be compensated by temperature change or by changing the rate of application of forces. Thus, hard, brittle polymers are softened by increase in temperature to respond to stress like soft, flexible ones. A single master-curve can be constructed for a polymer to include the data for a wide range of temperature and rate.

The preparation of a master curve for polymer is shown in Figure 3-6. In general polymers can be compared with each other at their glass transition temperatures and equal logarithmic changes of absolute temperature will produce approximately equal changes in mechanical properties.

3-8 FILM FORMATION

1. Non-Reactive Binders

a. Soluble

A typical example is a lacquer containing as binder high molecular weight cellulose acetate butyrate dissolved in a highly volatile ketone solvent. The solution is viscous because of the dissolved high molecular weight binder. Applied to a surface, the coating smooths out due to surface tension, while the solvent gradually evaporates. As evaporation proceeds, the coating becomes more and more viscous as polymer particles interfere with each other's motions, and finally, when the film contains only a small amount of solvent, say 10-30%, it will be hardened to the point where no substantial flow will occur.

Further evaporation of solvent will cause shrinkage. Adhesion to the substrate will resist reduction in surface area and cause tension in the film. Loss of thickness alone will take up virtually all the shrinkage. Beyond a certain point, the shrinkage will cause tensile stresses which will be relieved only slowly by molecular motions, and the film which results will be hard and under a gradually lessening tension as the molecules slowly flow.

b. Non-Soluble

Are made typically from an aqueous dispersion of a synthetic polymer latex, e.g. a rubber latex. The binder consists of spherical particles of rubber of 0.2 microns diameter. The rubber particles repel each other in the aqueous suspension because they are all electrically charged with the same polarity. Although the rubber is of high molecular weight and the concentration of rubber is high, the aqueous dispersion is of low viscosity - because the molecules of rubber are not dispersed and extended in the water.

When the coating is applied the water starts to evaporate and the particles of rubber get closer together. Eventually they touch each other while some water remains in the interstices. Evaporation of additional water results in a compression of the mass of latex particles. If they are soft the latex particles will coalesce into a film. If they are high in molecular weight the film will be strong.

Another important example is a fine-particle dispersion of a high molecular weight binder and pigment in an organic solvent mixture which swells the particles of binder but does not dissolve them. The solvent mixture is designed so that the less volatile components are strong solvents for the binder. Application of the coating is at low viscosity because the polymer molecules are not extended into the solvent phase. After application the poor solvents evaporate first leaving behind solvents that dissolve the binder and cause its molecules to extend and fill the volume. The remainder of the film forming process is like that of a soluble non-reactive binder.

2. Reactive Binders

a. Soluble binders of lower molecular weight than needed for strength are applied from solution using enough solvent to accomodate the mode of application desired. Reactions are caused to occur by heating, exposure to air, exposure to water vapor, high energy radiation, etc. Sometimes a reactive solvent is used which forms part of the binder when it is reacted after application. In that case little solvent need be evaporated during the film formation.

b. While the low molecular weight of reactive binders allows the use of relatively small quantities of solvents, it is sometimes desired for(air-pollution control, for example) to use solvents which are not particularly good solvents for the binders. In such cases the binder is often used in the form of a suspension in mixtures of less volatile good and more volatile poor solvents, and the binder dissolves as solvent evaporates. Finally the reactions which increase the molecular weight are allowed to occur.

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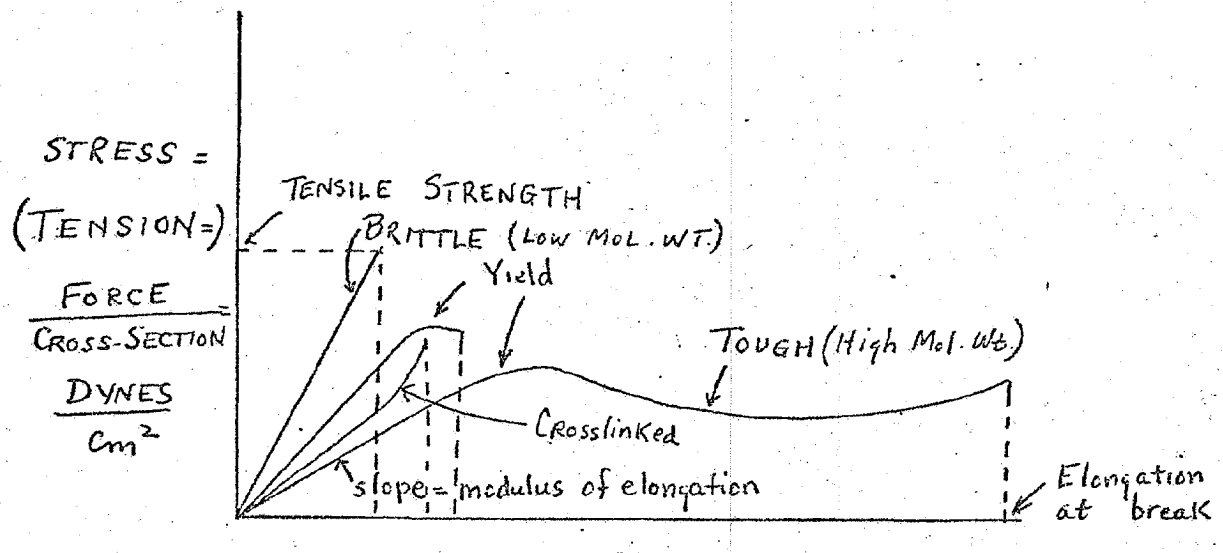
FIG 3-1 - FOUR TYPICAL STRESS-STRAIN CURVES



STRAIN = ELONGATION = $\Delta L/L$

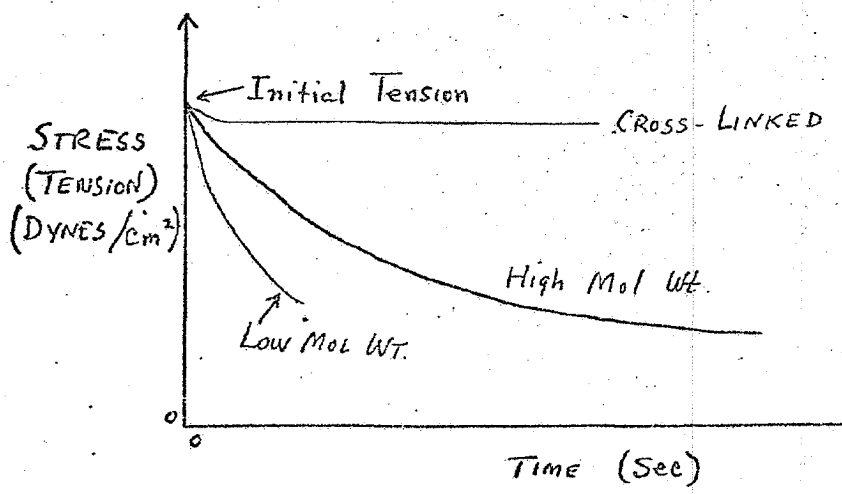


FIG 3-2 STRESS-RELAXATION AT CONSTANT LENGTH

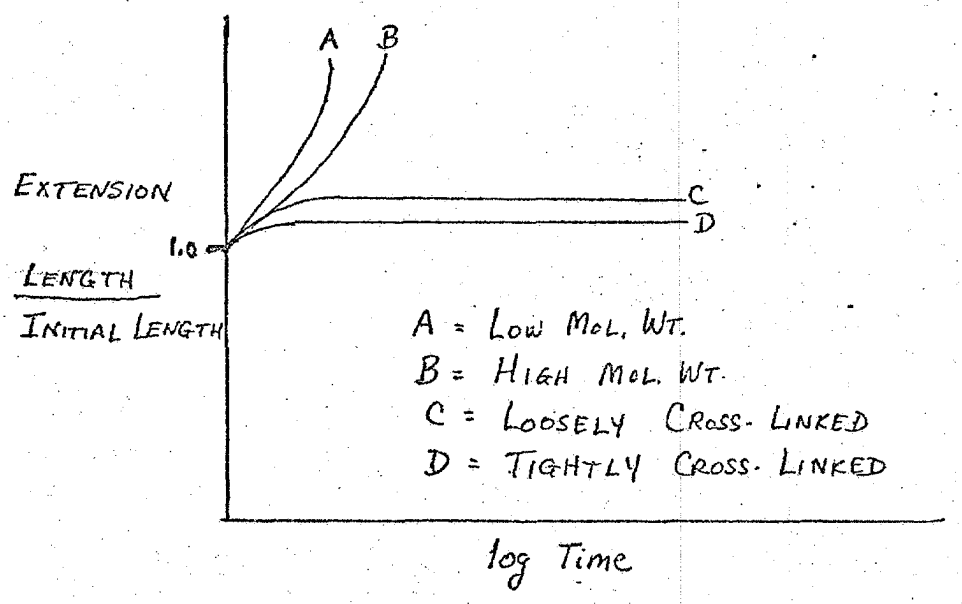


FIG 3-3 EXTENSION AT CONSTANT STRESS FOR FOUR POLYMERS

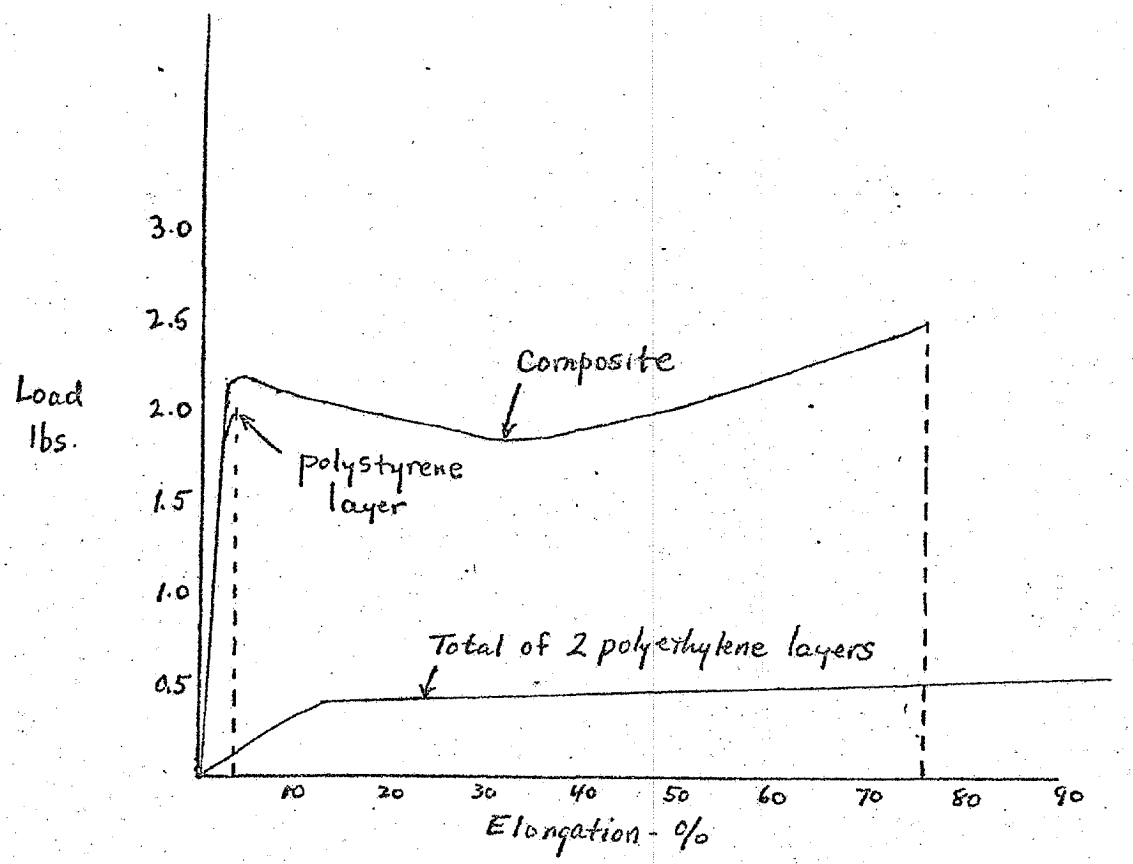
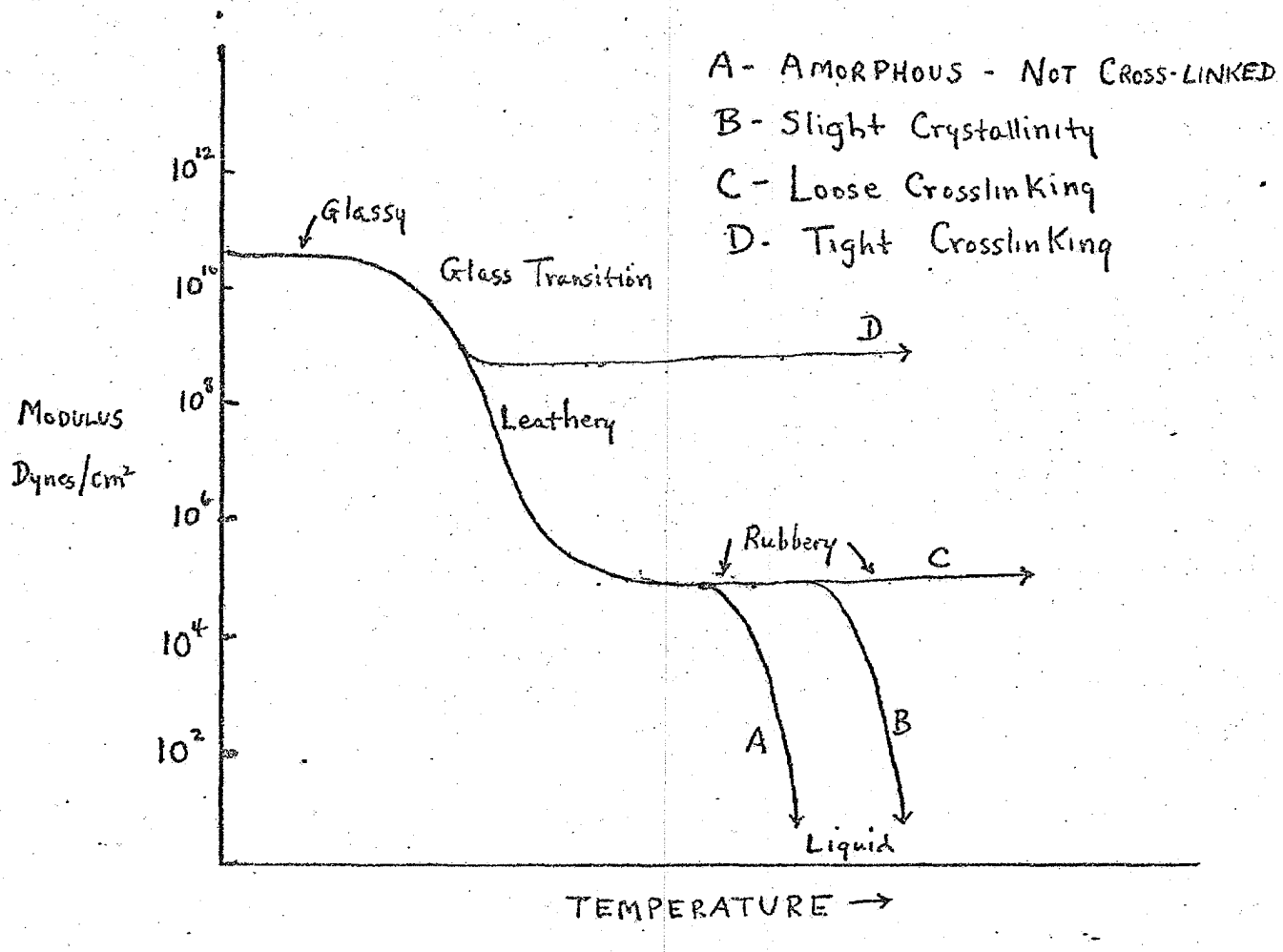


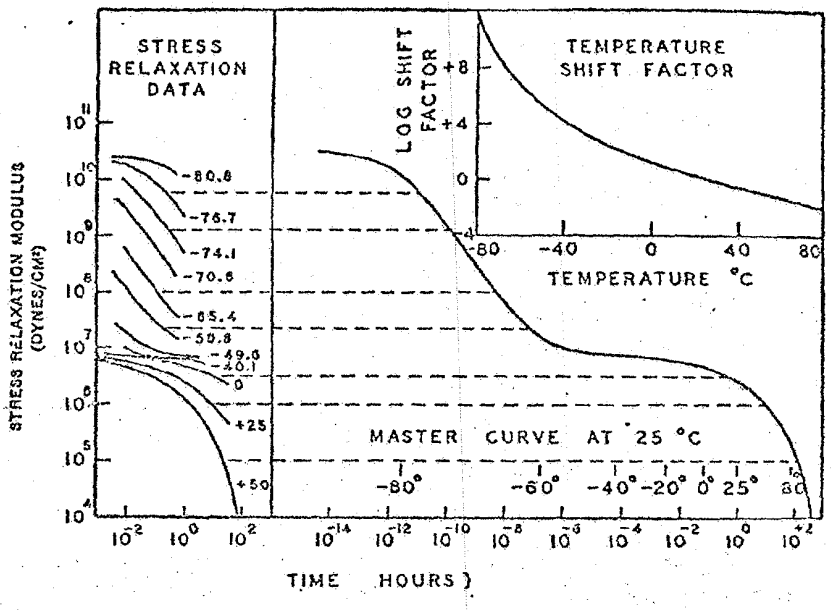
FIG 3-4 - Stress - Strain Diagram for a 3 Layer Film - Polyethylene - Polystyrene - Polyethylene

(W. J. Schrenk and T. Alfrey - Polymer Eng. & Sci 9 396 (1969))



EFFECT OF TEMPERATURE ON STIFFNESS

Fig 3-5



~~Figure 1-25.~~ Time-temperature superposition principle (ref 117).

Time-temperature superposition principle illustrated with polyisobutylene data. The reference temperature of the master curve is 25°C. The inset graph gives the amount of curve shifting required at the different temperatures.

From Deanin - p. 164

Fig 3-6 TIME - TEMPERATURE SUPERPOSITION

E. Catsiff and A.V. Tobolsky - J. Coll. Sci 10 375 (1955)
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BINDERS - CHEMICAL STRUCTURE AND SYNTHESIS

CHAPTER 4

4-1 SYNTHESIS OF BINDERS

The molecular weight needed in a dried surface coating for strength exceeds about 50,000 and, for some materials, it is in millions.

Certain compounds of low molecular weight on the order of 100-300 can be applied to a substrate surface as fluid liquids and converted on the substrate to the high molecular weight needed by chemical reactions induced by oxygen, ultra-violet radiation, electron irradiation, etc. In many cases it is desirable, in order to meet application requirements, to apply the binder in the form of a product of intermediate molecular weight on the order of 1000-10,000, to be converted on the surface to the required molecular weight. In still other cases, it is desirable to apply the binder at the final high molecular weight.

The higher molecular weights needed are conveniently achieved by combining the small molecules comprising one compound or a small number of compounds. Polymerization refers to processes whereby the small molecules - monomers - are built up into large ones - polymers.

4-1-1 Common Types of Compounds for Polymerization

a. Through Multiple Reactive Groups - The reaction of a dihydric alcohol with a dibasic acid which occurs liberating water, results in the formation of a polyester. Its molecular weight can be adjusted by the ratio of the alcohol and acid and by the extent to which the reaction is allowed to proceed. Reaction of diamines with diacids or of diols with diisocyanates are other examples of this type.

b. Through Double Bonds

1. Vinyl Polymerization

Under suitable conditions of temperature, pressure, and catalysts, ethylene polymerizes, as do many other compounds containing a single terminal double bond to form long-chain compounds.

2. Conjugated-Diene Polymerization

Generally the conjugated structure acts like a single double bond with addition either in the 1, 2, or 1, 4 position. Because of the presence of a double bond in the chain when the addition is of the 1, 4 type, cis and trans configuration of the chain are found.

3. Hetero-double Bond Polymerization

The polymerization of formaldehyde to form a polyether by anionic or cationic initiators and the polymerization of isocyanates are examples.

c. Ring-Opening

Cyclic compounds containing a heteroatom often can be made to form a chain e.g. ethylene oxide polymerizes to form a linear polyether, polyethylene glycol, $- [CH_2 - CH_2 - O]_{\overline{n}}$

4-2 STEP-GROWTH POLYMERIZATION

Step-Growth Polymerization is typified by esterification of a dibasic acid with a dihydric alcohol to form a polyester. As each monomer unit is added, the polymer formed is no more likely to react than a previously unreacted monomer unit. As a result, the monomers virtually disappear before any substantial fraction of high molecular weight is formed. There is considerable reaction between polymer molecules containing reactive chain ends until the reactive chain ends disappear or conditions are changed so that the reaction is stopped. The average molecular weight tends to be low until reaction of functional groups uses them up.

4-3 CHAIN-GROWTH POLYMERIZATION

Chain-Growth Polymerization is typified by free-radical polymerizations of olefinically unsaturated monomers, and involves the addition of a monomer molecule to a free radical to form another free radical available to add another monomer unit, and so forth. A monomer unit, having added a free radical, is overwhelmingly more reactive than the other monomer units. Free radicals needed to initiate chains are available from the decomposition of a variety of initiators and are usually in small number. Once a free radical has formed and reacted with a monomer unit the molecule continues to grow until all the monomer is gone or until a side reaction results in either chain transfer, termination by combination of two radicals, termination by transfer of a hydrogen atom (disproportionation) or reaction to form an inactive radical. During almost the entire course of the polymerization process, the reaction vessel may contain substantial quantities of monomer along with polymer of high molecular weight.

4-4 FUNCTIONALITY IN CHAIN-GROWTH POLYMERIZATION

High molecular weight, $10^4 - 10^7$ or so - is readily achieved in chain growth polymerizations using pure divalent monomers, for example, methyl methacrylate, even at low degrees of conversion. If a quadrivalent monomer (for example glycol dimethacrylate) is mixed with a divalent monomer, the first chains produced will have reactive unsaturation, one for each molecule of the glycol dimethacrylate incorporated in the chain. This unsaturation in the chain is about as free to react as the unsaturation in unreacted monomer units. New chains of polymer forming will include unsaturation from these partly reacted dimethacrylate units, and branched and cross-linked polymers will be formed. The amount of polyvalent unsaturation that will produce cross-linking depends on the kinetic chain length, and the average number of monomer units that combine before a termination reaction under the specific reaction conditions. Under typical reaction conditions for an acrylic resin only about 0.1% of a tetravalent unsaturation is sufficient to yield cross-linked products.

4-5 FUNCTIONALITY IN STEP-GROWTH POLYMERIZATIONS

In the manufacture of large molecules by the combination of small ones, their valency - the number of places on each of the small molecules at which they join - determines the maximum chain length, the formation of branches, and cross-linking.

If each of the small molecules has exactly two sites for connection they may unite in a chain limited in length only by the time allowed for the combination reactions to occur. If almost all the molecules are divalent and occasional ones are monovalent, chains will be long and the attachment of a monovalent unit ends a chain at that point.

A branch results when a molecule which is trivalent (or polyvalent) unites in the chain. Mixtures of bivalent and multivalent functional molecules result in cross-linking when sufficient reaction has occured. The attachment of sufficient monovalent molecules can prevent cross-links from forming. A cross-linked polymer can be considered as a network of long chains connected at branch points in such a fashion that flow is limited by the tensile strength of chains and extension to maximum length is limited by the covalently bonded bonding links in the chain.

The formation of large networks or cross-linked polymers is usually calculated from composition by starting at any point and calculating the probability of reaching a branching molecule before a terminal (monofunctional) group is reached. If the branching group is trivalent and the probability of reaching a branch point is less than that of reaching a terminal monofunctional unit, the chain will always be limited.

Assuming that reactivities of the various functional units can be determined, the probability of the formation of interlaced networks can be calculated. (Flory - Chapter IX, p. 347 et seq.).

In step-growth polymerizations, the molecular weight is usually limited by stopping the reaction (by reduction of temperature, for example) before all the functional groups have reacted, in which case the polymer is capable of further reactivity later. The molecular weight is sometimes also limited by use of monovalent reagents. It is increased with branching by use of trivalent or polyvalent reagents in carefully controlled amount.

4-6 PURITY OF REAGENTS AND SPECIFICITY OF REACTIONS IN POLYMERIZATION

To be suitable for polymerization to substantial molecular weight without crosslinking, the reactions must be extremely clean. The probability of reaction of a divalent unit in a polymerization as a divalent unit must approach 100%, to obtain high average molecular weight. In ordinary synthetic work to produce low molecular weights a yield is considered high at 90%. This requirement of high yield means that the monomers need to be pure if high molecular weight without crosslinking is to be achieved. Furthermore side reactions of the reactive groups which make them unreactive must be minimum.

In the preparation of low-molecular weight materials which are to be tightly crosslinked after application, purity and absence of side reactions may not be important. Usually the exact amount of branching is not very important, and variations in reactivity and purity will be compensated by number of crosslinks.

4-7 POLYMERIZATION THRU MULTIPLE REACTIVE GROUPS

Relatively few reactions are used for the production of high molecular weight by reaction of difunctional compounds with each other. The prime examples are reactions of carboxylic acids with alcohols to form esters, esters with alcohols to form esters, amines with acids to form amides, phenols with acid

chlorides, and diisocyanates with alcohols to yield polyurethanes. Examples are given in Figure 4-1 of reactions suitable for polymerization through multiple reactive groups. Figure 4-2 illustrates the formation of polymers by similar efficient reactions.

4-7-1 Chemistry of Alkyd Resins

Alkyd resins are organic polyesters derived from polybasic acids and polyhydric alcohols. Alkyd resins are of low molecular weight - 2000-10,000-but they contain unreacted hydroxyl, carboxyl, and generally fatty acid esters. They are usually converted on the substrate surface to infusible form by further reaction with oxygen or with additives reactive with hydroxyl groups. In some other cases the alkyd resin is simply a plasticizer for a film-forming strong resin like nitrocellulose and is not converted to insoluble form. In all cases where polymers are mixed for reaction the compositions must be proper for compatibility.

Alkyd resins are usually made from phthalic anhydride, glycerine, and a drying or non-drying triglyceride oil. Other dibasic acids,e.g. adipic are occasionally substituted for phthalic anhydride and other alcohols, e.g. pentaerithritol,are substituted for glycerin. Typically the alkyd resins contain free hydroxyl, carboxyl and oil-acid ester end-groups. In alkyd resins which harden by oxidation the oil acids would be of highly unsaturated type.

Alkyd resins which are to be used with urea or melamine resins (See 4-7-3) do not require air-oxidizing groups but can be made to harden by reaction of hydroxyl groups with the methylol groups of the urea or melamine resin. Often cocoanut oil is used in such alkyd resins. The long chains of the cocoanut soften and flexibilize the cross-linked resin.

Alkyd resins are manufactured in several steps. Usually the oil is reacted with glycerin by alcohol interchange using basic catalysts to produce "monoglyceride" - really a mixture of mono-, di-, and triglyceride-and the "monoglyceride" is reacted with phthalic anhydride. The amount of each reagent and the extent of esterification are adjusted to yield products of suitably high molecular weight and functional groups. A preliminary calculation is made to determine the extent of the esterification reaction when infinite networks are built up making the product unusable. The extent of reaction is usually observed during its course by periodic measurement of acid number. Viscosity is measured also during the course of the reaction and plotted as a function of the acid number and time. The reaction is stopped by cooling when the viscosity is judged to have reached a suitable value. See Fig. 4-3.

4-7-2 Calculation of Extent of Reaction at the Gel Point

The preliminary calculation for the critical extent of reaction at the point of gelation p can be applied to synthesis of alkyd resins as well as to other step-growth polymerizations and is based upon the following:

f = no. of functional groups per monomer molecule (valency, or for a mixture of monomers, the average number per monomer unit).

N_o = no. of monomer molecules initially, expressed in mols, for example.

$N_o f$ = no. of functional groups originally present, expressed in mols.

N = no. of molecules after reaction, expressed in mols.

$2(N_o - N)$ = number of functional groups reacted.

$\frac{2(N_o - N)}{N_o f}$ = p = fraction of functional groups reacted or extent of reaction

$\frac{N_o}{N} = X$ Obviously when the mass is gelled the number of molecules N is reduced drastically and N_o/N increases drastically.

$$p = \frac{2N_o}{N_o f} - \frac{2N}{N_o f} = \frac{2}{f} - \frac{2}{Xf}$$

$$p = \frac{2}{f}$$

EXAMPLE:

INGREDIENT	N_o	f	$N_o f$
isophthalic acid	3 mols	2	6 (carboxyl)
pentaerithritol	2 mols	4	8 (carboxyl)
cocoanut oil acid	1 mol	1	1 (carboxyl)
	6 mols	2.5	15

$$f = \frac{15}{6} = 2.5$$

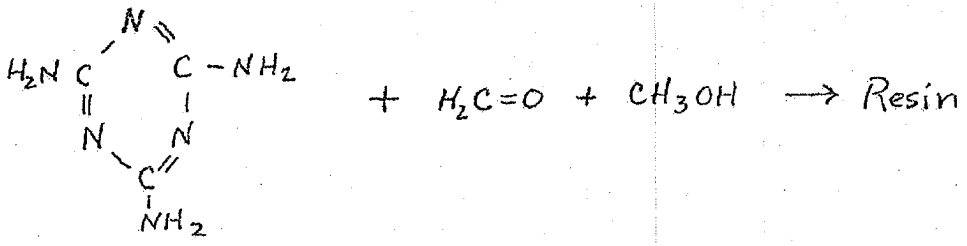
$$p = \frac{2}{f} = \frac{2}{2.5} = 0.8$$

At the gel point, according to this example, 0.8 x 15 = 12 mols of functional groups will have been converted to ester - obviously 6 hydroxyl and 6 carboxyl. Since there were originally 7 mols of carboxyl, one will not have been reacted. Since there were originally 8 mols of hydroxyl, 2 mols will have been unreacted.

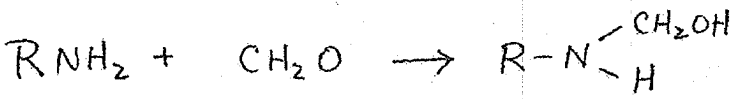
This preliminary calculation is easy and approximate. It does not take into account the formation of rings which can use up reactive groups without contributing to network formation. It also should fail under conditions where f is high and gelation occurs while X is relatively low. More exact treatments are available which take ring formation and high values of f into account.

4-7-3 Melamine Formaldehyde Resins

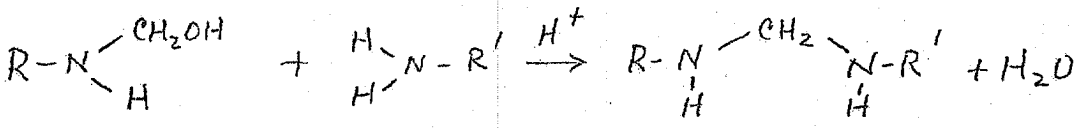
These products are made by reacting melamine with formaldehyde and an alcohol under slightly acidic conditions.



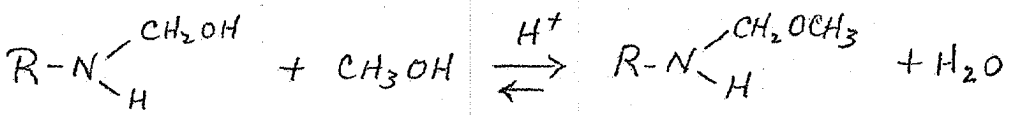
The first step is probably the formation of a methylol group on the amine group.



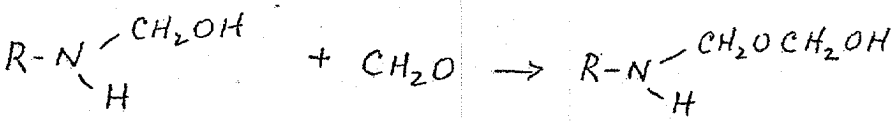
The methylol group can react with another amine to yield a methylene bridge.



It can also react with an alcohol to form an ether



and with more formaldehyde to form methylene ether groups.



When therefore melamine, formaldehyde and an alcohol are mixed in acid medium the product will contain methylene bridges, methylene ether bridges and alkyl ethers of the methylol melamines. The 6 hydrogen atoms of the melamine are not all equally reactive after some steps in the synthesis so that, in general not all will be substituted. Generally, however, a branched molecule will be obtained with free methylol, etherified methylol with or without methylene ethers and free amine groups. The melamine rings will be connected to each other through nitrogen and methylene bridges. Because of the large number of functional groups the melamine-formaldehyde resins are easily cross-linked. during manufacture, and good control of conditions of the synthesis is needed to get large molecules without cross-linking.

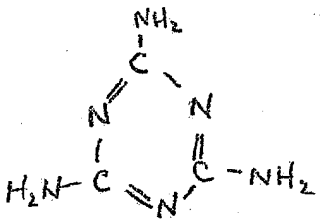
The methylol groups are most active in further condensation; the etherified methylol groups are active only under acidic conditions. If alcohols are used in insufficient quantity, the melamine resin is water soluble, not organic solvent soluble, and unstable.

In the presence of excess formaldehyde and methanol all six of the amine hydrogens can be replaced to form hexamethoxymethyl melamine. This is relatively unreactive because it contains only etherified methylol groups.

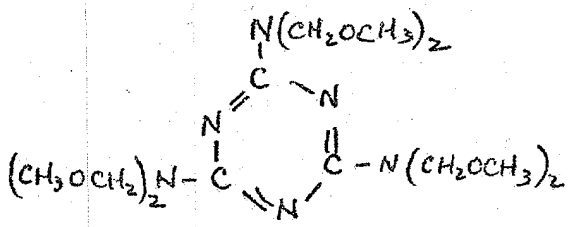
Melamine resins react with hydroxylated compounds to displace the alkyl group from the alkyl ethers. If a polyhydroxy compound like an alkyd resin is reacted with a melamine resin, many points of attachment will be possible on each molecule and cross-linking will be obtained.

The ability to form a compatible - single phase - mixture of a melamine resin with an alkyd resin is dependent on chemical structure and on molecular weight. The relatively small molecule of hexamethoxymethyl melamine is therefore most widely compatible with hydroxylated organic polymers.

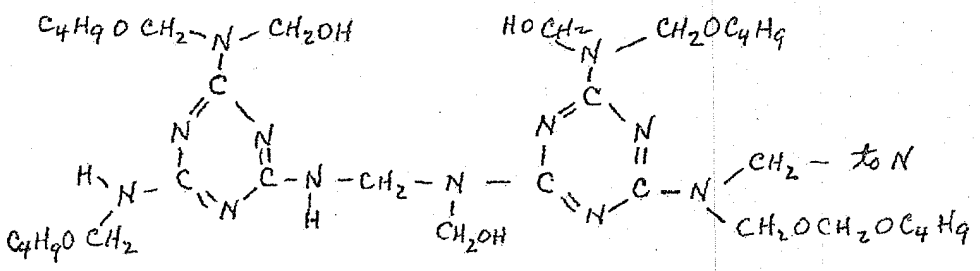
Melamine



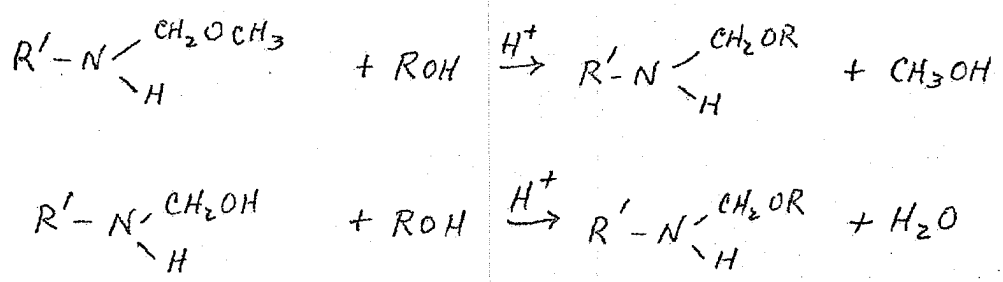
Hexamethoxymethyl Melamine



Hypothetical Butylated Melamine Resin To Show Structure Types



Reaction of Melamine Resin With Hydroxylated Polymer



The liberation of water or an alcohol by reaction of melamine resins with hydroxylated polymers can be the source of bubbles if the reaction occurs at temperatures above the boiling point of the liberated small molecules. Whether or not bubbles occur will depend on the diffusion rate of the small molecules out of the film, the rate of formation, and the presence of nucleating sites. Film thickness and hardness tend to reduce the permeation rates, but a sufficiently hard film might prevent the blowing of a bubble altogether.

4-7-4 Other N Resins

Many compounds containing amine nitrogen can be reacted in similar fashion. Urea is the most common one. It forms compounds analogous to those of melamine and is cheaper. Urea-formaldehyde resins react with hydroxylated compounds in the presence of acids like the corresponding melamine products.

4-7-5 Phenolic Resins

Phenol reacts with formaldehyde by displacement of o- and p- hydrogen atoms and the formation of methylol groups. Methylol groups react only slowly with phenols under alkaline conditions to liberate water and form methylene bridges. "Resols" are phenol and formaldehyde reaction products made in alkaline medium. They contain usually only one or two aromatic rings per molecule and contain methylol groups attached to the o- and p- positions on the aromatic rings. Resols are made with an excess of formaldehyde over phenol.

Phenol reacts with formaldehyde under acid conditions to form methylol groups but the methylol groups react more rapidly under acid conditions. As a result the resins, called "Novolaks", have methylene bridges attaching typically 5 or 6 aromatic rings and essentially no free methylol groups. The size of the typical molecule, its branching, and crosslinking depends on the functionality of the phenol and the ratio of phenol to formaldehyde.

When large unbranched or uncrosslinked molecules of a phenol-formaldehyde polymer are desired, phenols substituted in ortho or para position must be used so that the phenolic molecule will be reactive at only two sites.

A molecule of a phenol-formaldehyde adduct containing free methylol groups in the ortho position adds to a double bond in a drying oil to liberate a molecule of water and form a chroman ring which includes six atoms - oxygen from the phenol, two carbons from the double bond, a carbon from the methylol group and two carbons from the phenolic nucleus. Accordingly the oils can be built up with phenolic compounds to improve certain of their properties.

4-7-6 Epoxide-Based Resins

The epoxide group is a three-membered ring containing two carbon atoms and an oxygen atom. The epoxides are reactive with acids to form esters, with amines to form amine-alcohols and with other epoxide groups to form polyethers. Terminal epoxide groups are particularly reactive. Reactions of the epoxide to open the ring are base-catalyzed, and the tertiary amines are often used as catalysts.

A particularly important group of epoxides is exemplified by the diglycidyl ether of Bisphenol A (2-2' di-4-phenylol propane) and the higher molecular weight homologues.

Epichlorohydrin reacts with the sodium salts of phenols to form a chlorohydrin and then a glycidyl ether of phenol and sodium chloride (eliminating the phenolic hydroxyl). The glycidyl ether can also react with more phenol to open the epoxide ring and attach another molecule of the phenol.

Use of an excess of epichlorohydrin and a dihydric phenol results in low molecular weight compounds containing two epoxide groups per molecule. The molecule will also contain a secondary hydroxyl group for each dihydric phenol combined in the molecule. The first member of the series is a liquid. The higher diepoxides of this series are solids of low-melting point.

4-7-6-1 Film Formation from Epoxide-Based Resins

a. All of the Bisphenol A - diepoxide products can be reacted with drying-oil fatty acids to yield air-drying binders called epoxy-esters. The reaction with drying-oil acids esterifies the epoxide and the hydroxyl groups.

Esterification of the epoxide-based resins with drying oil acids (or with non-drying fatty acids) increases their solubility in hydrocarbon solvents. The esters, if they contain residual hydroxyls, can be mixed with urea-formaldehyde or melamine-formaldehyde resins and cross-linked during baking.

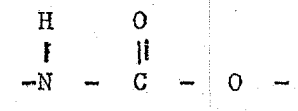
b. The epoxide resins can be reacted with urea-formaldehyde or melamine-formaldehyde resins during baking to produce cross-linked films with excellent adhesion to steel, low permeability to water, excellent hydrolytic resistance, and excellent flexibility.

c. The reaction of the epoxides with amines proceeds rapidly at room temperature. The mixtures are therefore not stable long after mixing. Coatings can be made by mixing the amine and epoxide as a spray during deposition on the substrate. Polyamides used for room temperature reactions with epoxide-containing resins are condensation products of fatty acids with polyamines and contain free amine groups.

Reactions like that of epoxide and amine, which yield no volatile products and little shrinkage are particularly useful for adhesives and finishes because (1) they fill rough surfaces well and (2) they do not produce high strain in the film during conversion to a solid. In addition, thick films are readily formed without the bubbling associated with gas-yielding reactions.

4-7-7 Polyurethanes

Polyurethanes are an important group of binders for coatings. They contain multiple urethane groups



Urethane

per molecule. A urethane group is introduced into binders by the reaction of an isocyanate radical with an alcoholic hydroxyl radical. A dihydric alcohol when mixed with a diisocyanate yields a linear polyurethane. The reaction proceeds rapidly at room temperature and yields no volatile products. The molecule is terminated by reactive isocyanate or by hydroxyl, depending on which is provided in excess. If molecules are desired which are not reactive, a monofunctional isocyanate or alcohol is also added, the total number of isocyanate groups and hydroxyl groups being equal. If branched or cross-linked products are desired, polyfunctional isocyanates or polyhydric alcohols can be used.

Some useful isocyanates are: 1,6 hexamethylene diisocyanate, tolylene 2,4 diisocyanate, diphenyl methane 4,4' -diisocyanate. The reactivities of the two-NCO radicals on tolylene 2,4 diisocyanate are not the same, the para-NCO reacting more rapidly than the ortho-NCO.

The isocyanates are relatively expensive, volatile, and toxic. It is often convenient to use them to react together long molecules containing two alcoholic hydroxyl groups, for example hydroxyl-terminated polyesters or hydroxyl terminated aliphatic polyethers. Used in this manner the added cost for the required isocyanates can be low.

Aliphatic polyester urethanes are subject to hydrolytic damage and polyether urethanes are subject to oxidative attack. Urethanes from aromatic isocyanates turn yellow and lose integrity in sunlight while those from aliphatic isocyanates tend to be more durable.

As a (relatively non-volatile polyisocyanate) building block for large molecules - particularly cross-linked ones - isocyanate-terminated branched polyesters can be made by reacting hydroxyl-terminated polyesters with an excess of a diisocyanate. The cyclic trimers of diisocyanates, e.g. the trimer of tolylene diisocyanate, is a useful triisocyanate of low volatility.

The isocyanates group reacts with common compounds other than hydroxyl - amines, carboxylic acids and water for example. The reactions of isocyanates to form urethanes are clean enough to allow the production of useful high molecular weight linear products. However, side reactions do occur. The urethanes themselves are subject to attack by isocyanates.

Blocked isocyanates are reaction products of isocyanates with a blocking agent. The blocked isocyanates are not reactive at room temperature, but they liberate the reactive isocyanate and the blocking agent on heating. Typical blocking agents are phenols and aldoximes. The use of blocked isocyanates permits the formulation of fluid coatings, stable at room temperature, which react to form polyurethanes on heating.

4-7-7-1 Film Formation from Polyurethanes

a. Polyurethane lacquers can be applied from solution in solvents at high enough molecular weight (and relatively low concentration) to produce strong films.

b. Polyurethane coatings are applied mainly as enamels at lower molecular weight and higher concentration. The final high molecular weight and cross-linking are achieved after application to the substrate.

1. Air-Curing - A polyurethane from a polyol and a diisocyanate contains in its structure esterified drying-oil acids. Oxygen causes the drying-oil components to combine with each other and increase the molecular weight.

2. Moisture-Curing - A binder of low molecular weight contains free isocyanate groups. After application, atmospheric moisture reacts with the isocyanate groups to form polyureas and liberate CO_2 which diffuses out.

3. Heat-Curing - A binder contains blocked isocyanates and reactive alcohol groups in its structure. On heating to a sufficient temperature the blocking agent is liberated and urethane formation proceeds to raise the molecular weight.

4. Two-Package Systems - Di- or poly-isocyanates are mixed with polyols just before use. To reduce the hazard of toxicity, one must choose isocyanates of low volatility. Diphenylmethane diisocyanate, lower molecular weight condensates of excess (volatile) diisocyanates with polyols and polymerized diisocyanates which contain free isocyanate groups are useful.

4-7-8 Silicone Polymers

Low molecular weight silicone polymers are used in coatings. These contain the - Si - O - Si - O - linkage, with one or more of the remaining valences of silicon attached to carbon. The carbon can be an alkyl or an aryl group and the group attached to carbon can contain other functional groups.

The polymers are usually derived from the hydrolysis of a silicon halide or ester as in Fig.4-4. If exactly two of the attachments to silicon are carbon atoms, the polymer is linear (or macrocyclic). The introduction of a trifunctional (three ester groups) molecule introduces a branch. The use of a monofunctional unit terminates a chain. Terminal hydroxyl and silicon ester groups continue to be reactive.

Alcoholysis of a silicon ester substitutes an alcohol. Alcoholysis by means of an alkyd resin of a silicone chain possessing ester groups yields a larger molecule possessing alkyd and silicone polymer structures.

Silicone polymers are resistant to high temperatures and are durable in sunlight exposure. They are used with other polymers to impart high durability.

Silicone polymers made with phenyl groups attached to silicon are more resistant to heat than those made with methyl groups.

4-8 POLYMERIZATION THRU DOUBLE BONDS

Many compounds containing a double bond can be polymerized. The most common ones used in organic coatings are styrene, alkyl methacrylates and acrylates, vinyl acetate, acrylonitrile. These materials tend to form rather stiff polymers compared with those from ethylene, propylene, isobutylene which form relatively soft, rubbery polymers. The polymerization of these monomers is brought about by several kinds of catalysts but is exclusively a chain-growth process; during the course of the process monomer exists along with polymer.

4-8-1 Free Radical Catalysis

4-8-1-1 Production and Properties of Free Radicals

Free radicals are compounds, usually quite reactive, containing an odd electron. They are produced by a variety of processes. Thus, for example, an electron striking an organic molecule at high velocity can remove a hydrogen atom producing two free radicals - the hydrogen atom and the larger molecule remaining.

A characteristic of free radicals is a high rate of combination with other free-radicals. Free radicals also will abstract and combine with hydrogen atoms from organic compounds, leaving a new free-radical and destroying its own free-radical structure. Free-radicals will combine with oxygen to produce a peroxy free-radical. The reactivity of free-radicals varies with their structure - a peroxy free-radical is often less reactive than its parent.

Free-radicals are usually produced for polymerization by the reactions of peroxides or persulfates or by the decomposition of certain azo compounds. The radicals produced will tend to combine with each other very rapidly but the rate of recombination will obviously increase with the concentration of the radicals. In the usual polymerization the concentration of free-radicals is usually quite low - of the order of 10^{-15} per cm^3 as a maximum, compared with about 10^{22} small molecules of other kinds per cm^3.

4-8-1-2 Steps in the Growth of a Polymer Molecule

The elementary steps in the formation of a single polymer molecule by free-radical polymerization are initiation, propagation, and termination. Fig. 4-5. In the initiation step, a free-radical from the decomposition of a peroxide, azo compound, or the like, combines with a monomer molecule creating a molecule with a new free-radical end-group. During the propagation step the free-radical reacts with successive monomer molecules, at each step maintaining its free-radical character. The rate of propagation is independent of the initiator chosen. During the termination step, the radical end of a molecule is inactivated by (1) combination with another radical, or by (2) losing a hydrogen atom to a second free-radical and forming one saturated and one unsaturated molecule, known as disproportionation, or (3) by abstraction of a hydrogen atom from a molecule of solvent, polymer, monomer or special additive to form a new free-radical. The special additives known as chain-transfer agents have specially reactive hydrogen atoms, easily abstracted and leaving a free-radical which can start a new chain.

The most important commercial monomers are given in Fig. 4-6. These are unstable in the sense that polymerization results in a large liberation of energy. Free radicals are available from many oxidation - reduction reactions and even from cosmic rays to start such reactions. Accordingly inhibitors are added to the monomers before shipment in the amount of 50-200 parts per million. The inhibitors react with free-radicals preferentially. However, they are used up to some extent during storage. The initiator provides more free-radicals and these destroy the inhibitors before polymerization can proceed to an appreciable degree. Thus polymerizations have an induction period. Another cause of inhibition is the presence of dissolved oxygen, from storage in contact with air or from leaks into the apparatus. The important inhibitors are hydroquinone and its methyl ether, aromatic amines, copper salts.

4-8-1-3 Chain Transfer Agents

Free-radicals will abstract an atom - usually hydrogen-from a variety of compounds - to form a new radical free to start a new polymer chain radical. Mercaptans are the most useful chain transfer agents. When they start a new chain it has a sulfide end-group.

Hydrogen atoms are readily removed from tertiary carbons, less readily as substitution decreases. They are also readily abstracted from a carbon attached to an aromatic ring or an allylic hydrogen. The new radical formed from abstraction of an allylic hydrogen is relatively inactive, so that allyl groups tend to stop acrylic polymerizations - not merely start new chains. Xylene and other substituted benzenes are often used as solvents when chain transfer is desired.

4-8-1-4 Polymerization Processes

Bulk: Monomers are brought to a proper temperature and catalyst is added. The catalyst should be chosen so as to yield free-radicals in sufficient amount throughout the course of the polymerization reaction. The heat liberated during polymerization is absorbed by cooling the walls or by cooling vapors of the monomer. Heat transfer is often poor especially at the end of the reaction, when the viscosity is high. The high viscosity tends to reduce rates of termination by reaction with other polymeric radicals and

thereby increases rates of polymerization and molecular weight in later stages of the polymerization. Polymerization in bulk is not used for the manufacture of organic coatings.

Suspension Polymerization is a special form of bulk polymerization. Globules of monomer and oil soluble catalyst are suspended in water using a small amount of water-soluble polymer or a powder to coat the monomer droplets. and reduce their rate of coalescence. Strong stirring is essential to maintain globule size, usually between 50 and 250 microns diameter. Heat is transferred readily from these small globules to the continuous aqueous phase and from there to the cooled walls of the vessel. When polymerization is complete the globules of polymer are separated from the water, washed and dried. They can then be dissolved in solvents if desired.

Solution Polymerization is used for many polymers which are ultimately to be used in solution. Monomer, solvent and catalyst are mixed at an appropriate temperature and the heat of reaction is absorbed through the walls or by cooling of solvent vapors. The choice of solvent helps reduce molecular weight by chain-transfer mechanisms.

Emulsion Polymerization is frequently used for surface coatings. The final product is a stable suspension of polymer particles in water, so fine that settling is negligible. Typically the particle diameter is 0.1 to 0.3 micron. A mixture is made of an emulsifier - say sodium lauryl sulfate, water, monomer, and a water-soluble catalyst - say ammonium persulfate. Heat is applied to start the formation of free-radicals. Initiation occurs initially in the aqueous phase, but after the addition of a few monomer units the growing molecule becomes insoluble in water and aggregates into a cluster or joins other such molecules in a cluster, absorbing emulsifier on its surface. Polymerization then occurs in the clusters of polymer molecules utilizing polymer free-radicals and monomer absorbed by the polymer particles from solution in water, supplied in turn from a pool of monomer or large droplets of monomer. Stabilization is achieved by the electronic repulsion of the charged emulsifier absorbed on the surface. Additional stabilization can be provided by carboxyl or hydroxyl groups or other hydrophilic groups in the polymer.

If the emulsifier is anionic the particles will be charged negatively. If the emulsifier chosen is cationic the particles will be charged positively.

The particles in emulsion polymerizations are so small that two polymer radicals in a single particle tend to find each other and terminate rather than continue to react with monomer. A fine particle of a emulsion polymer will generally have no reactive radicals or one reactive radical chain during the course of its growth. If the polymer is stiff enough the larger particles will contain for significant times more than one growing chain - a cause of increase in rate.

Polymerization in organosol form has been investigated in the last few years. A mixture of monomer, stabilizer, and initiator is made in a non-solvent for the polymer. The stabilizer is a non-ionic polymer molecule, part of which has strong attraction to the polymer and part has strong attraction to the poor solvent. Polymerization proceeds as in aqueous emulsion. Molecular weights tend to be lower than in emulsion because of the presence of compounds reactive to free-radicals in the solvents. The particles formed can be fine enough not to settle appreciably. They are stable because of the preferred attraction of their stabilizer coating to the solvent.

4-8-2 Anionic Polymerization

Certain monomers can be polymerized by the addition of alkali metal alkyls, aryls, alkoxides or amides. The growing chain is negatively charged - anionic - and the closely held counter-ion is the positively charged alkali metal. Because of the close influence of the cation, the rate of the propagation step depends on the choice of initiator. The chains are terminated by formation of a metal hydride, by transfer mechanisms to other organic compounds, or by reaction with traces of water or other compounds containing active hydrogen. (See Figure 4-7). When chain transfer or hydride processes are avoided, the molecules are rather uniform in size. They are all started at about the same time and remain active to polymerization.

A special case of anionic polymerization is that initiated by the coordination catalysts - Ziegler-Natta catalysts-mixtures of an alkyl or aryl of a metal from Groups I-IV and a compound of a transition metal from Groups IV-VIII. The most prominent example is the catalyst prepared from triethyl aluminum and titanium tetrachloride. The catalyst is insoluble and polymerization is initiated and propagated at sites on the surface of titanium trichloride at which aluminum triethyl is coordinated. The propagation reaction is highly specific and directional, resulting in tacticity. See Figure 4-8. Water and oxygen are destructive of the polymerization catalyst.

Anionic polymerization of ethylenically unsaturated monomers is rarely used for the preparation of surface coatings. However, it is used in research when specific structures or molecular weights are needed.

4-8-3 Cationic Polymerization

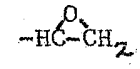
Certain monomers are readily polymerized by the addition of (1) strong acids, or (2) metal halides (Friedel-Craft's Catalysts) in combination with a co-catalyst - usually water or an active hydrogen compound or (3) carbonium salts. The growing chain is positively charged.

Butadiene is polymerized for can-coatings using a boron fluoride catalyst to yield polymers in which some of the units are combined in 1,2 and others in 1,4 arrangement. The polymer thus contains pendent vinyl groups and internal double bonds.

Cationic polymerizations are not used much in the manufacture of surface coatings. See Figure 4-9.

4-9 TYPES OF REACTIVE GROUPS USED IN POLYMERS

Polymer molecules consist of chains of atoms on which other atoms or radicals may be attached at terminal points or along the chain e.g. halogen, OH, COOH, epoxide. These atoms or radicals are capable of useful chemical reactivity either with or without the addition of other compounds under conditions different from, or the same as, those used in the initial polymerization. They also frequently provide properties associated with adhesion, pigment dispersion and other manifestations of surface activity. Vinyl monomers with functional groups they introduce during free-radical polymerization:

MONOMER	FUNCTIONAL GROUP
Hydroxyethyl methacrylate	-OH
acrylic acid	-COOH
methacrylic acid	-COOH
maleic anhydride	
maleic acid half esters	-COOH
fumaric acid	-C-COOH -C-COOH
glycidyl methacrylate	
dimethylaminoethyl methacrylate	$-N(CH_3)_2$
itaconic acid	COOH | CH | -C-COOH

Particularly in polymers of low molecular weight often made by reactions of multiple functional groups e.g. alkyd resin, but also in low molecular weight vinyl polymers, functional groups are used or added to provide cross-linking. These can be reactive with air or with melamine or urea resins which contain $-N-CH_2OH$ or NCH_2OR, where R is usually an alkyl group.

4-10 DRYING OILS AND DERIVATIVES

4-10-1 Natural Drying Oils

A series of oils are extracted from seeds. These consist generally of esters of glycerine and unsaturated fatty acids. Various fatty acids are contained in any one sample of oil and are combined in groups of three, perhaps not randomly but also not systematically. Some oils consist predominately of fatty acids of a certain type.

The unsaturated fatty acids oxidize spontaneously in air. Catalysts-most prominent are cobalt, manganese, and lead - accelerate the oxidation rate. In the course of the oxidation hydroperoxides are formed, particularly on allylic carbons and these react through free-radicals to yield hydroxyl, carbonyl and acid groups, and radical combinations form carbon to carbon links between adjacent molecules of fatty acid. High temperatures accelerate the rate of drying.

The oils from highly unsaturated acids form cross-linked polymers on air drying, insoluble but swollen in all solvents. The cross-linking is accelerated by use of larger molecules than glycerin on which more than three fatty acid molecules can be attached. Some of these larger molecules can be made by standard polymerization processes. Oil modified alkyd resins and epoxy esters of drying oils are examples.

The oxidation rate and cross-linking rate depends on the particular acids present. Some of compounds formed in the oxidation absorb blue light preferentially, and are therefore yellow. Yellowed oils are usually bleached by sunlight. The oils and other oil-derived products therefore differ in the amount of yellowing. The choice of oil (and fatty acid) used is made partly on the basis of drying rate, partly on the basis of yellowing tendency, and partly on the basis of durability in sunlight - which also is a function of oxidation rate. Of the common oils, cocoanut oil is the most resistant to oxidation but it is non-drying and non-discoloring. It is used as an ingredient in alkyd resins for durable finishes which do not rely on oxidation of the oil for film formation.

4-10-2 Derivatives of Natural Drying Oils

The drying oils having double bonds can have cis- and trans forms associated with each double bond. Isomerizations to shift the location of the double bonds and the cis-trans structure can be accomplished with heat and catalysts. These changes naturally must affect rates and products of oxidation.

The heating of castor oil eliminates a molecule of water from each ricinoleic acid to produce some conjugated structures. It makes possible air-oxidation and copolymerization with styrene (which requires conjugated structures).

Maleinized oils are the reaction products of maleic anhydride with the unsaturated fatty acid portion of an oil molecule. Two routes of addition seem to be followed and internal rearrangements occur.

1. An allylic hydrogen is removed and it with the rest of the fatty acid adds across the maleic double bond to form a succinic acid derivative without affecting the unsaturation of the oil component.

2. Addition of maleic anhydride across conjugated double bonds by Diels-Alder mechanism.

3. Shifts of non-conjugated to conjugated double bonds. The maleinized oils carry acid groups making them soluble or dispersible in alkaline water.

4-10-3 Bodied Oils and Blown Oils

The blown drying oils are deliberately oxidized with air at high temperatures. The bodied oils are heated mainly in the absence of air. Polymerization and isomerization occurs in both instances. The molecular weight suggests dimers and trimers of the oils. The amount of unsaturation decreases. The temperature - about 300-350°C - indicates that there are many reactions which occur. None of the C-H bonds can be regarded as stable under these conditions.

4-10-4 Copolymerized Oils

Styrene, cyclopentadiene, and α- methyl styrene are copolymerized with dehydrated castor oil and with other oils with conjugated unsaturation. Such oils are harder when polymerized and more viscous as liquids than the untreated oils.

4-10-5 Synthetic Drying Oils

There have been many attempts to make synthetic drying oils i.e., materials which oxidize and dry like oils on exposure to air. An example which received considerable study is the vinyl dioxolane ester. Its reaction on exposure to air have been studied in detail.

4-11 COPOLYMERIZATION

In a free-radical polymerization of a vinyl monomer the radical-containing chain-end is capable of reacting with a new monomer molecule similar to the one just added but it is capable of adding to another type of monomer molecule if present. In general, then, a mixture of monomers will yield polymer chains containing a mixture of the monomers. However, any one radical chain end may be more reactive to one monomer than another, and different types of chain ends will be more reactive or less reactive to a given monomer. As a result the ratio of monomers incorporated into a polymer chain and their sequence depends on the ratio of monomers present and on the reactivities of radical chain ends and monomers. The prediction of reactivities and the calculation of copolymer compositions is described in Flory pp. 178 - 199.

Reactivities and copolymer ratios will be different for non-free radical vinyl polymerizations.

Copolymerizations are also used in step-growth polymerizations to obtain particular properties.

Analytical expressions for the rates and sequences of polymerization can be derived from the knowledge of reactivities of the monomers. In general, as a polymerization reaction proceeds, the monomer composition will drift. Computer methods allow one to calculate the sequences of monomer units and their change during the course of the polymerization.

Certain copolymerizations of two monomers result almost exclusively as alternating monomer units. The alternation is a consequence of the relative reactivities of the two types of radical chain ends with the two types of monomers. Example - styrene/maleic anhydride in free-radical polymerization. Within wide limits of the initial ratios of styrene and maleic anhydride, the first polymer formed will be the alternating polymer. Only after almost all of the maleic anhydride is used up will there be any sequence of styrene monomer units.

Polymer molecules already formed will often contain structures which are susceptible to attack by free-radicals, and new polymer molecules can be attached to these points by continued reaction with fresh monomer which may be different from those already present. When such susceptible points are along the chain of a polymer molecule the second polymer will be grafted to the first - as branches may be grafted to the trunk of a tree. If such groups exist at chain ends, block copolymers are said to be formed.

In block and graft polymers there are long sequences of one kind and long sequences of another kind. The long sequences of block and graft copolymers are attached and cannot separate from each other. Solvents for one sequence will therefore suspend the other.

The long sequences of block and graft copolymers retain the rigidity as well as the intermolecular attractions of the corresponding polymers unattached in graft or block form.

4-11-1 Functions of Copolymerization

1. Change of useful temperature range: The glass transition temperature of a random copolymer is a function of the glass transition temperature of each of the corresponding homopolymers and the ratio of the different monomers.

At the glass transition temperature, segments of about 10-50 monomer units in length become freed to move. This temperature depends on chain flexibility. Random copolymers have glass-transition temperatures which often lie between the glass transition temperatures of the corresponding homopolymers. The actual position of the glass transition temperatures is usually given as in the ideal case where there is no substantial attraction or repulsion between the elementary monomers.

$$\frac{1}{Tg} = \frac{W_1}{Tg_1} + \frac{W_2}{Tg_2} + \frac{W_3}{Tg_3} + \text{etc.}$$

W_i = Wt. fraction of monomer
T_g = glass transition temperature of copolymer
Tg_i = glass transition temperature of homopolymer i.

Such an equation can hold only if the elements of length which are freed to move at the glass transition temperature have a composition approximating the average. The equation cannot be expected to hold for polymers containing long sequences and bulk phase structure of monomers different from other long sequences and phase structures. Accordingly, block and graft copolymers characteristically do not follow this equation but show instead two or more glass transition temperatures more or less characteristic of their long sequences.

Ideal behavior has been demonstrated for copolymers of styrene and acrylates. Acrylonitrile/acrylamide copolymers. styrene/methyl methacrylate yield lower than ideal glass transition temperatures for the mixtures, while vinylidene chloride/ methyl acrylate, methyl acrylate/methyl methacrylate and dimethylsiloxane/ phenyl methyl siloxane yield higher than ideal glass transition temperatures. (Miller - Structure of Polymers, Reinhold, 1966 p. 477)

Glass temperature vs. composition curves higher than ideal are explained by mutual attractive forces between the comonomers which tend to increase density and stiffness. Curves lower than ideal are explained by repulsion between the monomers tending to reduce density and stiffness.

2. Change of solubility characteristic: Copolymers are intermediate in solubility characteristics between the corresponding homopolymers.

3. Change of crystallinity: Copolymerization tends to reduce crystallinity.

4. Change of reactivity: Introduction of cross-linking groups. Drying oil acids or alcohols: vinyl dioxolanes: 2, 3 dihydropyran-2H-methyl or allyloxy groups for oxygen-induced cross-links: OH, COOH, NH_2, isocyanate.

5. Introduction of polar groups for wetting and adhesion. Most prominent are -OH -COOH, $-NH_2$, $-N(CH_3)_2$.

4-12 NATURAL POLYMERS

Proteins, starches, celluloses, gums gutta percha and natural rubber are examples of natural polymers which have wide applicability. In the organic coatings industry these are often used as intermediates for the preparation of special more useful products.

Proteins are polypeptides of high molecular weight. Casein has been used in many water based finishes to provide viscosity and film-forming ability particularly in the presence of polymer latices for water-based finishes.

Starches and cellulose are condensation products of sugars. They contain acetal linkages and many hydroxyl groups per molecule. These hydroxyls are available for esterification or etherification. Reactive groups can be added to provide cross-linking. The cellulose esters - cellulose nitrate and cellulose acetate butyrate are valuable polymers for coatings.

4-13 OUTSTANDING PROPERTIES OF LONG SEQUENCES OF THE MONOMERS

Methyl Methacrylate	Hardness, Heat stability, light stability, alkali resistance.
Styrene	Heat stability, low water permeability, non-staining, alkali resistance, hardness.
Vinyl acetate	High water-permeability, adhesion, grease-resistance, yellowing with heat, hydrolytic instability.
Acrylonitrile	Solvent resistance, light stability. Yellowing with heat.
Vinyl chloride	Alkali resistance, water resistance, toughness, yellowing with heat and light, toughness (can be stabilized against heat and light).
Vinylidene chloride	Water resistance, alkali resistance, yellowing by heat and light, toughness.
Vinyl fluoride	Durability (stabilized), toughness, alkali resistance.
Alkyl Acrylates	Rubbers at room temperature, tough, intermediate durability.

4-14 REFERENCES ON BINDERS AND POLYMERS IN GENERAL

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R. H. Yocum - E. B. Nyquist - Functional Monomers - Dekker, New York (1973) Vol. I and II - summarizes the uses of monomers normally introduced in small quantities for special chemical and physical properties.

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Vol. 1	- Vinyl	-	G. E. Ham
Vol. 2	- Ring Opening	-	Frisch and Reegen
Vol. 3	- Step Growth	-	D. H. Solomon

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Journal of Polymer Science - John Wiley & Sons - New York, N.Y. 10016, issued in three series - Chemistry, Physics, Letters.

Journal of Paint Technology - Federation of Societies for Paint Technology, Philadelphia, Pa. 19107.

Journal of Applied Polymer Science - John Wiley & Sons - New York, N.Y. 10016.

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J. W. Prane - New Polymers for Coatings for the 70's - Progress in Organic Coatings 1 3 (1972).

W. J. Elms - R. D. Spitz - Acrylic Non-Aqueous Dispersion Variables, Journal of Paint Technology 46 #594 40 (1974).

Polymerization of Phenyl Glycidyl Ether in the presence of Tertiary amines and alcohols - M. F. Sorokin et.al. Polymer Science USSR 14 343-352 (1973).

Density Changes of Amorphous Polymethyl Methacrylate during Orientational Stretching - M. F. Miligan and N. I. Shishkin - Polymer Science USSR 14 400 (1973).

Esterification:

$$ROH + R'\overset{O}{\overset{\|}{C}}OH \leftrightarrows RO\overset{O}{\overset{\|}{C}}R' + H_2O$$

Transesterification:

$$ROH + R''\overset{O}{\overset{\|}{C}}OR'' \leftrightarrows R'\overset{O}{\overset{\|}{C}}OR + R''OH$$

Amide Formation:

$$RNH_2 + R'\overset{O}{\overset{\|}{C}}-OH \leftrightarrows R\overset{H}{N}-\overset{O}{\overset{\|}{C}}R' + H_2O$$

Urethane Formation:

$$RNCO + R'OH \longrightarrow R\overset{H}{N}-\overset{O}{\overset{\|}{C}}OR'$$

Ether Formation:

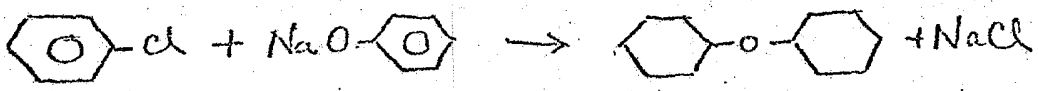


FIG. 4-1 SOME EFFICIENT REACTIONS SUITABLE FOR POLYMERIZATION THRU MULTIPLE FUNCTIONAL GROUP

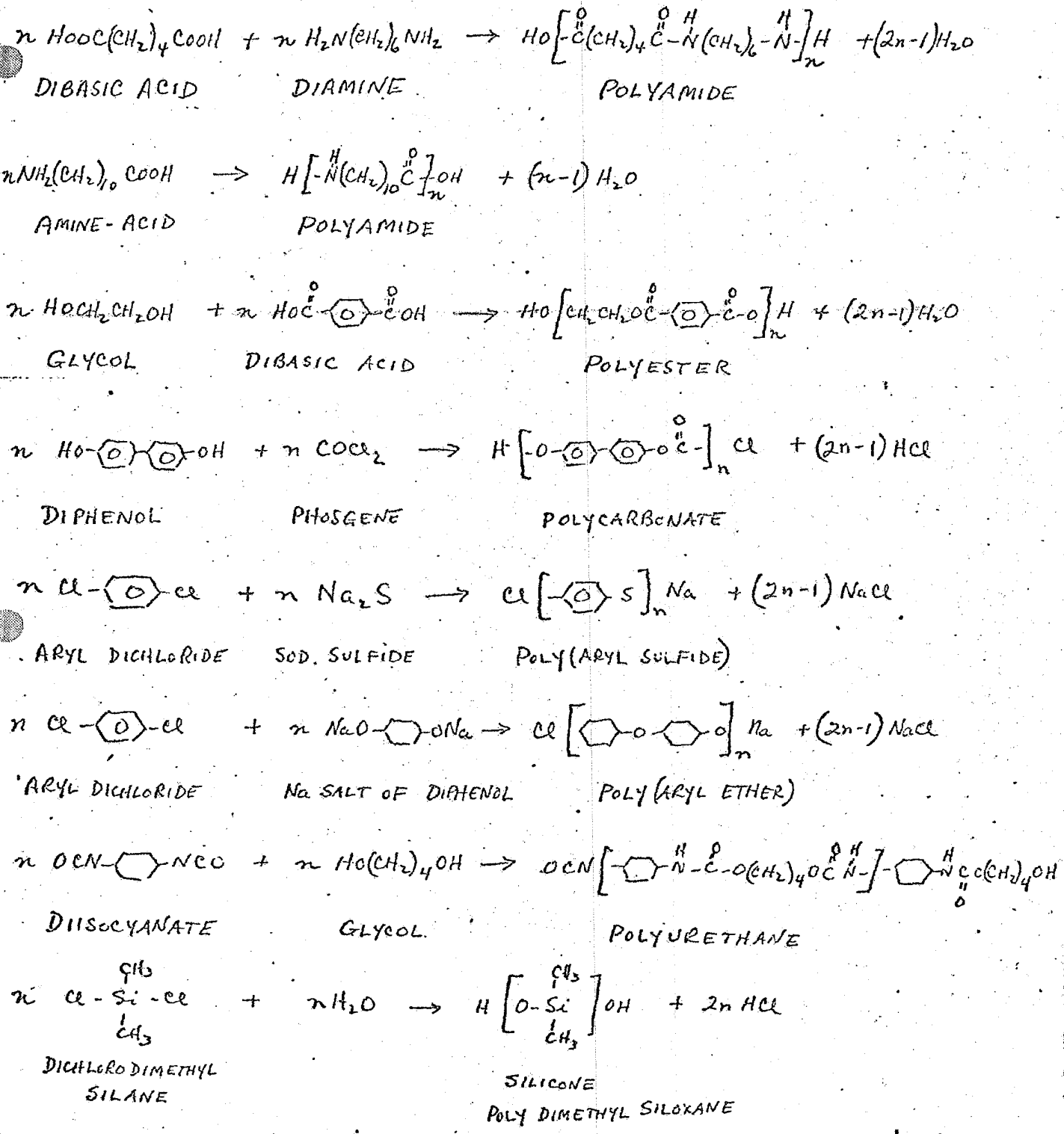
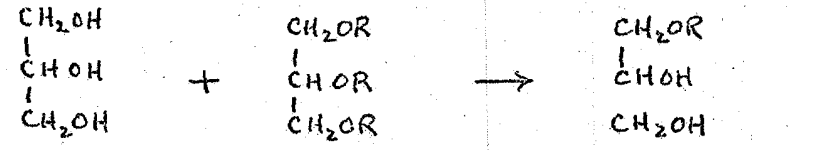


FIG. 4-2 POLYMERIZATION THRU MULTIPLE FUNCTION GROUPS

FIG. 4-3

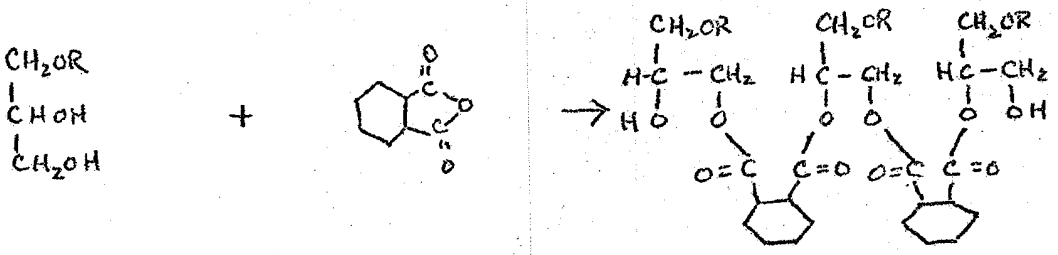
STEPS IN ALKYD RESIN MANUFACTURE - SIMPLIFIED

1. "MONOGLYCERIDE"



Glycerin + Oil → Monoglyceride

2. ESTERIFICATION OF "MONOGLYCERIDE" WITH DIBASIC ACID



"MONO" + PHTHALIC ANHYDRIDE → ALKYD RESIN

"MONO" - Monoglyceride (2), diglyceride (2), triglyceride, glycerine in statistical ratios.

MONO AND ALKYD - Oil acids of many kinds in every oil
Isomerization and polymerization occurs with unsaturated oils.
Molecular weight depends on ratios of reacted molecules - wide mol. wt. distribution.
Many structures possible.
Many substitutions of alcohols and acids for those indicated.

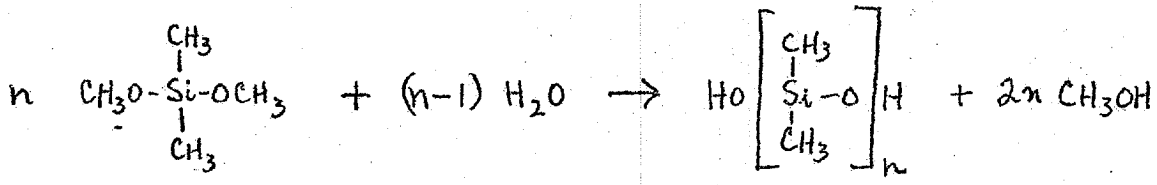


FIG. 4-4 - PREPARATION OF A SILICONE POLYMER

Initiation:

$$R\cdot + M \rightarrow RM\cdot$$

Example: $HO\cdot + \overset{|}{C}=\overset{|}{C} \rightarrow HO\overset{|}{C}-\overset{|}{C}\cdot$

Propagation:

$$RM\cdot + M \longrightarrow RMM\cdot$$

Example: $HO-\overset{|}{C}-\overset{|}{C}\cdot + \overset{|}{C}=\overset{|}{C} \rightarrow HO-\overset{|}{C}-\overset{|}{C}-\overset{|}{C}-\overset{|}{C}\cdot$

Termination:

By Combination:

$$RMM\cdot + RMMM\cdot \longrightarrow RMMMMMR$$

By Chain Transfer:

$$RMM\cdot + R'H \longrightarrow RMMH + R'\cdot$$

By Disproportionation:

$$RCH_2CH_2\cdot + \cdot CH_2CH_2R' \rightarrow RCH_2CH_3 + CH_2=CHR'$$

FIG. 4-5 ELEMENTARY STEPS IN THE FORMATION OF A POLYMER MOLECULE BY FREE RADICAL REACTION THRU DOUBLE BONDS

FIG. 4-6 IMPORTANT COMMERCIAL MONOMERS FOR FREE-RADICAL POLYMERIZATION OF BINDERS

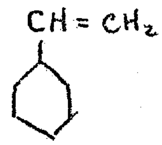
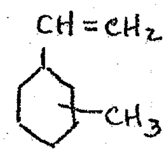
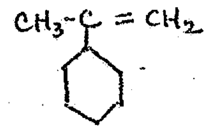
HYDROCARBONS:			
	Styrene	Vinyl toluene	α-methyl styrene
HALOGENATED HYDROCARBONS	$CH_2{=}CHCl$	$CH_2{=}CCl_2$	$F_2C{=}CF_2$
	Vinyl chloride	Vinylidene chloride	Tetrafluoroethylene
Vinyl esters	$CH_2{=}CHO\underset{\displaystyle O}{\underset{\Vert}{C}}CH_3$		
	Vinyl acetate		
Acrylics	$CH_2{=}\overset{\displaystyle CH_3}{\overset{\vert}{C}}{-}\underset{\displaystyle O}{\underset{\Vert}{C}}{-}OCH_3$	$CH_2{=}CHCN$	$CH_2{=}CH{-}\overset{\displaystyle O}{\overset{\Vert}{C}}{-}OR$
	Methyl Methacrylate	Acrylonitrile	Alkyl Acrylates
	$CH_2{=}CH{-}\underset{\displaystyle O}{\underset{\Vert}{C}}NH_2$		
	Acrylamide		

FIG. 4-7 ANIONIC POLYMERIZATION

Initiation:

A) Alkali Metal Alkyls, Aryls, Alkoxides, Amides

$$Na^+ NH_2^- + CH_2=CHR \longrightarrow H_2N-CH_2-\underline{C}HR \quad Na^+$$

Carbanion

or B) Alkali Metals - (Alkali Metal = M•)

I

$$M\bullet + CH_2=CHR \longrightarrow \bullet CH_2-\underline{C}HR \quad M^+$$

$$2\left[\bullet CH_2\underline{C}HR \quad M^+\right] \quad M^+ R\underline{C}HCH_2CH_2\underline{C}HRM^+$$

Dicarbanion

II

$$M\bullet + A \rightarrow M^+A^-\bullet$$

$$M^+A^- + CH_2=CHR \longrightarrow \bullet CH_2-\underline{C}HRM^+ + A$$

$$2\bullet CH_2-\underline{C}HRM^+ \longrightarrow M^+RH\underline{C}-CH_2-CH_2-\underline{C}HRM^+$$

Propagation:

$$\sim\sim \underline{C}HR\,M^+ + CH_2=CHR \longrightarrow \sim\sim CHRCH_2-\underline{C}HRM^+$$

Termination:

A $\sim\sim CH_2-\underline{C}HRM^+ \longrightarrow \sim\sim CH=CHR + MH$ Hydride

or B $\sim\sim CH_2-CHRM^+ + CH_2=CHR \longrightarrow \sim\sim CH=CHR + CH_3-\underline{C}HRM^+$

or C $\sim\sim CH_2-\underline{C}HRM^+ + CO_2 \rightarrow \sim\sim CH_2-CHR-\overset{O}{\overset{\|}{C}}-O^-M^+$ Inactive

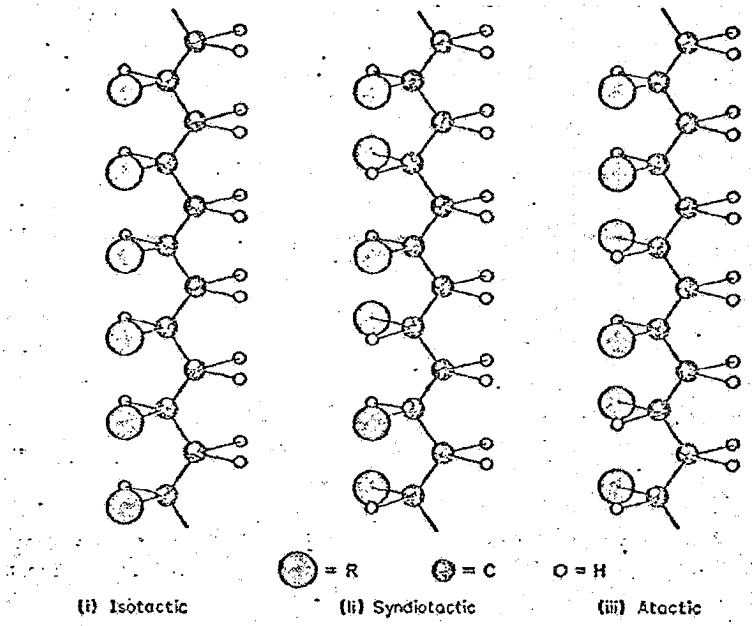


Fig. 1.6 *Diagrammatic representation of vinyl polymers* $[-CH_2-CHR-]_n$

FIG. 4-8 TACTICITY OF POLYMERS

Drawing from Organic Polymer Chemistry - K. J. Saunders - Chapman and Hall, London, 1973

FIG. 4-9 CATIONIC POLYMERIZATION

A. Ordinary Acids - e.g. $HClO_4$, H_2SO_4, HCl

Initiation: $H^+A^- + CH_2{=}CHR \longrightarrow CH_3\text{-}\underset{+}{C}HR\ A^-$

Propagation: $CH_3\text{-}\underset{+}{C}HR\ A^- + CH_2{=}CHR \longrightarrow CH_3\text{-}CHR\text{-}CH_2\text{-}\underset{+}{C}HR\ A^-$

Termination:

Transfer to counter-ion

$$\sim\!\sim CH_2\text{-}\underset{+}{C}HR\ A^- \longrightarrow \sim\!\sim CH_2\text{-}CHR + HA$$

Transfer to monomer

$$\sim\!\sim CH_2\text{-}\underset{+}{C}HR\ A^- + CH_2{=}CHR \rightarrow \sim\!\sim CH\ CHR + CH_3\text{-}\underset{+}{C}HR\ A^-$$

B. Metal halides (Friedel-Crafts Catalysts) + Co-catalyst (active hydrogen e.g. alcohols, water, acids)

Form complex protonic acid. Rea ct mainly as above.

C. Carbonium Salts e.g. Triphenyl methyl chloride

Initiation:

$$\phi_3C^+\ Cl^- + CH_2{=}CHR \longrightarrow \phi_3C\text{-}CH_2\text{-}\underset{+}{C}HR\ Cl^-$$

Propagation and Termination as above.

PIGMENTS AND PIGMENT DISPERSION

CHAPTER 5

5-1 SIZE, SHAPE, SURFACE CONTOUR

Pigments are solid materials divided into fine particles. Fine pigments can be 0.02 microns in diameter (or other characteristic dimension). Coarse pigments can be of 100 microns diameter. (Surface coatings are usually 25-50 microns thick). Characteristically, pigments are almost completely insoluble in water and organic chemicals. For some uses, however, (for example, inhibition of corrosion, fungicidal action) their solubility, though small, is important.

A few pigments are made by condensation of non-crystalline, roughly spherical fine particles from a vapor. Many are mined and crushed, or precipitated as crystals, and crushed. Their surfaces are rounded. Washing and drying of a filter cake containing the pigment are common operations. Sometimes chemicals are added to pigment slurries to aid in filtration, and these remain, to some extent, stuck to pigment surfaces. Small amounts of common soluble salts also remain from the water used for washing.

The surfaces of crystalline materials have compositions which depend on the direction of cleavage. The surfaces therefore differ in their affinity or absorption characteristics.

The surface area of a pigment depends on the particle size and shape. The surface area of a particle increases with the square of diameter or other characteristic dimension but the surface area per gram of pigment is inversely proportional to the diameter. Over the range of sizes from 0.02 microns to 100 microns, the surface area per gram changes by a factor of 5000.

The qualities of a pigment's surfaces help to determine the rheological properties of a fluid coating containing them and can also affect the mechanical properties of a dried film containing them. For many pigments the chemical nature of the surfaces is unknown, trade-secret or non-uniform.

5-2 FUNCTIONS OF PIGMENTS

FUNCTION	NOTABLE EXAMPLES
A. Appearance	
1. Provide Color	Phthalocyanine blue, chrome yellow, carbon black
2. Provide hiding	Titanium dioxide, chrome yellow, voids
3. Provide roughness	Calcium carbonate, coarse silicas
4. Provide enhanced roundness	Aluminum flake, "Afflair"

B.	Alter Rheological Properties:	
	1. Produce thixotropy, pseudoplasticity	Clays
C.	Economy:	
	1. Substitute for more expensive binder.	Clays, calcium carbonate
	2. Build structures in the dried film to include air (thereby increasing hiding).	Clays, calcium carbonate
D.	Reservoir for Active Material:	
	1. Anticorrosive	Zinc chromate, zinc dust
	2. Antibiotic	Copper dust, zinc oxide
E.	Fireproofing:	Antimony oxide
F.	Electrical conductivity:	Carbon black, maganese dioxide
G.	Stabilization of Polymer:	Antimony oxide
H.	Ultra Violet Protection:	Titanium dioxide, iron oxide Carbon black
I.	Reduce permeability:	Mica

5-3 AGGLOMERATES

When supplied as a filter cake or as a dry powder the individual particles usually consist of clumps of particles held together by the universal forces of attraction which operate between surfaces in close proximity and by solid materials which cement the particles together. The cements may be of material deposited from the continuous phase of the pigment dispersion when it is dried.

5-4 DISPERSION

In the preparation of surface coatings, the agglomerates of pigment are separated and sometimes made finer by breaking crystals. Dispersion usually refers to the process of separating the individual particles in the agglomerates or clumps of particles and mixing them, more or less uniformly, into a liquid continuous medium.

Dispersion is usually accomplished by strong shearing forces in a paint mill. The shearing forces within the liquid are transmitted by it to the agglomerates, tending to break them. Higher shear is necessary to break small agglomerates than large ones, and to separate agglomerates of fine pigment particles to their ultimate size than coarse ones.

Grinding usually refers to the breaking of hard agglomerates or large pigment particles - usually crystals - but it often refers to dispersion as well.

5-5 FLOCCULATION

Dispersed pigment particles are subject to Brownian motion of vibration and rotation due to random collisions with molecules of the medium. The particles will occasionally collide - more strictly they approach each other within about 4A. Whether or not they will stick to each other after a collision depends on the difference between two competing forces: (1) the attractive forces of the particles for each other and (2) the attractive forces of the liquid for the particles. If the net attractive force between pigment particles if sufficient, particles will stick together after collision. The process will then continue until essentially all the particles are stuck to others. Flocculation refers to the process by which the suspended particles after collision form clumps or floccs. In the surface-coating industry flocculation is the rule, and must be controlled if the flow properties are to be uniform.

5-5-1 Control of Flocculation

Flocculation is a function of forces between pigment particles and molecules of the liquid phase. Coating of a pigment with a material having a strong attraction to the liquid phase is effective in preventing flocculation provided this coating has also a strong attraction to the pigment surface. Surface-active agents, such as soaps, usually have, on one molecule, types of chemical groups which differ in affinity. Such surface active groups are used to prevent or control flocculation of pigment dispersions.

The surface active agents coat the pigment surface. One part of their molecule has affinity for the liquid phase. An additional effect of the surface active agent is the limit that the agent provides to the close approach of the two pigment surfaces which have strong mutual attraction when close.

Flocculation can be produced by the addition of long molecules which are attracted and stick to the pigment particles, but which are long enough and have enough attractive groups to form bridges between pigment particles.

When soaps or other ionized materials are coated on pigment particles to keep them apart by electrical repulsive forces, the addition of salts reduces their repulsion and may cause flocculation. Also, changes of pH can cause reduction in ionization of the surface-active agent and hence flocculation.

5-6 SETTLING

Settling of particles under the action of gravity proceeds at a rate proportional to the net force of gravity on the particle and inversely proportional to the viscous resistance to its movement. If the rate of settling due to gravity becomes comparable with the rate of diffusion due to Brownian motion there is no substantial settling. Carbon black particles of 0.05 micron, when dispersed individually, for example, do not settle appreciably.

The force of gravity on a spherical particle suspended in a liquid is given by:

Eq. 5-1

$$f_g = \frac{4\pi r^3 (d - d_1)g}{3}$$

f_g = gravitational force (dynes)

r = particle radius (cm)

d_1 = density of liquid (g/cm^3)

d = density of particles (g/cm^3)

g = acceleration of gravity (dynes/g)

The resistance to motion of a particle is proportional to its velocity and the viscosity.

Eq. 5-2

$$f = 6\pi\eta r v$$

f = viscous force (dynes)

η = viscosity (poise)

v = particle velocity

The steady state rate of settling, reached almost immediately, is such that $f_g = f$. It follows that:

Eq. 5-3

$$v = \frac{2r^2 (d - d_1)g}{9\eta}$$

If the particle considered consists actually of a mass of finer particles the resistance to motion will be governed by the size of the mass, its average density, and the porosity. Masses of particles that are stuck to each other settle much faster than individual particles.

In a weightless environment, settling would not occur, but flocculation would go on as usual.

Equations (5-1) to (5-3) apply to a single particle settling in an otherwise motionless fluid. A particle falling through a liquid actually causes liquid to flow with it. Another particle, if close enough behind, is caught up in the liquid flow from the first particle and its fall is then more rapid. Accordingly settling rates of concentrated suspensions may be perceived as more rapid than simple Stokes Law equations would predict. Actually they are rates of fall in a convective liquid.

5-6-1 Hard and Soft Settling

Pigments which are well dispersed in a less dense liquid and which have little net attractive force for each other pack closely when they settle on top of each other. They can slide past each other. They act lubricated and rearrange themselves to occupy the lowest levels in the fluid. Pigments which have strong inter-particle attraction do not slide over each other. They form loose, highly porous, structures when they settle. Therefore, liquid paints formulated with pigments

large enough and dense enough to settle, must be flocculated to produce soft-settling even though other properties might suffer. When pigment particles approach each other in a gas, for example air, the new attractive force between the particles is always larger than the attractive force for the rarified molecules of the gas. As a result, pigments do not settle in air to a close-packed condition, and the finer the pigment the larger its volume per pound.

5-7 HIDING AND COLOR

To obtain maximum utility from a pigment it is necessary to break agglomerates and flocculates down to the size of the primary particles. If flocculates are needed it is preferable to keep them loose to maintain color and hiding. See Chapter 8.

5-8 GRINDING AND DISPERSION PROCESSES

5-8-1 Shear Processes

A mixture of pigment and liquid medium is subjected to shear between surfaces that are in relative motion, and much farther apart than particle dimensions. Agglomerates which are subjected to sufficient shear are broken. Roller mills, dough mixers, high-speed stirrers and simple mixers are of this type. (Shear force can be expressed in terms of the force applied by each cm^2 of one moving surface. The shear rate is given by the quotient of the relative speed divided by the distance apart).

5-8-2 Hard-body Contact

Freely moving hard-surfaced materials can move closer to each other than pigment-particle dimensions. When they do they crush pigment particles between the hard surfaces. However, the devices making use of hard-body contact - ball and pebble mills, attritors, sand mills - do not produce hard-body contact if the viscosity is high. When the viscosity is high the hard grinding surfaces do not get as close to each other, and the devices operate as high-shear force devices operating in a more-or-less homogeneous medium, much like a dough mixer or roller mill.

5-8-3 Cavitation

A liquid subject to tension develops cavities filled with vapor at low pressure. When the tension is relieved the cavities collapse and the momentum of the liquid moving into the cavities is dissipated rapidly in a small volume. The forces involved in cavitation are large enough to break molecules and produce free radicals. Sonic and ultrasonic devices of sufficient intensity function this way. Some cavitation must occur also in high speed stirring devices, in low speed high-shear-stress rubber mills and in roller mills. Cavitation is also produced on vibration from hard impact.

5-8-4 Selection of Grinding and Dispersion Equipment

The selection of grinding processes depends on the quality or fineness required and on the types of hard agglomerates or crystals to be broken. For the breaking of crystals, ball mills, pebble mills or attritors are needed. These provide the highest, though local,

compressive and shear forces. For softer agglomerates, and, particularly for the fine particle pigments, high viscosity, low-speed rubber mills, using viscous suspensions, and sonic waves of high intensity function best. Sand mills are effective for pigments of all but the finest size, provided that hard crystals need not be broken. Some products, particularly those of low gloss, do not need much reduction of particle size or agglomerates. Simple stirring at intermediate viscosities is low in cost, but results in some loss in hiding and utilization of colored pigments. When mixtures of coarse and fine pigment are mixed together, the coarse ones act much like sand in a sand-mill or pebbles in a pebble mill, to exert high shear on smaller particles between them. Accordingly simple mixing equipment can operate like a sand mill in securing relatively good dispersion of fine pigments - provided coarse pigments are present in sufficient volume.

Simple mixers disperse pigments effectively when the particles are large, the agglomerates are soft, and the vehicle possesses adequate wetting characteristics. Two types of operation are (1) high viscosity low shear rate and (2) low viscosity high shear rate. Usually the high viscosity devices have a relatively large volume within which the shearing action occurs and this volume is exchanged slowly. The low viscosity devices operate with a small mixing zone and the material in this zone is exchanged rapidly.

5-9 COMPOSITIONS SUITABLE FOR PIGMENT DISPERSION

Pigment dispersion is usually accomplished by using as large a loading as possible of pigment consistent with the rheological requirements of the equipment. The composition to be dispersed or ground is called a mill-base. The mill base will also comprise water or solvents and will generally contain a surface-active component which will stabilize the pigment dispersion somewhat against flocculation.

The fluid used or vehicle can be a polymer solution which will be all or part of the binder in the final film. The surface-active agent can be a separate material with no other function, or it can be identical with all or part-of the binder polymer. Usually it is preferable to let the binder perform the surface-active function, because of the water-sensitivity introduced by the usual surface-active agents. If the fluid is a polymer-latex, sufficient surface-active agent must be present to protect not only the latex but the pigment against flocculation.

5-9-1 Compositions for Rubber Mill

The pigment will usually be a highly colored, finely divided one requiring extreme forces. The vehicle for the mill base must be selected to properly wet and disperse the pigment and produce a coherent, tacky mass which holds together like a sheet of rubber. For this purpose the vehicle must contain a polymer of adequate molecular weight - say 50,000 or above. Plasticizers (or some high-boiling solvent) may be used to reduce the viscosity of the highly pigmented mill-base to manageable levels.

5-9-2 Compositions for 3-roll Mill

The molecular weight of polymers used in the vehicle of the mill base need not be high. Sufficient surface active agent is needed to prevent flocculation. Pigment loading should be as large as possible consistent with a fluid mill base. Clearances can be adjusted to compensate somewhat for viscosity.

5-9-3 Compositions for Pebble and Ball Mills

The compositions should contain maximum pigment and minimum fluid portion. The viscosity of the mill base and the rotational speed of the mill should be such as to produce a cascading action rather than centrifuging or cataracting of the balls or pebbles. The balls or pebbles are filled preferably to the half-way mark in the mill to obtain maximum power input.

5-9-4 Compositions for High-Speed Mixers

High-speed mixers operate by providing a small volume near the mixing blades within which the shear rate is high. The passage of material through this volume is rapid enough to produce a high rate of production. In general, such mixers are suitable for pigments of intermediate size containing no hard agglomerates. The viscosity of the composition must be low to obtain rapid passage through the mixing zone.

5-9-5 Compositions for Sand Mills

Commercial sand mills operate within certain tolerances of stirring speed and feed rates. Densities and viscosities of the pigment-vehicle mixture can be adjusted to optimum values but wide ranges are economical.

5-10 SURFACE-ACTIVE AGENTS

A. Nonionic surface-active agents usually consist of molecules containing one or more highly polar groups and relatively non-polar groups. Either the polar or the non-polar group may be attracted preferentially to the pigment, the other to components of the vehicle.

B. Anionic surface-active agents are metallic salts or acids consisting of a (usually) large negatively charged portion which is held on the surface making it negatively charged and a positively charged portion which is of lesser importance - not absorbed, but attracted to a slight degree to the negative surface. The positive ions are dispersed throughout the medium - usually water or strongly polar material. The negative ion may be held to the surface by a non-polar portion of the ion or by a polar portion.

C. Cationic surface-active agents are salts or bases consisting of a (usually) large positively charged portion which is absorbed on the surface. The negatively charged portion is attracted, but slightly, to the positively charged surface.

D. Amphoteric surface-active agents contain ionizable groups of both positive and negative types on the same molecule which is held to the surface.

When ionizable surface-active compounds are used with particles in aqueous environment they may be ionized and the coated particles carry an electric charge. When such surface-active agents are used in non-polar environment, the ions of the surface-active agent do not separate and the particles will not be charged. In such cases they act as though they are non-ionic.

Surface-active agents for a particular fluid-pigment combination are absorbed on the pigment surface. If the amount of surface-active agent is insufficient, the pigment particles will attract and touch each other and a weak structure will be set up; If the amount of surface-active agent is increased sufficiently the particles no longer set up such a structure and the viscosity drops, permitting a higher pigment loading. Generally, for economy, the pigment-loading is as high as possible, and additional binder components are added after the grinding step.

If polymers containing a plurality of absorbing groups are the surface-active agents they can usually bridge between pigment particles. The dispersing action of the mill tends to loosen such attachments and redistribute them until molecules do not bridge between particles. The most favorable arrangement of a surface-active polymer is as a coating on a single pigment particle, and all pigment particles fully wrapped. When the pigment particle is sufficiently covered it will no longer flocculate in that medium provided the medium is sufficiently attracted to the surface-active agent.

When incompletely covered particles (even though well dispersed in a mill) meet up with additional surface-active polymeric material they may be bridged by the polymer, and localized clumps appear - known as seed. Additional grinding or dispersing action is then needed. To insure that seeding does not occur, an excess of polymeric surface-active agent is needed during a grinding or dispersion step. However, the excess should be minimal because the viscosity otherwise increases unnecessarily and reduces the amount of pigment that can be dispersed.

Surface-active agents suitable for pigment dispersion can be of low molecular weight (e.g. butanol is surface active for rutile titanium dioxide in xylene) of film-forming high molecular weight (nitrocellulose for carbon black dispersions), or of intermediate molecular weight, (alkyd resins.)

5-11 PIGMENT PACKING

Uniformly sized cubes can be packed by hand into dense structures with no voids. Uniformly sized spheres can be packed by hand into dense structures but the void space will be 26%. Experiments to pack uniform spheres by random motions yield about 36% voids. The packing of spheres non-uniform in size can be calculated. Obviously void space can be decreased by packing fine spheres in the large void spaces between large spheres. Plate-like and needle-like pigment particles yield much larger void volume than spheres.

Many of the properties of a fluid suspension are a function of the volume fraction occupied by the pigment. When the pigment volume is raised the viscosity rises. The rise with pigment volume is sudden if the interparticle attraction is low (good dispersion) and is somewhat more gradual as the interparticle attraction is high.

Oil absorption measurements yields information on the degree to which the pigment particles, by virtue of their shapes and surface characteristics, will pack closely when stirred. The more pigment that can be added to the oil before stirring becomes impossible, the lower is the oil absorption value, and the higher the pigment content in an economical dispersion process.

5-12 PIGMENT VOLUME, CRITICAL PIGMENT VOLUME CONCENTRATION

In the formulation of coatings, the volume fraction of a film occupied by pigment is much higher than it usually is in bulk plastics. The need for achievement of color, hiding, and certain protective values in thin films often requires as high a pigment concentration in the film as possible.

The pigments vary strongly in their densities. The volume occupied by a pigment is regarded as more significant than the weight fraction with respect to the rheological properties that are important in manufacture of coatings and in their mechanical properties afterward.

As pigment volume concentration is increased a concentration is reached where there is insufficient binder to fill the voids between the pigment particles when the vehicle is dried. This is the critical pigment volume concentration. At values beyond the critical pigment volume concentration, the film becomes laden with voids, it becomes weaker, more porous and more easily adhered to.

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CORROSION OF IRON AND ALUMINUM

CHAPTER 6

The corrosion of iron and aluminum to produce oxides and hydroxides proceeds because of the energy liberated during the oxidation. The mechanisms by which the oxidations occur will depend on the conditions.

In the absence of water and at ordinary temperatures, iron and aluminum corrode very slowly. A thin layer of oxygen atoms forms on the surface and the reaction stops. Aluminum mirrors, thin enough to be partly transparent, deposited on glass by vacuum deposition and kept dry, remain highly reflective for years. The corrosion of iron is similar to that of aluminum in many ways.

6-1 ELECTROCHEMICAL CORROSION

The rate of corrosion increases markedly in the presence of electrically conductive films of water, and the corrosion becomes spotty. Electrolytic cells are formed of anodic and cathodic areas, connected by metal and electrolyte. In the anodic areas iron is converted to Fe++ (and in the presence of oxygen, ultimately to Fe+++).

In the absence of oxygen iron rusts slowly. The reaction yields hydrogen.

At the anode: $Fe \rightarrow Fe^{++} + 2(e)$ (1)

At the cathode: $2H_2O \rightarrow 2H_2 + 2OH^- - 2(e)$ (2)

The overall reaction is:

$$Fe + 2H_2O \rightarrow Fe^{++} + 2OH^- + H_2 \quad (3)$$

In the presence of oxygen, hydrogen is not evolved. The reaction rate is increased. In the rusting process the anodic areas become acidic and the cathodic areas become basic.

The overall reaction can be written as:

$$2\ Fe + 2H_2O + O_2 \longrightarrow 2\ Fe(OH)_2 \quad (4)$$

and this can be divided among anodic and cathodic areas as:

$$2\ Fe + 4H_2O \longrightarrow 2\ Fe(OH)_2 + 4H^+ + 4(e) \quad \text{(Anode)} \quad (5)$$

$$O_2 + 2H_2O \longrightarrow 4OH^- - 4(e) \quad \text{(Cathode)} \quad (6)$$

The production of acid at the anodic areas and base at the cathodic areas according to (5) and (6) can cause side-reactions with coatings or other materials present. In any case, the hydrogen ions and hydroxyl ions will tend to diffuse and react with each other.

$Fe(OH)_2$ reacts with oxygen to form ferric hydroxide with intermediate formation of mixed hydroxides and Fe_3O_4. In rusting, the formation of Fe+++ occurs at some distance from the metal. When $Fe(OH)_3$ is formed at the metal surface in sufficiently dense form the metal is protected by it.

6-2 INHIBITION OF CORROSION

6-2-1 Passive Inhibition

The rate of corrosion is reduced by reducing the ionic conduction between cathodic and anodic areas, or by placing barriers to the passage of oxygen. Barriers to ionic conduction are set up by putting in contact with the metal or its oxide an organic coating of low affinity for water and ions. The barrier properties to water of known organic coatings are insufficient to prevent the passage of enough water to provide an ionic environment, but if ions must diffuse through the coating the rate will be low. Therefore, it is important to have no path for ions or a high concentration of water. This means a high level of adhesion that is not unduly weakened by water.

6-2-3 Active Inhibition

The rate of corrosion is reduced by a separate chemical reaction.

a. Anodic Inhibition - The addition of chromate, nitrite, or hydroxyl ion in sufficient amounts causes pronounced inhibition of the anodic reaction. Some of the inhibition is used up and a protective ferric oxide film which is a poor conductor of ions or electrons is formed on the metal. The addition of chloride to the electrolyte causes an increase in permeability of the oxide film and tends to destroy the anodic inhibition.

The anodic inhibition reaction can occur only if relatively clean metal comes in contact with a sufficiently high concentration of anodic inhibitor. If there are thickly rusted areas or pits into which the inhibitor can diffuse only slowly, these will not be subject to the action of the inhibitor in sufficiently high concentration, and there will be no sufficient inhibiting action. In fact, insufficient inhibitor accelerates corrosion in aqueous systems and is the cause of pits - local high corrosion rates.

Red lead, zinc chromate, and strontium chromate pigments are used in metal protective paints. These pigments are protective also in pure water, and their value probably depends to some degree on the inhibition of the anodic reaction.

In the absence of oxygen the corrosion of iron proceeds more slowly, hydrogen is liberated and the ferrous form of iron is obtained. Rusty iron exposed to water in the absence of oxygen turns black, as it does on painted rusty steel. In other words, after rusty steel is painted, reaction of the red rust with iron to form black oxide proceeds, accompanied by dimensional changes. It is therefore important to remove rust before painting.

b. Cathodic Inhibition - If sufficient electromotive force is applied between an iron surface and another surface in an electrolyte in such a way as to make the iron surface the cathode, the iron surface will not corrode. The reaction at the cathode will usually be the formation of base and hydrogen, both of which diffuse away.

The reaction at the anode will depend on its chemistry. If a corrosion-resistant anode is used, the formation of acid and oxygen is expected. If the anode is an active metal, like zinc, it will dissolve. If a piece of zinc is connected with good contact to a piece of iron and both are immersed in water together, the zinc will dissolve and the iron will remain unattacked. For this method of protection of iron to work there must be a sufficiently high e.m.f. between the steel and the adjacent liquid, and this means a sufficient current density. The zinc must dissolve at a rate sufficient to provide the minimum current density required.

Cathodic protection of steel is accomplished by use of zinc-rich paints. Good contact with the substrate and low electrical conductivity of the electrolyte are essential. For this purpose silicate binders are often used together with powdered zinc pigment. Zinc-rich epoxy-based paints are also used for protection of steel.

6-3 THE PROTECTION OF STRUCTURAL STEEL FROM CORROSION:

Clean steel corrodes rapidly in moist air or water forming hydrated metal oxides. The portion of oxide next to the metal is of Fe++ while the outer portion is Fe+++. It is usually porous, and contains water, chlorides, and sulfates. When steel is oxidized at elevated temperatures (during manufacture of castings, etc.) a dense layer of adherent oxide or mill-scale is formed. The mill scale is brittle and mainly Fe_3O_4 , but, as long as it is intact it protects the metal below it from further corrosion, painted or not. If the mill-scale is damaged mechanically, or it becomes loosened from the metal through repeated temperature changes, corrosion can occur with large-scale detachment of mill-scale and paint.

If the mill scale is partly removed by corrosion or damaged mechanically, paints will generally protect poorly over it. Sandblasting will produce a clean iron surface which, however, will oxidize rapidly. The sandblasted steel surface is best protected with a paint containing an anodic inhibitor like chromate or red lead; or alternatively, by zinc dust whose particles are in electrical contact with each other and the metal, and which protects by cathodic inhibition.

Often it is impractical to sand-blast, and wire-brushing is used to remove coarse, thick, rusty spots. This wire brushing usually leaves large areas of porous hydrated iron oxide in contact with the metal. The prognosis for painting is poor for such surfaces even if inhibiting pigments are used. The best one can do is provide an adherent binder which remains flexible enough to withstand the dimensional changes (due to temperature variation and corrosion) and yet relatively impermeable to water. Penetration of the binder into the rust to leave a dense structure after drying is also considered desirable if removal of the rust is impractical. For this purpose low molecular weight and low-solvent-content are desirable (evaporation of some solvent after the film has hardened can leave voids).

6-4 ADVANTAGE OF ACTIVE INHIBITORS

The protection of steel from corrosion by the use of active inhibitors, i.e. chemicals which react in the aqueous environment to protect anodically or cathodically, is to be distinguished from the passive protection provided by a relatively impervious paint. A small damage which cuts through a paint formulated to protect actively will not result in corrosion, but it will result in corrosion when a passive protection is used.

6-5 METAL PRETREATMENTS

Chromate pre-treatments for iron and aluminum provide adherent oxidized surfaces (largely oxides, basic phosphates, and chromates, that temporarily protect the metal from electrolytic corrosion, which adhere strongly to the metal, and to which organic coatings adhere strongly. A few hours soaking in water, in the absence of a protective organic coating, causes corrosion of the temporary protective layer. The usual organic coatings adhere poorly to untreated steel and aluminum and protect much better with the metal treatments.

6-6 FILIFORM CORROSION

When corrosion conditions are mild, corrosion under a painted surface will often occur in filiform patterns (resembling worms) rather than as spots or as uniform disintegration of the surface. Filiform corrosion is specially common on steel or aluminum painted with flexible coatings.

6-7 MEASUREMENT OF CORROSION

The tendency of metals to corrode in moisture is highly dependent on details of their chemical composition and physical treatment. Stress in metals is known to increase solutions rates. Fine cracks are known to concentrate corrosion when anodic inhibitors are used. With the best of precautions rusting occurs in spotty form because iron near rusted areas is generally more prone to rust than iron near unrusted areas.

Corrosion is often measured in terms of weight loss, in terms of area rusted, or in terms of number of pits and depth. Each of these measures is significant to some degree. No one of the measures tells a complete story.

When painted steel panels are exposed to a particular corrosive condition it is common to find variations that are of practical significance between supposedly identical panels.

6-8 ACCELERATED CORROSION TESTS

1. Humidity Cabinet - Painted panels are exposed to the vapor space above water at about 110°F. They are filled by water (osmotic) or by rust and water. The coating is softer and more permeable than at room temperature. The deposit of water on the surface is quite spotty and dependent on very small differences in temperature.

2. Water Soak - The exposure is the same as the humidity cabinet exposure except that it is more uniform. Generally the paints will be exposed to a greater salt content than in the humidity cabinet.

3. Salt Spray - Painted panels are usually scratched with a knife before exposure. There are usually no osmotic blisters in the paint because of the salt content in the spray. The penetration of salt and water to the metal provides rapid corrosion. Cathodic areas adjacent to anodic corroding areas are alkaline and the alkali often attacks the binder causing swelling and softening. The coating is usually loosened from the areas adjacent to the scratch. The distance from the scratch over which loosening occurs is taken as a measure of the attack.

4. Tidewater Exposure - Painted panels are alternately soaked and dried. Cyclic expansions and contractions are superimposed on the corrosive environment.

5. Bimetallic exposure - This in effect attaches a electric cell to produce anodic and cathodic areas of higher potential than would be obtained with only one metal. The use of a more noble metal (say copper) on steel increases the corrosion rates.

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DEGRADATION AND STABILIZATION

CHAPTER 7

All organic coatings change with the passage of time. Their useful life depends on their chemical nature, their physical structure, the durability of the substrate to which they are attached, and their environment.

Organic coatings usually are required to have a variety of properties selected to best match the use for which they are intended. The changes brought about by elements of the environment usually affect one or another of the required properties adversely.

Substantial increases in useful life are often made by the addition of stabilizers in small amounts. Sometimes these are added also for the purpose of reducing adverse changes brought about during the conversion of the coating from liquid to solid form (e.g. yellowing which occurs during the baking process).

7-1 INTEGRITY AND ADHESION

Catastrophic failures in integrity are usually evident as cracks. Sometimes these are long and widely separated. They can also be close enough together to appear to the naked eye as roughened surfaces. Gradual failures are usually evident as loss of gloss or chalking. Such failure occurs mainly in coatings which are pigmented.

Failures in adhesion are evident as blisters or peeling or as chipping under commonly applied stresses.

The stresses responsible for loss of integrity and adhesion can be externally applied, as in bending the substrate. They can also be the result of differential dimensional changes due to temperature changes, absorption of water, swelling or de-swelling with solvents, and evaporation of components.

Clear films exposed outdoors fail eventually by developing many fine cracks. Cracks can result from stresses due to shrinking when the temperature is reduced. The stresses are also produced when the films have lost enough of their substance by evaporation or solution. Loss of molecular-weight can reduce toughness causing even small temperature changes to produce cracks.

Films pigmented so that sunlight does not penetrate deeply usually fail by chalking, i.e. losing vehicle and exposing pigment, which is washed away. Microcracks between vehicle and pigment may possibly occur first.

7-2 PROTECTIVE PROPERTIES

The protective properties of a coating depend on low permeability to damaging environmental chemicals. Cracks ruin protective value. In the absence of cracks chemical changes in the coating can result in large permanent stresses. The stresses can result in a reduction of density with

a consequent increase in permeability. The chemical changes can also result in increases in permeability to water when strongly polar groups are formed by chemical changes. Failure of the substrate is often a result of failure of the protective properties of the coating in the case of wood or steel.

7-3 COLOR

Changes of color often are the cause for repainting. Color changes occur through the use of non-durable pigments, through changes in the vehicle, through the deposition of dirt, the growth of microorganisms. The formation of long conjugated double-bond systems is a principal cause of yellowing. Some chemical groups are particularly effective in causing yellowing e.g. phenols and aromatic amines.

7-4 GLOSS

Films which are initially smooth or glossy develop roughness by losing vehicle faster than pigment through evaporation or solution, by developing fine cracks or by developing blisters. Blisters usually result from collection of water from osmotic forces, or from swelling by water, with resulting expansion and detachment.

7-5 CLARITY

Clear films often develop opacity on exposure. The opacity is the result of the development of inhomogeneities of refractive index. The inhomogeneities can occur in vehicles consisting of mixtures as the result of phase-separation due to thermodynamic incompatibility or due to the absorption of water. Sometimes voids occur due to selective removal of parts of a binder where the remainder is too rigid to contract and fill the voids.

7-6 REQUIREMENTS IN THE BINDER TO MAINTAIN IMPORTANT PROPERTIES

To secure a long useful life it is important to maintain a high molecular weight, to preserve the chemical constitution, and to preserve the phase structure.

7-6-1 Molecular Weight

A minimum molecular weight is necessary for the bulk of the binder in order to obtain adequate elongation without fracture (integrity). In some cases, as in high-molecular weight polyvinyl chloride, substantial amounts of low-molecular weight plasticizers can be added usefully. These soften the binder and weaken it, particularly at elevated temperatures, but lower the minimum useful temperature.

7-6-2 Chemical Constitution

Given a high molecular weight the chemical structure determines the forces holding the binder together and attaching it to pigments and substrates. The chemical structure also affects the affinity for water and solvents.

7-6-3 Phase Structure

Certain balances of binder properties, for example, good impact resistance and hardness, or long useful temperature range, are often achieved by mixtures of polymers which are not homogeneously dispersed. The polymers are separated into phases which have optimum size for achievement of a particular property balance. The phase structure is often developed by evaporation of a solvent or change of temperature, but the development is not instantaneous because migration of polymers is slow and the phase structure therefore changes slowly. Certain binders form slowly into domains of crystallites, and these melt sharply at their melting point, but form slowly on cooling. The intrusion of a separate phase, e.g., water, between binder and pigment or between binder and substrate can cause weakness or loss of adhesion. Water can also affect the mutual solubility of the components of a binder and cause them to separate.

7-7 THE ENVIRONMENT: ELEMENTS OF THE ENVIRONMENT WHICH AFFECT USEFULNESS OF COATINGS

7-7-1 Oxygen

The reaction of oxygen with polymers is favored by the release of the large energy of oxidation. However, at ambient temperatures, oxidation is slow. The oxidation process is known to be a chain reaction in which free radicals are important participants. During the course of the chain reaction, hydroperoxides and peroxides are formed first. These undergo further change.

7-7-2 Light

a. Solar Ultra Violet:

The radiation which reaches us from the sun contains virtually no light of wave lengths shorter than 290nm. Radiation of 290 to 400 nm., called solar ultra violet, is invisible but has chemical effects. Figure 7-1 is a plot of intensity of radiation as a function of wave length. The effect of light on polymers generally increases with decreasing wave length (provided it is absorbed) at such a rate that the region of wave length 290-320 nm., in spite of low intensity, is the most responsible for degradation of organic coatings. For this reason, organic coatings exposed behind glass are generally much more durable than those exposed directly. Solar ultra-violet is the principal initiating cause of oxidation of coatings by oxygen.

b. Effect of Sunlight on Organic Compounds:

The energy contained in a quantum of 290 nm light is sufficient to break any C-C, C-H, C-O or C-N linkage if applied appropriately. Actually, quantum yields from light in the degradation of polymers are estimated at 10^{-3} - 10^{-5}. Most of the absorbed radiation, therefore, is converted into heat without direct chemical effect.

The effect of sunlight on polymers is to initiate free-radical formation and subsequent oxidation by oxygen. Furthermore, the heat produced by absorption of sunlight accelerates other chemical reactions and increases the mobility of small molecules within the polymer, accelerating their migration and evaporation.

The exposure to light and oxygen causes a different balance of effects in different polymers, but in general there are change of color, change of solubility, and volatility. On a molecular level, there is oxidation, main-chain scission, side-chain scission and cross-linking.

Sunlight varies in wave length, composition, and intensity with latitude and with angle in the sky. It has secondary effects on polymers through its action in producing ozone.

c. Mechanisms in Oxidation:

The initial effect of light and elevated temperature is to form free radicals - molecules having atoms which possess an unpaired electron. These are usually localized on specific atoms. Once free-radicals are formed, chemical reactions can proceed, even in the dark, to result in oxidation products. The usual oxidation products of hydrocarbons and many polymers are carbon dioxide, carbon monoxide, water, hydroperoxides, alcohols, ketones and acids. There is also temporary growth of polymer chains by combination, and there is scission of polymer chains to form fragments.

The usual sequence of oxidation is given in Figure 7-2 for a simple aliphatic hydrocarbon. All of the products of reaction are subject to further oxidation until ultimately everything is in the form of CO_2, H_2O or other volatile products.

The creation of a free radical by absorption of sunlight requires the presence of a chemical species which absorbs in the solar ultra-violet region (such as aromatic rings, double bonds, carbonyl, or hydroperoxide). While the polymeric substances used as binders may not, in ideal cases (e.g., polyethylene), have such absorption, they all possess such absorbing species in actual cases combined in molecules of polymer or near molecules of polymer. The energy picked up by the absorbing species must be transferred in sufficient amounts directly or indirectly, to a critical part of the polymer for a free radical to form on the polymeric chain. (Only a small fraction, estimated as 10^{-3} - 10^{-5}, of the absorbed quanta yield free radicals).

Free radicals are created also by high temperatures and by a variety of oxidation - reduction reactions. The sequence of reactions followed after free radicals are once present is the same, regardless of the mode of initiation. During the sequence free radicals tend to proliferate because absorption of a molecule of oxygen on one free-radical results in a peroxide which decomposes to two free radicals.

Free radicals are not all equally reactive. A relatively inactive free radical tends to stop the proliferation, as does the spontaneous combination of two free radicals.

Carbon-hydrogen bonds vary in the case with which hydrogen atoms are removed to form free-radicals. The order of reactivity is usually given as in Figure 7-3.

The oxidation rates of various polymers and the hydrogens chiefly responsible are given as in Figure 7-4.

Important effects on the integrity of polymers are produced by molecular weight decrease due to scission of the long polymer chains. In the case of polypropylene and other hydrocarbon polymers reactions as in Figure 7-5 are postulated as initiated by ultra-violet light. The light is absorbed by hydroperoxides, ketones and aldehydes and results in breakdown of molecular chains leading to brittleness and shrinkage.

The formation of a free radical on structures like polyisobutylene - where a carbon atom is completely substituted - can result in chain scission as in equation (9) of Figure 7-5. Chain scission reactions are also present in thermal decomposition of acrylates and methacrylates and styrene polymers.

Cross-linking occurs as a result of the combination of radicals in separate chains of a polymer. Chain scission and cross-linking reactions occur simultaneously on the exposure of coatings. As a result some binders are cross-linked after exposure but contain a substantial fraction of low-molecular weight. Cross-linking cannot occur unless the radicals are mobile enough to meet each other. Rigid molecules do not favor this condition. The higher alkyl acrylates, soft mobile polymers, tend to cross-link.

Free-radical depolymerization is the reverse of the free-radical polymerization and results in liberation of monomer. Some depolymerizations as that of polymethyl methacrylate, yield monomer almost quantitatively. (Equation (10) Figure 7-5).

7-7-3 Water

Water is soluble to some degree in all polymers. Its partial pressure in air is of the order of 20 mm of mercury depending on temperature and humidity. It is present to some degree in surface coatings all the time. The amount of water absorbed depends on the chemical structure of the film. Hydroxyl, amino, carboxyl, amide and other polar groups favor absorption of water. The film generally expands on absorption. The most prominent degrading effect of water is hydrolysis of esters, amides, etc. present in organic coatings, resulting in chain-scission and reduction of molecular weight. Coatings often contain carboxylic acid groups in their structure in order to obtain good wetting, good pigment dispersal and reactivity to produce cross-links. Some fraction of these carboxylic acid groups remain as such in a hardened paint film. On exposure to alkaline water the carboxylic acids react to form salts, which absorb more water than the unionized carboxylic acids. The water softens and expands the film, often loosening it from the metal. Alkali formed at cathodic areas during corrosion is similarly active.

a. Osmotic Effects:

One of the important mechanisms by which water affects coatings is the formation of osmotic blisters. The formation of a blister is due to the migration of water from the outer surface to a region underneath containing a higher concentration of a water-soluble but slowly diffusing substance, for example salts. Salts might be introduced as impurities in pigments or vehicles or left on a surface prior to painting by poor washing or cleaning procedures. The driving force of osmosis is the concentration difference of salt or other soluble substance. This force diminishes if

the salt is free to migrate out of the film. The pressures available from osmotic effects are calculated approximately from equation 7-1.

$$P = \frac{n}{v} RT \qquad \text{Eq7-1}$$

P = Pressure in atmospheres
T = Absolute temperature
R = .082 1. atm./mol.
$\frac{n}{v}$ = Molar concentration difference in moles/1.

For a 0.1 M glucose solution (or other molecular or ionic species) the driving force for osmosis is a pressure of 2.5 atmospheres. A crystal of salt or its saturated solution can have much higher osmotic pressure, depending on its solubility and on the number of ions it produces.

The rate of permeation depends on the diffusion rate in the coating, which depends in turn on solubility of water in the coating and on mobility of the polymer segments.

b. Hydrolysis:

The hydrolysis of polyesters, polyamides etc., is usually accelerated by acids or enzymes or by increase of temperature. Esters of aromatic acids and the neo-acids are much more resistant to hydrolysis than simple aliphatic esters. Methacrylate ester units in polymers are more resistant to hydrolysis than the corresponding acrylates.

7-7-4 Ozone:

Ordinarily the ozone concentration at the earth's surface is low enough to be almost negligible. However, the concentration increases to important levels near 100 ppm in the presence of light, NO, oxygen and hydrocarbon vapors. The formation of ozone at ground level is complex and the subject of much study in connection with air-pollution.

The principal effect of ozone on polymers is to react with double-bonded compounds to form ozonides, which then split to break the double-bonds completely (Figure 7-6). The principal practical degrading effect is the crack propagation in rubbers under stress. Ozone produces compounds which react faster with oxygen and which absorb solar ultra-violet.

7-7-5 Temperature:

An increase of temperature increases rates of hydrolysis and some of the steps in the oxidation by oxygen. It also softens polymers and allows them to yield under stress. One of the principal effects of sunlight is to increase the temperature and reactivity of exposed organic coatings. Drops in temperature increase stiffness and brittleness while they cause contraction. The temperature of the coating closely approximates that of the substrate but the coefficient of thermal expansion as a result of a change of temperature is either a compressive or a tensile stress and the accompanying strains. Even when they are small compared with a measured elongation to break, they can result in eventual cracking

of the coatings. Occasionally a single, but large, reduction of temperature will cause failure by cracking - as on cooling an automotive finish in liquid nitrogen or "dry-ice".

Increase of temperature is often perceived to cause yellowing and embrittlement. Yellowing is usually caused by oxidation, which yields conjugated double-bond systems (in some cases quinones). Temporary enbrittlement is caused by reduction of temperature. Permanent embrittlement is caused by reduction of molecular weight due to chain scission brought about by oxidation or hydrolysis. Increase of hardness and brittleness is also brought about by substitution of polar constituents for non-polar ones during oxidation and hydrolysis, and by the formation of many tight cross-links which restrict the motion of chains. (The polar molecules often have intermolecular forces which stiffen the structures).

7-7-6 Micro-Organisms:

Various forms of fungi, particularly mildew, live on finishes. They produce spots, most often black, which are disfiguring, and make it necessary to repaint. Organic coatings subject to high humidity and high ambient temperatures are particularly prone to mildew growth. Enzymes produced by the organisms damage the coating by chemical action. Soft finishes are more likely than hard ones to have objectionable mildew growth.

Mercury compounds and zinc compounds have traditionally been used to prevent mildew growth. Various proprietary organic compounds have replaced mercury for this purpose.

7-7-7 PHYSICAL PROCESSES WHICH CHANGE ARRANGEMENT OF MOLECULES OF THE BINDER

a. Extraction, Migration, Evaporation:

These processes, which remove small molecules from polymeric films, cause shrinkage of the films and produce tension which can result in cracking. Oxidation and hydrolysis often produce small molecules. The rate of diffusion outward decreases mainly with increasing viscosity or hardness of the coating and with increase of the molecular weight of the diffusing species. Plasticizers, e.g., di 2-ethyl hexyl phthalate, which soften and make films more flexible, are lost to polymeric substrates by migration. When plasticizers are necessary for painting plastic substrates - particularly thick samples - they should be non-migratory. The tendency to migrate or to be extracted is measured by a partition coefficient, the tendency to evaporate is measured by a vapor pressure, but the rate of these processes is a function also of diffusion rates. Large molecules tend to have low diffusion rates.

Evaporation and extraction of oxidized or hydrolyzed vehicles leaves pigment behind. The surfaces become less glossy as a result. In addition, the exposed pigments are sometimes of high tinctorial power. They produce metallic reflections (anomalous dispersion), the effect called "bronzing".

b. Mechanical Working:

Mechanical working of polymers, when in extremely viscous condition as in a rubber mill, causes long polymer chains to break, leaving free radicals at the breaks. The free radicals react with other susceptible groups or oxygen. It is probable that all abrasions of plastics of high molecular weight, including finishes, result in similar formation of free radicals and new chemicals at the points where molecules are broken.

High molecular weight - above about 200,000 - molecules are more susceptible than low to mechanical degradation. Ordinarily, little mechanical degradation occurs at molecular-weight lower than 20,000. High molecular-weight increases the probability of scission because the long molecules resist the shearing action and extension to a greater degree, and are therefore subject to larger forces. In other words, each link in the polymer chain bears the sum of all the forces extending.

Mechanical elongation also changes the phase structure, resulting often in voids or crazing of glossy polymers, in orientation of polymer chains, and in distortions of dispersed particles.

c. Swelling:

Coatings absorb not only water but a variety of organic solvents. When swollen, the coatings are softer (more easily damaged) and more permeable. The swelling results in a compressive stress on the coatings. In addition strains left in the original coating may cause cracks to develop when the coating absorbs small but weakening amounts of solvents, detergents or water.

The amount of solvent absorbed in a binder depends on mutual attractive forces between the binder and the solvent, on competing attractions of molecules of binder and solvent for their own kind, and on limitations to swelling set by the density of crosslinks (in the case of enamels) or crystallinity.

Swelling cannot be avoided completely by crosslinking. It can often be reduced by crosslinking to negligible levels for the intended purpose. A density of one crosslink for every five or ten atoms of a chain makes a rather substantial reduction in swelling.

d. Cyclic Stress:

Repeated stress due to swelling and contraction brought about by temperature changes, mechanical action (bending), and swelling-deswelling by water or solvents, result in cracks.

7-8 ACCELERATED WEATHERING

The environment provides the materials and energy which cause changes in organic coatings. These are rarely provided singly, and there are many interactions. In the laboratory, individual active agencies are often studied separately. Attempts are made, as in accelerated weathering tests, to combine some of the various agencies causing deterioration in a way to simulate and accelerate the effects of natural exposure.

It is usual in accelerating the effects of exposure to lengthen exposure time to light and water, to increase temperature, and to provide more or less frequent cycling of hot-cold, wet-dry, and light-dark. However, light sources do not duplicate sunlight in the critical wave-length region, increase of temperature above the usual ambient temperatures causes mechanical relaxations and creep not ordinarily obtained, the temperature range is not as large as outdoors, the hydrolytic effects of water cannot be accelerated much beyond the long, wet periods of natural exposure, the effects of temperature on reaction rate varies with the reactants, and the extractions, evaporation and migrations of material that occur in natural exposure cannot take place the same way in accelerated exposure. The chemicals present during accelerated tests and the stresses to which they are subjected are different from those in natural weathering.

The result is that there are many disappointments in accelerated weathering tests. The usual purpose is to determine within an error of about 10% the relative durability of several coatings which may differ in binder and/or pigment. The usual accelerated weathering results are found not to correlate that well with outdoor exposures. (The situation is complicated by inconsistent weather patterns which yield non-reproducible outdoor weathering).

Gross differences in accelerated weathering are no doubt significant, and the kinds of failure in accelerated weathering can alert one to problems that will be found later in outdoor exposures. Exceedingly long life in accelerated weathering tests, as with fluoropolymers, is usually found to be significant.

7-9 STABILIZATION:

7-9-1 Ultra-Violet Absorbers

To obtain protection from ultra-violet light and from the ensuing oxidation, compounds are often added which absorb ultra-violet light but convert it into heat. Soluble compounds which absorb in the sun-light spectrum without affecting the visible spectrum are particularly desirable because they cause no change of color or opacity. Pigments, particularly carbon black and ferric oxides also absorb ultra-violet light and protect plastics, but they produce color and scattering of light.

The soluble ultra-violet absorbers sold commercially are usually of low molecular-weight and can be extracted by water or lost by vaporization. The usual ultra-violet screens (see Figures 7-7, 7-8) are either weak in absorption of critical wave-lengths or their absorption extends above 400 mu making them appear slightly yellow.

A special case of soluble U.V. absorbers is that in which a U.V. absorber is copolymerized into the polymer structure, making it non-extractable and non-volatile. A commerical monomer suitable for this purpose is shown in Figure 7-11.

Ultra-violet absorbing material is sometimes made in coatings by the action of light on phenolic esters of aromatic acids. For example phenyl benzoate, not a ultra-violet absorber, is converted into 2-hydroxy-benzophenone which is an ultra-violet absorber. The reaction is a light-induced Fries arrangement. (See Figure 7-9).

Ultra-violet light absorbers protect a coating by reducing the light intensity near the surface of the coating. The intensity of the light will diminish as the concentration and depth from the surface are increased. If a practical result is to be obtained, the amount of the ultra-violet absorber must be sufficient to decrease the ultra-violet light intensity substantially in that part of the film which is to be protected. In the case of a coating, which might be only 1 or 2 mils thick, the use of large concentrations of ultra-violet absorbers is necessary for protection compared with the amount used in bulk plastics, whose surface may not be particularly important.

Benzophenone differs in its response from o-hydroxy benzophenone when a quantum of U.V. light is absorbed. The benzophenone molecule (Figure 7-10) decomposes into carbon monoxide and two phenyl free-radicals which can accelerate the degradation of an adjacent molecule. The o-hydroxy benzophenone on the other hand is excited by radiation but the absorbed energy is dissipated in the molecule itself as heat without free-radical formation.

Substitution on the molecules of U.V. absorber affects the wavelength absorption curve and also the solubility. Long alkyl groups favor solubility in common vehicles, a common problem with ultra-violet absorbers. They also reduce volatility and solubility in water.

7-9-2 Antioxidants:

Antioxidants are used to interfere with the free-radical reaction to form non-reactive products. They are used in conjunction with U.V. screens or alone. They protect throughout the film.

Antioxidants are typically phenols substituted in the ortho and para positions, and aromatic amines.

7-9-3 Quenchers:

Quenchers are typically nickel complexes which pick up energy from atoms excited by ultra-violet light and dissipate the energy as heat. (See Figure 7-12). The quenchers also have some ultra-violet absorbing action, so their action is complicated.

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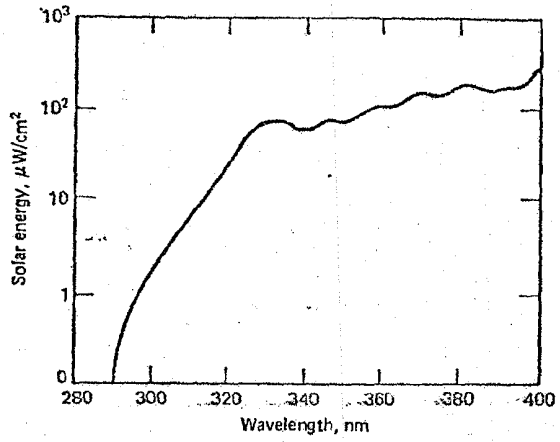
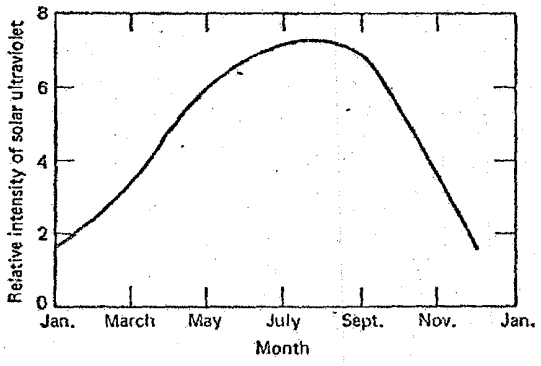


Energy distribution for solar ultraviolet radiation.



Seasonal variation in intensity of solar ultraviolet radiation at Kingsport, Tenn.

FIG. 7-1

FROM - ENCYCLOPEDIA OF POLYMER SCIENCE AND TECHNOLOGY-INTERSCIENCE, NEW YORK (1969) - ULTRA-VIOLET RADIATION ABSORBERS

Initiation:

$$RH \longrightarrow R\cdot + H\cdot$$

(Radiation, electrons, high temp, free radicals from other sources)

Propagation:

$$R\cdot + O_2 \rightarrow RO_2\cdot$$

$$RO_2\cdot + RH \rightarrow ROOH + R\cdot$$

$$\downarrow$$

$$RO\cdot + \cdot OH$$

$$RO\cdot + HR' \rightarrow ROH + R'\cdot$$

$$\cdot OH + HR' \rightarrow HOH + R'\cdot$$

Termination

$$2R\cdot \rightarrow R:R$$

$$RO_2\cdot + R\cdot \rightarrow ROOR$$

$$RCH_2-CH_2\cdot + \cdot CH_2CH_2R \rightarrow RCH=CH_2 + H_3CCH_2R$$

FIG 7-2 - TYPICAL RADICAL REACTIONS IN THE OXIDATION OF C-H BONDS

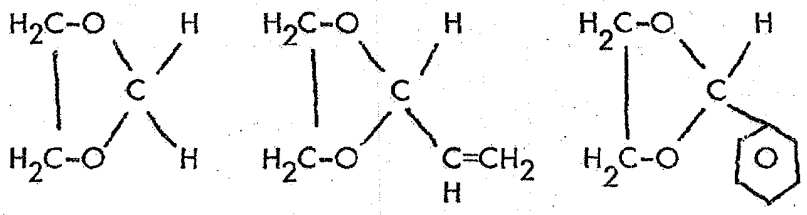
FIG. 7-3 C-H BONDS REACTIVE TO FREE RADICALS

I. ALIPHATIC

ALLYLIC
BENZYLIC $> 3^{\circ} > 2^{\circ} > 1^{\circ} >$ Vinylic

H on C attached to ether oxygen.

H on C attached to dioxolane



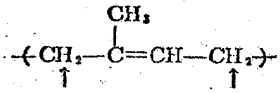
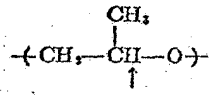
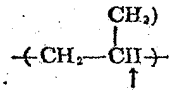
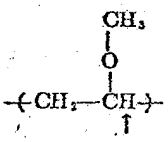
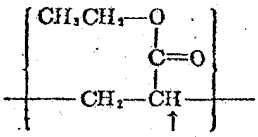
II. AROMATIC

Ring H's Most Stable

FIG. 7-4

274

Table 11-1 Relative rates of oxidation versus structure [3]

Structure	*Relative rate of oxidation*
	10
	9
	6.5
	2.8
	1.4

from RODRIGUEZ
PRINCIPLES OF POLYMER SYSTEMS
McGRAW HILL, NEW YORK (1970)
PAGE 274

FIG. 7-5
FREE RADICAL REACTIONS OF ALDEHYDE, KETONE, TERTIARY HYDROPEROXIDE

(1) $-\overset{|}{\underset{|}{C}}-CHO \xrightarrow{h\nu} -\overset{|}{\underset{|}{C}}\cdot + \cdot CHO$

(2) $-\overset{|}{\underset{|}{C_1}}-\overset{O}{\overset{\|}{C}}-\overset{|}{\underset{|}{C_2}}- \xrightarrow{h\nu} C_1-\overset{O}{\overset{\|}{C}}\cdot + \cdot\overset{|}{\underset{|}{C_2}}-$

(3) or $\longrightarrow C_1\cdot + CO + C_2\cdot$

(4) $R'-\overset{H}{\underset{H}{C_3}}-\overset{|}{\underset{|}{C_2}}-\overset{|}{\underset{|}{C_1}}-\overset{O}{\overset{\|}{C}}-R \xrightarrow{h\nu} R'-\overset{H}{\underset{|}{C_3}}=\overset{|}{\underset{|}{C_2}} + C_1=\overset{R}{\underset{OH}{C}} \rightarrow C_1-\overset{R}{\underset{|}{C}}=O$

(5) $R'-\overset{|}{\underset{|}{C_3}}-\overset{|}{\underset{|}{C_2}}-\overset{|}{\underset{|}{C_1}}-\overset{O}{\overset{\|}{C}}-H \xrightarrow{h\nu} R'-\overset{|}{\underset{|}{C_3}}=\overset{|}{\underset{|}{C_2}} + \overset{|}{\underset{|}{C_1}}=\overset{H}{\underset{OH}{C}} \rightarrow -\overset{|}{\underset{|}{C_1}}\overset{|}{\underset{H}{C}}=O$

(6) $\overset{|}{\underset{|}{C}}=O \xrightarrow{h\nu} \overset{|}{\underset{|}{C}}-O\cdot \xrightarrow{RH} \overset{|}{\underset{|}{C}}\overset{\cdot}{-}OH + R\cdot$

(7) $\sim\overset{CH_3}{\underset{H}{C}}-CH_2-\overset{CH_3}{\underset{OOH}{C}}-CH_2-\overset{CH_3}{\underset{H}{C}}-CH_2\sim \xrightarrow{h\nu} \cdot OH + \sim\overset{CH_3}{\underset{H}{C}}-CH_2-\overset{CH_3}{\underset{O\cdot}{C}}-CH_2-\overset{CH_3}{\underset{H}{C}}-CH_2\sim$

(8) $CH_3\overset{H}{\underset{|}{C}}-CH_2\cdot + O=\overset{CH_3}{\underset{|}{C}}-CH_2-\overset{H}{\underset{CH_3}{C}}-CH_2\sim$

(9) $R_1CH_2-\overset{CH_3}{\underset{CH_2}{C}}-CH_2R_2 \longrightarrow R_1CH_2-\overset{CH_3}{\underset{|}{C}}=CH_2 + R_2CH_2\cdot$

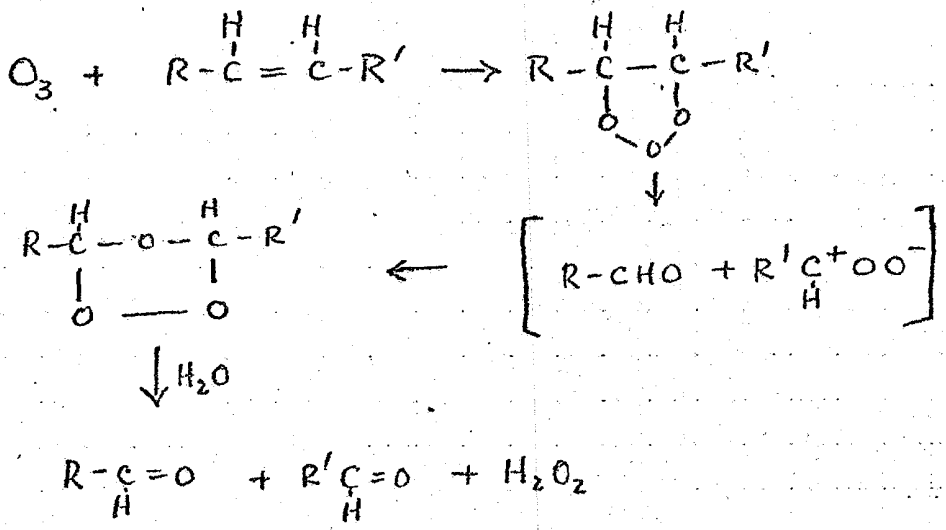
Highly Branched Structures

(10) $R-\overset{CH_3}{\underset{O=C-OCH_3}{C}}-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{O=C-OCH_3}{C}}\cdot \longrightarrow R-\overset{CH_3}{\underset{O=C-OCH_3}{C}}\cdot + H_2C=\overset{CH_3}{\underset{O=C-OCH_3}{C}}$

Depolymerization of Polymethyl Methacrylate

FIG 7-6

REACTION OF OZONE WITH UNSATURATED HYDROCARBONS



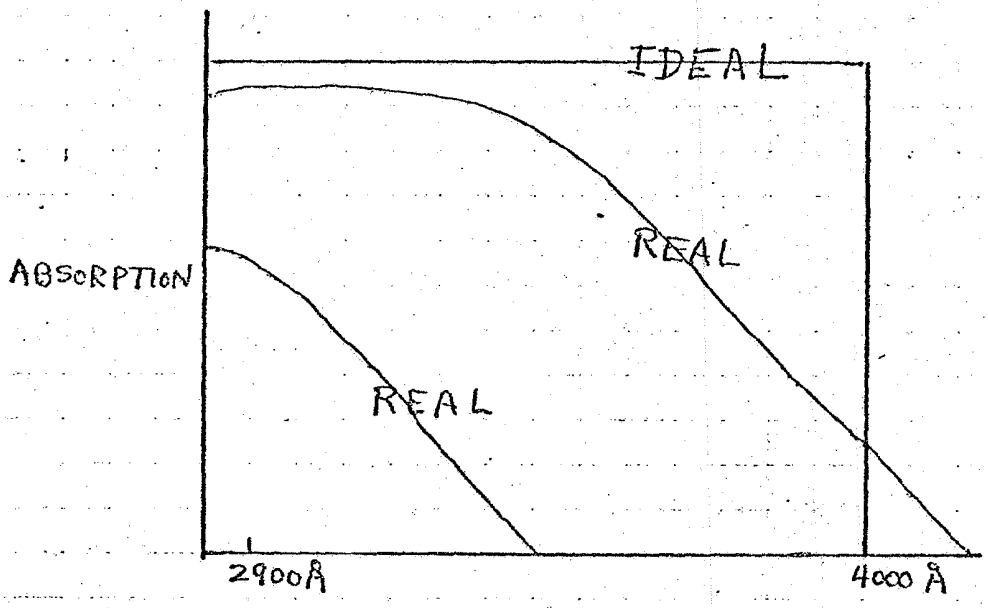
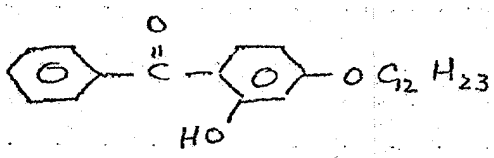


FIG 7-7 - ABSORPTION OF U.V. ABSORBERS COMPARED WITH IDEAL

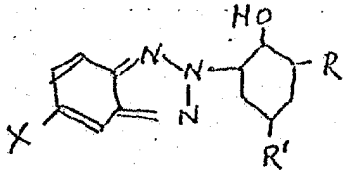
FIG 7-8

ULTRA-VIOLET ABSORBERS

1. 2-Hydroxybenzophenones (e.g. Uvinul Series, 4 dodecyloxy 2 hydroxybenzophenone)

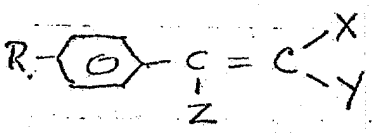


2. Benzotriazole-phenols (e.g Tinuvin Series)



X = Cl
R = H or Alkyl
R' = alkyl

3. Substituted Cinnamic Acid Derivatives

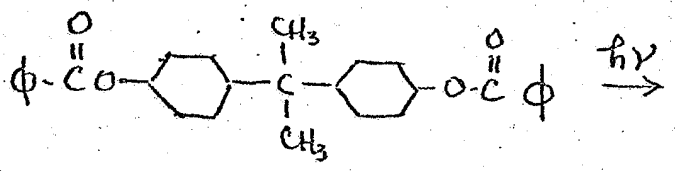


R = H, $-OCH_3$

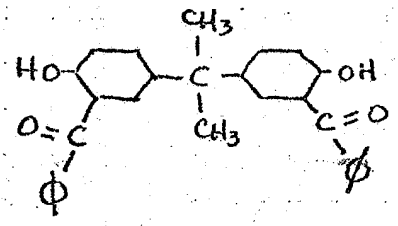
X, Y = carboxylic ester or -CN

Z = H, Alkyl, Aryl

Absence of Color
Relatively poor U.V. absorption



AROMATIC ESTER OF A PHENOL



UV LIGHT ABSORBER
AN o-HYDROXY BENZOPHENONE

FORMATION OF A UV ABSORBER ON EXPOSURE
PHOTOCHEMICAL FRIES REARRANGEMENT

FIG 7-9

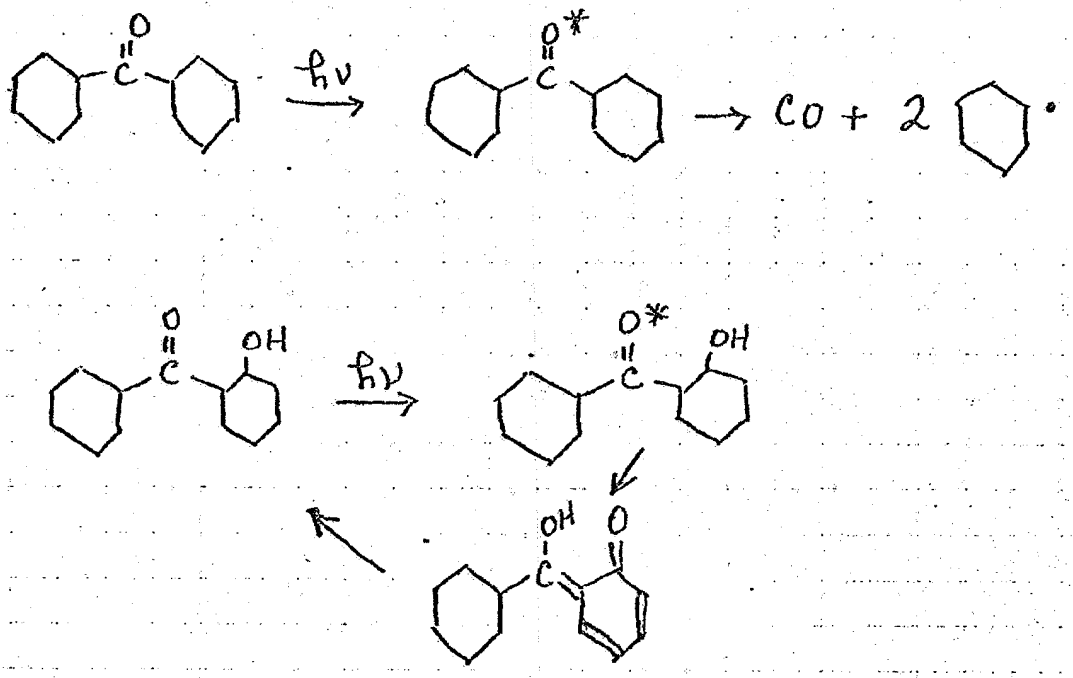


FIG 7-10 ACTION OF LIGHT ON BENZOPHENONE and o-HYDROXY BENZOPHENONE

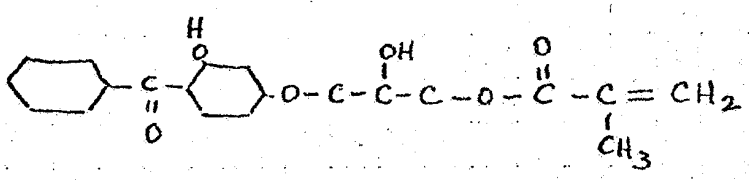
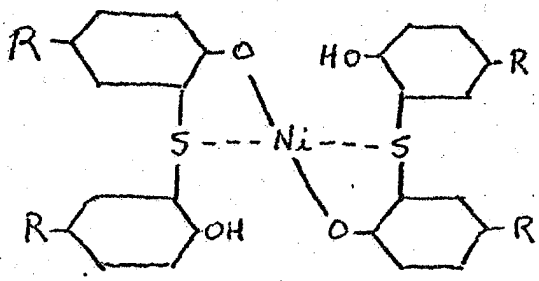
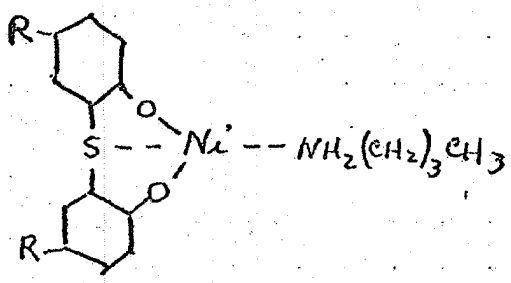


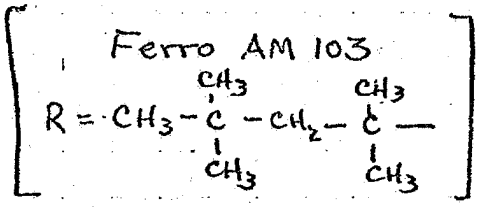
FIG 7-11

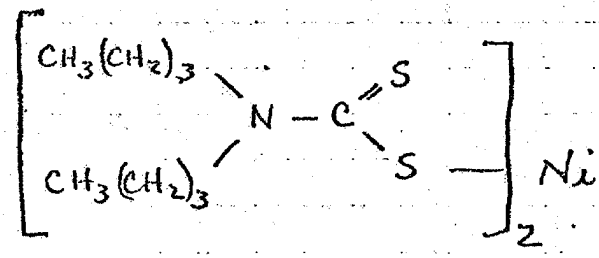
A UV ABSORBING ACRYLIC MONOMER





Cyasorb 1084





Nickel dibutyl dithiocarbamate

FIG 7-12

QUENCHERS OF ACTIVATED MOLECULES

(PLUS UV ABSORPTION)

APPEARANCE

CHAPTER 8

Organic coatings are often applied to yield certain appearance effects considered desirable. These effects are usually;

A. Uniformity of smoothness as perceived visually.

B. A particular degree of smoothness.

C. Hiding of the color of the substrate.

D. A particular color of the coating.

E. Particular directional light reflection effects.

The methods of achieving the desired effects and the obstacles to achieving them will be analyzed, and methods of measuring the various aspects of appearance will be discussed.

8-1 UNIFORMITY OF SMOOTHNESS IN SURFACE COATINGS

Ideally a coating should dry to a uniform desirable degree of roughness independent of the roughness of the substrate to which the coating is applied. Certain properties of the substrate and certain limitations of the coating tend to make the coatings non-uniform.

8-1-1 Origins of Non-Uniformity of Smoothness of a Surface Coating

a. Surface-contour of the substrate

Many of the substrates which are later coated are subject first to processes which incidentally produce rough surfaces not controlled for roughness. Other substrates are inherently rough. For example - sheet metals are roughened by chemical treatments designed for cleaning and conversion coating and by the forming and stamping operations. Welding produces ridges, pimples, and holes. Wood and concrete surfaces contain pores or holes and protruding fibers or granules. The organic coating is often used to hide the imperfections and to produce a uniform surface in spite of the variation in the substrate.

b. Absorption

Certain substrates, for example plastics or rubber, while appearing smooth, will absorb liquids from an organic coating. The amount absorbed will vary depending on inhomogeneities of chemical and physical properties of the substrate and can result in a blotchy appearance of the coating.

c. Wrinkling

A wrinkled surface is larger than an unwrinkled one covering the same substrate. It is usually produced by absorption of material into a very thin solid film formed at the surface of a fluid film. This absorption can occur by diffusion from the liquid of components of low molecular weight.

d. Non-Uniformity of Surface Tension or Surface Properties of the Coating or Substrate

The organic coating in the liquid state will sometimes dry to a non-uniform surface even over a substrate of uniform contour in response to variable surface or interfacial tension. The variation is induced by evaporation of solvents or water, absorption of gases, or non-uniform wetting.

e. Roughness Resulting from Irregularities in the Mode of Application

Brush marks left after brushing, "orange peel" appearance left after spraying, long striations left after roller-coating are examples of irregularities due to mode of application.

8-1-2 Effect of Contour of Substrate

Finishes vary in the surface smoothness when applied and dried over surfaces of variable roughness. While appearing smooth when wet they often appear to have penetrated into the depressions during the drying process and appear rough like the substrate. A coating is said to have good "filling" or "hold-out" when the coating's dry surface does not betray the roughness underneath. The property of filling is measured by comparing the contours of substrate and coating under carefully controlled conditions.

If a coating is applied over a smooth, non-porous, substrate having a measured depression etched in it, the coating will generally, after drying, betray the presence of the depression by a corresponding depression in the surface, somewhat less sharply defined.

Using duplicate depressions for a series of different organic coatings the degree of surface imperfection in the coating will be found to be dependent on the choice of coating, the film thickness applied, and on the conditions of drying of the coating.

Using a single coating but varying the width and depth of the depression, it will be found that (1) wide depressions will not fill up to the same level as narrow ones, and (2) that deep ones will not fill up to the same level as shallow ones, though to a greater fraction of their depth. While etched lines in a smooth surface are easily measured using a microscope, other kinds of roughness - e.g. that left by anodizing treatments on steel or aluminum - can be measured with a needle which is moved over the surface and which is connected to a transducer which converts the contour into electrical impulses; the electrical impulses are measured.

8-1-3 Effect of the Flow Properties of the Coating on Filling

If the coating were an ideal liquid (like toluene, water, or glycerine) and it were applied in sufficient quantity over a rough planar surface which it wets spontaneously, it would flow into depressions and off elevations until its top surface became minimum while the surface of the substrate was covered completely. The ideal liquid would therefore hide depressions and elevations completely if its thickness were greater than the amplitude of the roughness. However, such a liquid would be unsuitable for application as a coating because it would leave even small convex curvatures and edges without sufficient coating to provide color or protection. If any part of the surface was not horizontal the liquid would drain from it completely. Therefore a practical liquid coating must be formulated instead to flow rapidly for only a short time, then stop. The flow would then bring the surface over depressions almost but not quite up to the average level.

The processes which produce hardening of the film gradually slow the flow. Furthermore, to make application of the coating easy but prevent its running off vertical walls the coating is formulated so that its viscosity rises as its flow rate decreases. The effect is generally therefore for the flow into a depression to stop before filling is complete.

8-1-4 Effect of Coating Thickness on Filling

Organic coatings are usually applied as films of only about 0.0003" to 0.002" thick. It becomes impractical to hide surface imperfections which approach or exceed the film thickness. It is therefore common practice to smooth surfaces somewhat by filing off projections, and by filling depressions with solder or other filler, until the roughness is of dimensions substantially smaller than the thickness of coating to be applied.

8-1-5 Effect of Shrinkage on Filling

If the coating dries by evaporation of solvent, or by another hardening mechanism which involves shrinkage of the film after it can no longer flow appreciably under the weak forces of surface tension, thicker areas, i.e. those over depressions, will shrink more than thin ones and therefore reduce the filling or hold-out. Evaporation of solvents, absorption by substrates and contraction on cooling are causes of shrinkage.

Lacquers, which are of relatively high molecular weight and become rigid even when they still contain substantial amounts (say 50%) of volatile solvent, are poor in filling compared with enamels, which are fluid until virtually all of the solvent is gone. For this reason lacquers applied over rough surfaces must often be buffed to achieve mirror-like smoothness but enamels usually are not. Buffing a lacquer over a rough substrate to mirror-like smoothness before the solvent has evaporated completely results in some loss of filling later. Cooling a smooth enamel surface over a rough metal substrate usually results in loss of filling because the coefficient of thermal expansion is higher for organic polymers than for metal. (Pigmentation can reduce the thermal expansion coefficient).

8-1-6 Effect of Porosity of the Substrate

Porous substrates absorb organic coatings by capillary action provided the pores are large enough to accomodate the polymers and pigments. The end surface of a wooden board is a familiar example of such a surface. It will absorb large quantities of surface coatings, including pigment and vehicle, without showing the coatings on the surface.

The driving force of capillarity ends when the liquid coating has entered until its surface is at the end of the capillaries. The usual procedure for applying a coating to such a surface is therefore to apply only a small quantity, let soak in to the point of invisibility, let it dry to the point of insolubility, then apply the amount required to get the desired appearance. Application of a wet coat until it would absorb no more would take far larger amounts. It is not necessary for the first coat and the second coat to be similar in properties. The first coat may be called a sealer because of its function.

8-2 GLOSS, SHEEN

The gloss of a surface-coating is the most commonly used measure of smoothness. The highest gloss represents the appearance of a liquid film, a highly polished glass, or a mirror.

Certainly, no surfaces are smooth within tolerances approaching atomic dimensions. The irregularities in the surface scatter light, deviating it from the specular angle. The amount of light deviated and the degree of deviation will depend on the shape and dimensions of the irregularity; and for irregularities of magnitude near the wave-length of light, on the refractive index. When the irregularities become small (say less than one tenth) compared with the wave length of visible light the amount of light deviated becomes negligible for most practical purposes. (The wave length of green light is 5.5×10^{-5} cm).

The determination that a coating has a particular degree of gloss is made in a qualitative way by observing the reflection of images in the surface. Sharp images and high contrast are evidence of high gloss. In determining whether or not a surface is glossy, the observer usually discounts large-scale shallow imperfections (such as "spray-wave" or "orange-peel" or ripples on water) which are large enough to be easily resolved by the eye. The observer concentrates instead on the optical effects produced by roughness of a scale too fine for him to resolve with the naked eye at normal viewing distances.

Observers vary in the way they interpret the optical images they receive. Optical instruments can be used to obtain pertinent objective measurements. These measurements will be satisfying to most observers, but not to all. Instrumental measurements are used in specifications by industrial purchases of organic coatings. Rather loose descriptions (e.g., high gloss, semi-gloss, matte, flat) are used in trade-sales.

Often a surface will appear to have low gloss when viewed from an angle near perpendicular to its surface but will reflect highly when viewed at a glancing angle. The quality of high specular reflection at large angles from the normal is called "sheen".

8-2-1 Reflection from a Plane Smooth Surface of a Dielectric of Dimensions Much Larger than the Wave-Length of Light

All the optical clues used by an observer depend on the reflection of light from the surface, and particularly the degree to which the direction of reflected light deviates from the direction of reflection by a perfect mirror or plane surface (as of a liquid, for example).

If a parallel beam of light is directed towards a plane smooth surface of dimensions large compared with the wave-length at an angle i from the normal of the surface, the angle of incidence, some of the light is reflected from the surface at an angle -i from the normal, and in the same plane as the normal and the path of incidence. (All the remainder of the incident light enters the surface at an angle r from the normal, the angle of refraction - where it proceeds until it is scattered at all angles, reflected from surfaces and/or absorbed.

Fresnel's Law of Reflection describes the amount of light reflected from a surface as a function of refractive index and angle of incidence. Unpolarized light, after specular reflection from a plane surface, is plane polarized. It is as though the original beam of light has been in the form of two equal beams having perpendicular polarization, one in the plane parallel to the plane of incidence, the other perpendicular to it. Such polarized beams do not change their polarization on reflection but the amount reflected of each of the two polarized beams is different.

For reflection from a surface of an organic coating of refractive index n in air, and angle of incidence i the Fresnel equations are:

$$R_{\parallel} = \left[\frac{\cos i - \sqrt{n^2 - \sin^2 i}}{\cos i + \sqrt{n^2 - \sin^2 i}}\right]^2 \qquad \text{Eq. 8-1}$$

$$R_{\perp} = \left[\frac{n^2 \cos i - \sqrt{n^2 - \sin^2 i}}{n^2 \cos i + \sqrt{n^2 - \sin^2 i}}\right]^2 \qquad \text{Eq. 8-2}$$

$$R_T = (R_{\parallel} + R_{\perp})/2 \qquad \text{Eq. 8-3}$$

$R_{\parallel}$ = Reflection of light polarized parallel to the plane of incidence.

$R_{\perp}$ = Reflection of light polarized perpendicular to the plane of incidence.

R_T = Reflection of unpolarized light.

These equations yield graphs of reflected light as a function of angle as in Figure 8-1 and 8-2. The reflection is greatest at large angles (i.e. approaching 90° from the normal) and at high index of refraction. (Most surface coatings have an index of refraction between 1.45 and 1.60.)

Light which penetrates the surface is also plane polarized. The corresponding intensities are $R'_{\parallel} = 1-R_{\parallel}$ and $R'_{\perp} = 1-R_{\perp}$. The light which penetrates a coating will in general be scattered by pigments and depolarized before it issues. If it is reflected by large particles it will issue as polarized light.

In the case of normal incidence the fraction of light reflected is given by:

$$R = \left(\frac{n^2 - 1}{n^2 + 1}\right)^2 \qquad \text{Eq. 8-4}$$

8-2-2 Reflection from Surfaces Which Are Not Smooth

Equations 8-2 and 8-3 refer to perfectly smooth surfaces. If the surfaces are rough and coarse compared with the wave-length of light the light will be reflected from each of the elements of the surface according to its own angle to the ray of incident light. The reflection from a rough surface will generally be concentrated at the specular angle and within an angle of it whose size depends on the angular deviations of the elements of the surface. The total amount of light reflected from the rough surface will not be affected by the roughness but the amount reflected at the specular angle will decrease in compensation. If the dimensions of roughness approach the wave length of light, the direction of deviation and the amount are not given precisely by the laws which govern large objects - size and refractive index have pronounced effects on direction and amount of deviated light.

8-2-3 Glossmeters

Instruments for the measurement of gloss are described technically in ASTM D523-67. In these instruments an almost parallel beam of light strikes a painted surface. The amount of light reflected within a small deviation from the specular angle is gathered in a photoelectric cell receptor and measured. The amount reflected is compared with that from a piece of smooth black glass of index of refraction 1.567 arbitrarily set at 100% (or of a working standard of any other refractive index set appropriately according to its refractive index using Eq. 8-3).

Apertures are prescribed for the beam of light and the receptor. These apertures are measures of the permitted deviation of the incident beams from parallelism and the maximum deviation of the reflected beam that will enter the receptor. The apertures are provided so that the instruments will be insensitive to shallow elevations and depressions usually present in coatings (spray wave, orange peel), to correlate with subjective estimates of gloss for practical coating systems, for which the eye and brain discount the shallow, large, elevations and depressions.

Light which penetrates the surface and which is reflected after being scattered by pigments will be spread out almost evenly over the hemispherical solid angle. The amount scattered by the pigment which enters the eye or a photoelectric receptor of narrow aperture will generally be negligible (less than 1%) compared with the amount specularly reflected from a smooth surface. Color of the coating is therefore ignored when gloss is measured by a glossmeter.

TABLE 8-1

Standard Conditions for Measurement of Gloss. A Source of Light is Used with Aperture of 0.75° Parallel to the Plane of Measurement and 3° Perpendicular to the Plane of Measurement.

	Receptor Aperture		
Angle of Incidence	II to Plane of Measurement	⊥ to Plane of Measurement	Use
20°	1.8°	3.6°	High Gloss
60°	4.4°	11.7°	Semi-gloss
85°	4.0°	6.0°	Flats

Surfaces with large amplitudes of roughness give rise to low gloss which remains low even as the angle of observation approaches 90° from the normal. Relatively lesser amplitudes of roughness yield low gloss at low angles and high gloss at large angles. Therefore the angle of observation that permits discrimination (both by gloss meter and by eye) for glossy finishes is about 20°, while that for flat finishes is 85°. Most often gloss is measured and specified at 60°. The aperture of the gloss meter is different for the different viewing angles. (The eye's aperture remains constant, of course, at constant levels of illumination, and is about 0.5° - 0.3°, smaller than used in most glossmeters.)

In the practical measurement of the gloss of paints by glossmeters certain precautions must be observed - (1) during measurement the surface must not be either too convex or too concave, (2) the preparation of the surface for test must be representative of the surface as used, (3) the refractive index must be considered.

Different people use different clues for their subjective observation of gloss. Some note the reflection of a point or line and observe the haze in the relatively dark area around any bright image; others use their own "distinctness of image" criteria; others use a brightness contrast ratio between adjacent areas of an image. Hardly anybody can (like a glossmeter) remember the brightness of an image seen in one surface and compare it with the brightness of an image seen in another. It is therefore not surprising that subjective estimates of gloss do not always agree with instrumental measurements.

8-2-4 The Achievement of A Particular Degree of Gloss

The effect of the substrate must be distinguished from the effects of the coating. The effect of roughness of the substrate is corrected by using a smooth substrate. Roughness is obtained by use of particulate material of larger than 1 micron or by the use of initially finer particles which flocculate into larger clumps. When coarse pigments or flocculating pigments are used, shrinkage of the film on drying is essential to obtain the low gloss. Roughness, however, can also be obtained by microscopic distortion of the surface (e.g. wrinkling) during drying.

The smallest surface variations responsible for low gloss at low angles or incidence are of the order of tenths of a micron. Surfaces with such small irregularities, though not glossy at small angles, will show high gloss or "sheen" at large angles. To obtain low sheen it is necessary to provide irregularities of about 20 microns, approaching the usual topcoat film thickness of 25 to 50 microns. Large pigment particles are the most reliable method of providing low gloss, the other methods are influenced by conditions of application.

8-3 SCATTERING OF LIGHT

Light is scattered when heterogeneities exist in the refractive index of the medium in which light is propagated. When the heterogeneities are small enough the scattering is observed only against a black background using a brilliant source of light. Thus, molecules of air, as individuals or as temporary clusters, scatter light to produce the blueness of the sky. Polymer solutions, having larger heterogeneities scatter more, and the intensity of scattering is used to measure molecular weight. The usual suspensions of pigment particles scatter much more than equivalent concentrations of polymer solutions.

Colorless pigment particles consist of dielectric materials having a refractive index which depends on their density and on the polarizability of their molecules. Commercial white pigments are usually inorganic, crystalline and irregular in shape. The particles are usually somewhat anisotropic, complicating theoretical analysis of scattering.

Scattering of light by isolated dielectric spheres is described rather completely by the Mie Theory in terms of the angle of the scattered light from the incident beam, the intensity of the scattered beam as a fraction of the incident beam, and the polarization as a function of particle size, refractive index ratio of the sphere and the medium and wave length in the continous medium. The Mie Theory is regarded as verified in detail. Its teachings are applied usefully to non-spherical particles.

According to the Mie Theory, the scattering of light from a small spherical particle is symmetrical forward and back; completely polarized at 90° from the angle of incidence, proportional to the sixth power of the diameter and inversely proportional to the fourth power of the wave-length (measured in the continous medium). The special case of The Mie Theory for these small particles is familiar as Rayleigh's Law.

As the spheres are increased in size, the scattering increases asymmetrically in the forward directions, polarization at 90° decreases, and the change with wave length and particle diameter decreases. There exists a particle diameter for each refractive index and wave length for which the amount of scattering of isolated pigment particles is a maximum. The maximum value of scattering increases with refractive index, but slowly. Titanium dioxide in its rutile form is the commercial scattering pigment of choice because of its high refractive index.

Reflection of light from a coating to the eye represents mainly that scattered by the pigment particles (or other refractive index inhomogeneities) plus that reflected from the surface of the coating itself.

8-4 ABSORPTION

Dissolved dyestuffs i.e. those dispersed as small molecules, are predominately absorbers and they scatter little of the light which strikes them. Light which is absorbed is converted to heat or other energy. The amount of light scattered by a particle of a dye increases strongly with increasing particle-size and with refractive-index. Absorption is usually dependent on wave length even in the case of carbon black.

The refractive-index of dyestuffs with steep absorption bands becomes rather high-valued in the neighborhood of the absorption band (anomalous dispersion). For this reason, particles of blue phthalocyanine dye (which absorbs strongly in the red) scatter predominately red light, and the redness is a measure of the particle size.

The light absorption by a dissolved dyestuff follows the Beer-Lambert Law (Eq. 8-5) if the dissolved molecules do not inter-react.

$$I = I_o e^{-kcl} \qquad \text{Eq. 8-5}$$

where I_o = light intensity at entrance in the specimen

I = light intensity at distance in the specimen

c = concentration of dyestuff

k = coefficient of absorption

l = path length in the specimen

The light absorption of a dispersion of a pigment dyestuff follows a similar expression, but the coefficient of absorption for a dispersion of pigment will increase with decreasing particle size reaching a limiting value when the size is small enough that light is not largely absorbed within the dimensions of a single particle. For this reason, pigments with high light-absorption must be reduced to finer particles than pigments of low light-absorption to gain maximum economy of coloring power. Colored pigments sometime change color slightly with particle size.

8-5 HIDING BY SCATTERING AND ABSORBING PIGMENTS

Pigmented surface coatings should not reveal the reflectivity of the substrate. This means that the light which reaches the eye by reflection from the coated article should contain only a negligible fraction which has been reflected from the substrate itself.

The eye judges brightness of two adjacent visual fields of the same color by contrast, or by ratio of light intensities rather than by differences. A change of 2% in the brightness of adjoining areas of white light or of light of the same color is considered perceivable (assuming reasonable brightness levels and reasonable areas). At very low levels of illumination and small areas larger differences are necessary for perception.

Hiding by a perfect black coating - no scattering, only absorption - is possible only at low levels of illumination because the ratio of reflection from a white portion of the substrate to that from a dark one would always be the same, independent of the thickness of the black coating. If, under a constant illumination, the thickness of the perfect black were increased to the point where the eye would not respond to the small amount of light transmitted, increase of the illumination level would allow the difference to be observed once again.

Hiding is obtained conveniently by providing a light-scattering pigment in the film. Light reflected to the eye from this scattering pigment over both light portions and dark portions of the substrate reduces the contrast. When the contrast is reduced sufficiently the coating hides, and at all levels of illumination.

When light from a surface coating of marginally adequate thickness results in adjacent areas different in color from each other the ratios of brightness that will be just observable depend on the colors of the light i.e. on the wave-length distribution of the light which reaches the eye.

Although scattering or reflecting pigments are essential for hiding, the hiding produced by a mixture of scattering and absorbing pigments is often more efficient (i.e. accomplished with less pigment) than that produced by the use of a scattering pigment alone.

8-6 COLOR

The perception of color is governed by the physiological response of the observer to the wave-lengths of the light which reach his retina. In the case of coatings over a substrate, the color of the light by which the surface is illuminated and the reflection and absorption characteristics of the coating and the substrate determine the wave-length of the light the observer sees.

8-6-1 Illuminants

Visible light from the sun consists of a particular distribution of radiation of wave-lengths 380 to 770 nm wave-length. Radiation of 290 nm to 380 nm, is considered "ultra-violet" and has no effect on visual perception except when it falls on fluorescent materials - of relatively little consequence in organic coatings technology. The radiation of wave-lengths greater than 770 nm is considered "infra-red" and it also has no effect on visual perception. (Ultra-violet and infra-red radiation, however, have important effects on durability).

By agreement between scientific workers standard light sources have been defined which correspond roughly to daylight and to certain conditions of artificial illumination. The distribution of wave-lengths from incandescent sources follows, more or less, the laws of black-body radiation.

Fluorescent lamps have colors which possess more structure in the wave-lengths vs. intensity curve. Their color depends on the sharp-line spectrum of the gas contained and the nature of the phosphors with which the lamp is coated. Fluorescent lamps are usually not suitable for observation of color if the appearance under sunlight or incandescent light is important.

8-6-2 The Reflection and Absorption Characteristics of the Coating

A spectrophotometer measures the reflection of light as a function of wave-length. A curve of hundreds of values of reflectance can be obtained, each one corresponding to a narrow wave-length range about a nominal center and together covering the visible spectrum. The curve so obtained describes the color completely. Coatings with identical spectrophotometric curves will appear identical in color to all observers, normal or not, and for all light sources (illuminants).

Color results from the variation with wave-length of the intensity of light coming from the coating. The light from the illuminant is modified by the coating in several ways:

(1) Reflection of light from the surface - about 4% of the incident light depending on refractive index. This reflection of light is practically independent of wave-length.

(2) Reflection by scattering for pigments inside the coating. The absorption and reflection varies with wave-length.

(3) Fluorescence of certain pigments that may be contained in the coating.

In the case of coatings with glossy surfaces it is customary to observe the color in white light while excluding the light reflected specularly from the surface, which is uncolored (except in the rare instances of reflection from metals or dyestuffs at high concentration). Dull surfaces are observed without such an exclusion. When glossy coatings are observed in the real world the specularly reflected color adds to the color developed inside the coating. Colors of glossy coatings cannot therefore match the colors of non-glossy coatings over a variety of conditions of illumination.

8-7 THE KUBELKA-MUNK ANALYSIS OF REFLECTIVITY OF COATINGS

While the Mie Theory provides data bearing on the amount of light scattered by single particles sufficiently dilute so that their scattering is independent, it does not apply well to conditions in a paint film where there is multiple scattering - i.e. where light is scattered from one particle to another with changes in direction and where there are many particles close enough together (i.e. approaching the wave-length of light in separation) to affect each other's electrical surroundings.

The exact calculation from first principles of the reflectivity and absorption of a paint coating is exceedingly complex. A successful practical approximation is known as the Kubelka-Munk simplification. The Kubelka-Munk equations yield reflectivity of a coating as a function of reflectivity of the substrate, thickness of the coating, and parameters expressing the reflectivity and absorption characteristics of the pigments and vehicles used.

The degree to which hiding is obtained then depends on the closeness of reflectivity from adjacent areas of the coating applied over contrasting areas of the substrate.

According to the Kubelka-Munk analysis the paint film is considered as made up of many layers of thickness dx. In each layer, light is considered as arriving in diffuse form and the light flux in the film is divided into

(1) that proceeding into the layer from the direction of the surface and (2) that scattered in the layer and proceeding in the reverse direction to the surface. In each layer a fraction of the light flux Sdx is reversed by scattering and a fraction Kdx is absorbed and lost as heat. S & K each is a function of wave-length.

The Kubelka-Munk equations are used most conveniently of course for those coatings which have K and S values that vary only in a negligible way with wave-length i.e. whites, blacks, and mixtures of them. For coatings which have substantial variation of scattering and absorption with wave-length the Kubelka-Munk equations must be used one wave-length at a time over the visible spectrum 380-770 nm.

The reflection from a coating applied over a substrate is influenced by the reflectivity of the uncoated substrate because some light which penetrates to the substrate is reflected back, with some attenuation, through the film. As the coating's thickness increases, the amount of light penetrating to the substrate decreases, and the effect on the observed reflectance decreases. Beyond a specific film thickness for each coating the reflectivity no longer depends appreciably on the film thickness. The reflectivity of the coating (excluding surface reflectivity) when thickness no longer affects it is given as R_∞. The reflectivity under these conditions depends on the ratio of absorbing to scattering action in the film aline:

$$\frac{1 - R_\infty}{2R_\infty} = \frac{K}{S} \qquad \text{Eq. 8-6}$$

For a scattering, non-absorbing film K = 0 and the ratio $\frac{K}{S}$ is zero.

Under these circumstances R = 1 (perfect reflection). For a non-scattering film with some absorbing power S = 0 and the ratio $\frac{K}{S}$ is infinitely large.

Under these circumstances R = 0 (no reflection).

In a system of several pigments of concentrations C_1, C_2, C_3, etc., the pigments when dilute, contribute independently of each other to K and S so that:

$$\frac{K}{S} = \frac{C_1K_1 + C_2K_2 + C_3K_3 + \ldots}{C_1S_1 + C_2S_2 + C_3S_3 + \ldots} \qquad \text{Eq. 8-7}$$

where K_1, K_2, K_3, and S_1, S_2, S_3 refer to the contributions of the individual pigments to absorption and scattering. When concentrations increase to the point where particles are close together compared with the wave-length of light, the values of S and K usually decrease.

For incomplete hiding, the reflectivity of the substrate, Rg; the thickness, X; the scattering coefficient, S; and absorption coefficient, K; contribute to the reflectivity, R, of the film:

$$R = \frac{1 - Rg\ (a - b\ \coth\ b\ SX)}{a - Rg + b\ \coth\ bSX} \qquad \text{Eq. 8-8}$$

where $a = \frac{(S + K)}{S}$ and $b = \sqrt{a^2 - 1}$

The values of a, b, S and K can be calculated from a measurement of the reflectivity R of a film of thickness X over a substrate of reflectivity Rg and a measurement of reflectivity R_o of a similar film over a black substrate (Rg = 0) as follows:

(1) a may be found from the equation:

$$a = 1/2\left(R + \frac{R_o - R + Rg}{R_o\ Rg}\right) \qquad \text{Eq. 8-9}$$

(2) b is calculated from a:

$$b = (a^2 - 1)^{1/2} \qquad \text{Eq. 8-10}$$

(3) S is calculated from:

$$S = \frac{1}{bX} \coth^{-1} \frac{1 - aR_o}{bR_o} \qquad \text{Eq. 8-11}$$

(4) K is calculated from the values of S and a above:

$$K = S\ (a - 1) \qquad \text{Eq. 8-12}$$

Accordingly all the necessary parameters for the calculation of the reflectivity of a coating of any thickness over any substrate are calculated from measurements for a few conditions of substrate and thickness. Also the effect on reflectivity of addition of more scattering or more absorbing components are readily calculated.

In principle, the Kubelka-Munk equations can be used for the prediction of reflectivities over various substrates, for the effect on hiding of the addition of slightly more scattering or absorbing pigment, for the comparison of the value-in-use of different pigments, for the amount of light transmitted through a paint film. They will be most accurate for dilute suspensions but to some degree can be adjusted for higher concentrations and small changes.

In practice various nomograms and other calculation short-cuts have been developed for manual calculations, and computer programs are readily developed to help the formulator to develop combinations of pigments and vehicles to yield maximum hiding under pre-set conditions for cost and other required qualities.

One of the most frequently quoted results of the Kubelka-Munk analysis is the improved hiding (i.e. the reduction in contrast for coatings over a black and over a white substrate) obtained by the addition of small amounts of absorbing pigment to a scattering pigment. Thus, shaded whites need less white pigments (relatively expensive) than unshaded, clean pigments to achieve the same hiding.

8-7-1 Limitations on the Kubelka-Munk Analysis

The Kubelka-Munk equations are good enough to permit many types of useful calculations but they are only approximations:

(1) They take no account of reflection from the outside surface of the film. Some light is reflected from the outer surface without contact with absorbing or scattering pigment. Other light is reflected back internally when it approaches the surface from inside the coating. The Kubelka-Munk analysis actually calculates the reflectivity and absorption for the hypothetical situation where the continuous phase in the coating continues with the same refractive index to the eye of the observer.

(2) The values of S and K are assumed independent of location in the film. Often pigments will float selectivity to the surface.

(3) Where some of the hiding is due to scattering from air, as in many trade-sales products, the distribution of the air must be homogeneous for the equations to apply.

(4) The illumination of all layers of the coating must be diffuse and that includes the outermost layer.

(5) The scattering of light is regarded as uniform in all directions but is not except when illuminated uniformly in all directions.

(6) The distribution of pigments is assumed to favor scattering in no particular direction. In the case of non-spherical pigments, whose orientation is biased by application method and film shrinkage, errors are introduced. A notable example is metallic finishes - pigmented with plate-like aluminum surfaces usually oriented parallel to the surface.

8-8 WET/DRY HIDING; WET/DRY COLOR

When a surface coating is applied to a substrate it usually contains water or an organic solvent which is evaporated before the film is dry. In addition there may be chemical reactions that result in cross-linking, absorption of oxygen, and changes in density and refractive index.

The changes in hiding power as a result of changes in S and K during drying can be particularly large for coatings which are made from aqueous polymer latices or other aqueous vehicles for various reasons: (1) aqueous vehicles lose large amounts of water - lower in refractive index (1.33) than any of the binders that remain (1.48 - 1.60); the scattering power of all solid pigments will decrease during the evaporation because of the decrease of refractive - index ratio; (2) particles of pigment get closer to each other as water evaporates, reducing their scattering power; (3) elementary particles and small aggregates of TiO_2 are often coated with porous alumina or silica which contain air when dry and water when wet; the pores are often large enough to admit H_2O but not large enough to admit polymeric binders. Such particles have maximum average hiding when dry because the refractive index ratio is the quotient of that for TiO_2 divided by the average for the material surrounding the TiO_2; and (4) A polymer latex itself has some scattering power when wet but not appreciably when dry and coalesced.

The color of finishes also changes during the course of drying. Changes in S and K, migration of pigment particles, orientation of flake-like pigments are all responsible.

The film applied by an ordinary consumer using a brush or roller is not carefully measured for thickness. He can often apply enough to hide as he applies it, wet. The viscosity of the coating controls the applied film thickness only within broad limits. When the film dries, the consumer may find he needs another coat, largely because of the increase of refractive index of the binder as water evaporates. If the paint is one which permits the use of scattering by voids or rough surface-scattering (a special case of voids - i.e. scattering by air-coating interfaces) the change of hiding between wet and dry can be reduced or eliminated. Non-glossy paints often take advantage of hiding by voids.

Voids are effective when dispersed in a vehicle even without pigment provided their size is near optimum - about 0.5 micron. When the voids are much smaller than 0.5 μ they may be considered as reducing the refractive index of the vehicle, making pigment particles scatter more light. Voids also act as separators between pigment particles increasing their scattering power.

8-9 THE MECHANISM OF COLOR PERCEPTION

The eye has two types of mechanisms sensitive to light - rods and cones. The rods, useful only at low levels of illumination, yield no perception of color - only brightness. The cones produce the sensations of color provided illumination is sufficient. The sensitivity of rods and cones to light varies with wave-length. The cones are most sensitive in their perception of brightness at about 550 nm. The rods, important for night vision, are shifted in wave-length sensitivity compared with cones so that objects which are red in daylight appear black in dim moonlight while objects which are blue in daylight appear relatively light in weak moonlight.

The cones, according to accepted theory, have three mechanisms (including pigments) each sensitive to a range of wave-length which, however, overlap. See Fig. 8-3. The violet-sensitive mechanism peaks at about 450nm, the green-sensitive peaks at 550 nm and the red-sensitive at 600 nm.

The curve for the red-sensitive mechanism also has a very weak peak of response also in the violet. In addition to pigment response, other colored materials in the eye affect the total response.

Given a spectrophotometric curve of the light entering the eye, each ordinate is weighted (multiplied by a factor) to yield a stimulus value for each of the three color-mechanisms according to a curve representing a standard observer. See Figure 8-4.

The eye therefore sends to the brain for each perception of the color of an object only three pieces of information and these three pieces are each derived from the added effects of the many points on the spectrophotometric curve.

Obviously there will be many possible spectrophotometric curves which yield the same three pieces of information - they will yield the same perceived color to the standard observer in spite of different spectrophotometric curves. In that case, if the illumination is changed, if color filters are interposed between objects and observer, or if an observer is substituted with a different color sensitivity, the colors will generally appear different. Colors matched by eye in one color of illumination often are mismatched when viewed in other colors of illumination if the spectral reflectivities are in fact different. Such matched colors are called metameric.

8-10 THE DESCRIPTION OF COLOR

Colors are perceived as differing in terms of lightness, hue and saturation. They can be plotted in a three dimensional space as in Fig. 8-5.

Lightness refers to the perception of the amount of light coming from a surface. At any given level of lightness, colors will differ in saturation and hue. The pure spectral colors are of high degree of saturation Actual colors, of lower saturation, may be described as mixtures of spectral colors with various amounts of white or black. Hue refers to the qualities of the pure spectral colors and can be described as violet, blue, green, yellow, orange or red. The term "dominant wave-length" describes the hue more precisely. Hue can be described in terms of the angular coordinates of Fig. 8-5 saturation by the distance from the vertical axis and lightness by the elevation from the zero light level.

Three terms L, a, and b of Figure 8-5 describe the lightness, hue and saturation. Lightness increases as L increases; saturation increases as the resultant value of a and b increase. The hue depends on the relative numerical values of a and b. (a and b can each be either positive or negative).

8-11 THE INSTRUMENTAL EVALUATION OF COLOR OF COATINGS

The color perceived by a standard observer will vary principally with the reflectivity of the coating as a function of wave-length and with the wave-length distribution of the illuminant.

Several standard illuminants have been defined by the spectral distribution of their light in terms of the energy contained in small equal increments of wave-length. Figure 8-6. A standard observer has been defined by the response of his three color mechanisms to each wave-length of the visible spectrum. Figure 8-4. (The curves usually given for response as a function of wave-length are for an energy spectrum in which an equal amount of energy is contained per unit of wave-length difference).

A spectrophotometric measurement of the reflectivity of light from a specimen as a function of wave-length can be recalculated to yield the spectrum of light that would be reflected if the illuminant were a standard one - e.g. Illuminant C (approx. average daylight overcast sky). For each narrow band of wave-length, the intensity is multiplied separately by each of the tristimulus values for a standard observer $\bar{x}$, $\bar{y}$, and $\bar{z}$. All the products of $\bar{x}$ and intensity (one for each band of wave-length) are summed to yield the resultant of the $\bar{x}$'s and the corresponding values of the resultants for the $\bar{y}$'s and $\bar{z}$'s for the observed color. The resultant tristimulus values X, Y, and Z, respectively, then specify the color.

The interpretation of the tristimulus value in terms of dominant wave-length and purity can be done by first calculating the chromaticity coordinates:

$$x = X/(X + Y + Z),\ y = Y/(X + Y + Z) \text{ and } z = Z/(X + Y + Z)$$

Eq. 8-13

(Only two of these are needed because $x + y + z + 1$). The values of x and y are plotted, say as point G, on a graph Fig. 8-7 on which the values of x and y corresponding to pure spectrum colors and the value of x, y for illuminant C have already been plotted. The dominant wave-length is found by extending the line from the coordinates of C through the coordinates for the unknown to the intersection with the spectrum locus. The dominant wave-length is read off the curve of the locus. The purity is the ratio of the two segments of the line from the illuminant coordinate to the spectrum locus. In the case of Fig. 8-7 the purity is 20%. The brightness of the color is given by the Y value of the tristimulus coefficient.

Much of the problem of color description is eliminated by use of photolectric instruments which directly yield responses corresponding to the three physiological responses of the standard eye. See Fig. 8 - 8 which shows how closely these can be approached.

Instruments are often used for evaluating the degree to which colors depart from a standard. For that purpose a numerical value for the departure from standard is desired. To ascribe the deviation to a quantitative measure of saturation difference, lightness difference or hue difference, such deviations can be indicated by distances on the three dimensional graph of Fig. 8-5 provided units are provided for the measurements. A particularly convenient set of units is that which is proportional to the smallest difference in color perceptible to the standard observer. Under such conditions equal small distances on the three dimensional graph are equally significant. See Fig. 8-9.

Procedures for converting spectrophotometric curves to coordinates on the color scales and for evaluating differences are described in the ASTM specifications and in Judd.

A measure of perceived color difference between two colors differing in L, a, and b is given by ΔE where

$$\overline{\Delta E}^2 = \overline{\Delta L}^2 + \overline{\Delta a}^2 + \overline{\Delta b}^2 \qquad \text{Eq. 8-14}$$

Transformations of the differences in values of the chromaticity x, y between two colors have been designed to yield values of ΔE in terms of NBS units of perceived color difference (one unit is defined as the smallest practical difference in color) independent of location on the color diagrams. (L, a and b are given directly on the Gardner Color Difference Meter).

8-12 COMPLICATIONS OF DESCRIPTIONS OF COLOR

The subject of color matching by physiological response is complicated by many factors:

1. Atypical color vision; color blindness, atypical response curves.

2. Color perception varies with angle subtended by the field of view.

3. Color perception varies with previous exposure to bright colors.

4. Color perception depends on contrasting colors in the background.

5. Color varies with the direction of illumination and viewing.

8-13 OBTAINING A PARTICULAR COLOR IN A COATING

The problem of a particular color is usually complicated by other requirements - a particular film-thickness and adequate hiding, for example.

In principle, the Kubelka-Munk Theory in combination with values of K and S for the different available pigments can combine to provide a formulation for color-matching and hiding. The calculations needed are long and involved - a computer is highly desirable.

Sometimes a color which seems close to that desired has already been formulated. The deviations in spectral response from the desired color can often be compensated for by appropriate additions of other pigments whose effect is analyzed in advance using Kubelka Munk Theory. The theoretical calculations substitute for the intuitive and educated guesses of manual shaders. The calculation, considering the many possible errors in the mathematical analysis, come close to reality and reduce the number of trials necessary to produce a satisfactory color-match.

8-14 FINISHES WITH PRONOUNCED DIRECTIONAL REFLECTION

8-14-1 Metallics

The usual colored finish has an almost constant color and brightness independent of the angle of observation provided the specular reflection from the surface (in the case of glossy surfaces) is ignored. Certain metallic or other highly reflecting flake-like pigments can modify this characteristic.

Flake-like pigments of aluminum inside a coating (usually containing colored pigments) if they are oriented in the coating to favor positions near parallel to the surface, act like tiny mirrors to enhance reflection at angles close to the specular angle. These aluminum pigment particles are distributed throughout the film. Some are near the surface where the color of the light they reflect is modified by absorption of some of the light. The effect is to enhance reflection near the specular angle. Although the colors reflected by individual aluminum flakes are different, the particles are so close together that their reflections cannot be resolved individually and their effect is averaged by the eye. The optimum effect is achieved with colored but non-scattering pigments (extra-fine particles).

The "metallic appearance" is obtained only if the particles are not randomly oriented but favor orientation near parallel to the surface. Such orientation is produced when a film continues to shrink down substantially after its viscosity becomes too high for flow in response to surface tension or temperature difference effects.

The best metallic effects are produced when films of high molecular weight binders are laid down from dilute solution and dried at low temperature. Under such circumstances the films become solid even at a relatively high content of solvent.

The same characteristics that are responsible for poor filling are responsible for good metallic appearance.

8-14-2 Iridescence

The colors observed in a thin oil-film on water are due to interference at some wave-lengths and reinforcement at other wave-lengths between waves reflected at the specular angle from the top surface of the oil and the interface between oil and water. The colors vary with the thickness of the oil film, with its refractive index, and with the angle of illumination. To be effective the thickness must be of the order of the wave-length of visible light i.e. 0.5 μ or 0.02 mils.

Similar colors are seen in laminates of films if the thickness and the refractive indices are properly chosen. If the laminate is multi-layered, so that the total specular reflection is much higher than from a single layer, the laminate will look metallic. To merely yield metallic appearance, the thicknesses need not be chosen critically. Fig. 8-10.

The preparation of iridescent films as coatings by depositing multiple layers of transparent finishes is not easily accomplished because the thicknesses must be uniform and quite thin. Deposition of single layers as paints of the desired thickness range is done for laboratory purposes.

Iridescence is achieved in pigments by depositing an appropriate thickness of a highly refractive layer of TiO_2 on mica. Because the particles of mica are flat plates, and, in the usual finishes after application they tend to orient parallel to the surface, the colors reflected from the separate particles of mica tend to be nearly the same and the iridescence is preserved.

Iridescence is obtained from deposits of cholesteric liquid crystals. Many cholesteric substances possess a temperature range within which they spontaneously arrange in layers to yield brilliant colors. If cooled or heated to temperatures outside this range they lose their color at some rapid rate. If cooling is sufficiently rapid there is insufficient time for the rearrangement of the molecules and color is maintained. Conversely, the rearrangements can be made to slow down by appropriate substitutions on the cholesteric molecules. In such cases the lifetime of the cholesteric colors at temperatures far below the true liquid crystal range will be of the order of months or years - Irlux.

8-14-3 Retroreflective Surfaces

Surfaces which reflect a beam of light in the direction of the incident light are made by embedding transparent beads in a surface coating producing small lenses in the top surface of a finish. The finish might be clear. Each lens focuses light at a point which should be reflective.

The effect is similar to that observed when a headlight beam is directed at the eyes of a cat or dog at night. The eye directs a strong beam of light back towards the light source. The directional efficiency of such retroreflective surfaces depends on the sharpness of focus at the reflective surface. It therefore depends on accurate placement of the transparent beads into the surface and control of film thickness.

8-15 REFERENCES FOR FURTHER STUDY

Books

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U. S. Patent 3,766,061 - W. Mahler and M. Panar on Stable Cholesteric Iridescent Colors.

Optical Characteristics of Iridescence and Interference Pigments - R. A. Bolomey and L. M. Greenstein - J. Paint Technology 44 #566 (1972).

FIG. 8-1

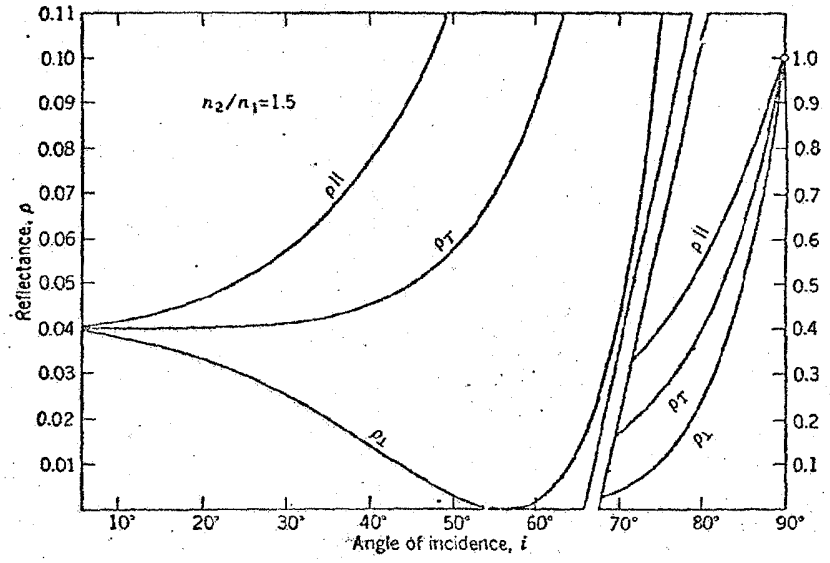


FIG. 3.1. Fresnel reflectance as a function of angle, i, of incidence on a boundary for which the refractive-index ratio is 1.5 (representative of an air-to-glass boundary). Note that the reflectance, ρ_T, for unpolarized light is the average of the reflectances for light plane polarized in ($\rho_\parallel$) and perpendicular ($\rho_\perp$) to the plane of the illuminating beam.

Figures from Judd and Wyszecki - Color in Business, Science, and Industry - Wiley, New York (1963)

FIG. 8-2

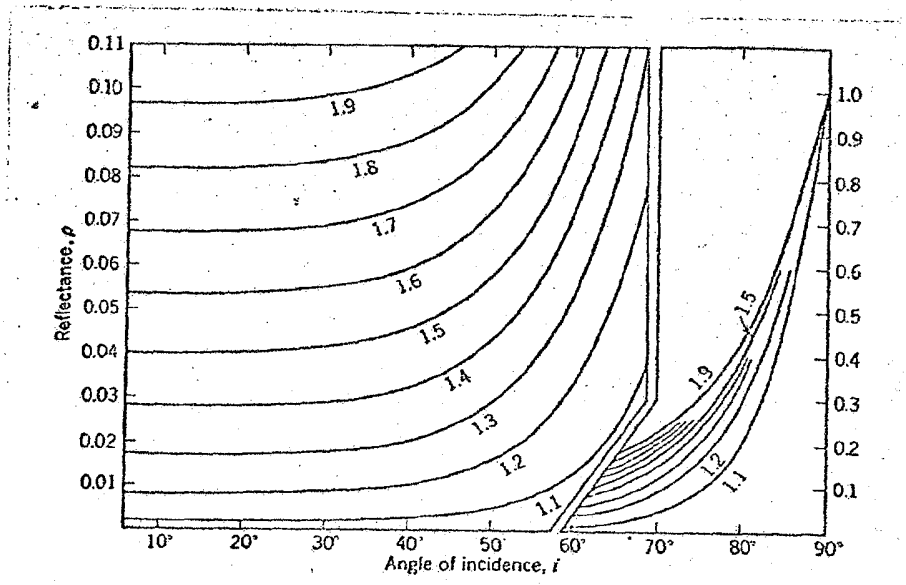


FIG. 3.2. Fresnel reflectance for unpolarized light as a function of the angle, i, of incidence for various values of refractive-index ratio.

FIG. 8-3

From Judd Color in Business Science and Industry Wiley, New York (1952)

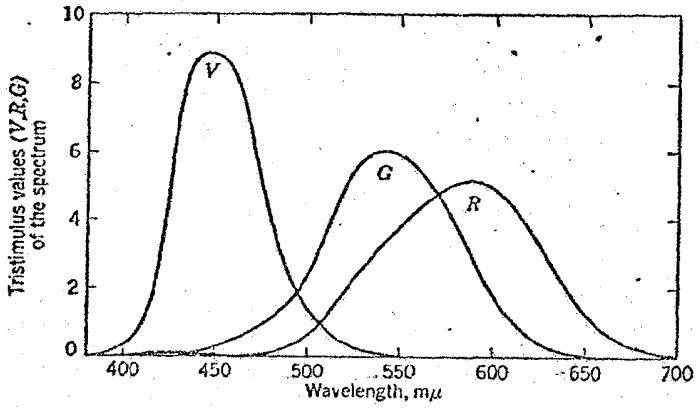


FIG. 8. Approximate spectral sensitivities of the presumed three cone photopigments. To get more precise spectral sensitivities these values must be divided by the spectral transmittances of the ocular media (Fig. 5) and the macular pigment (Fig. 6).

FIG. 8-4

From Judd and Wyszecki loc cit

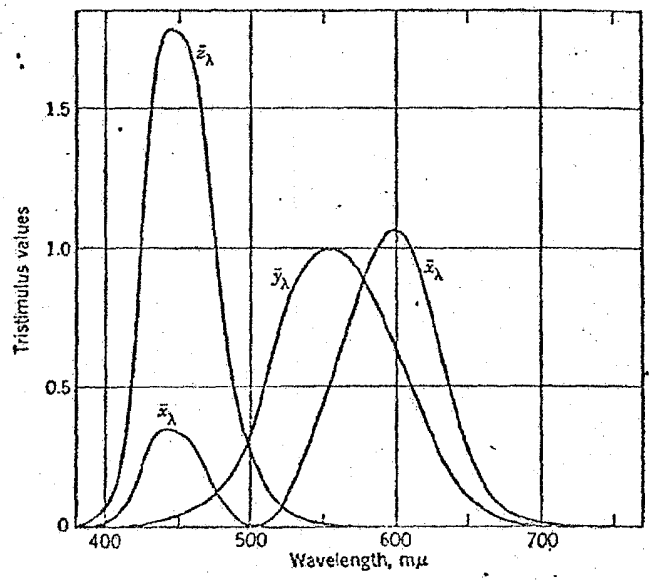


FIG. 1.13. Weighting functions used to reduce spectrophotometric data to colorimetric terms (tristimulus values, X, Y, Z). These functions define the standard observer recommended in 1931 for colorimetry by the International Commission on Illumination—the 1931 CIE standard observer.

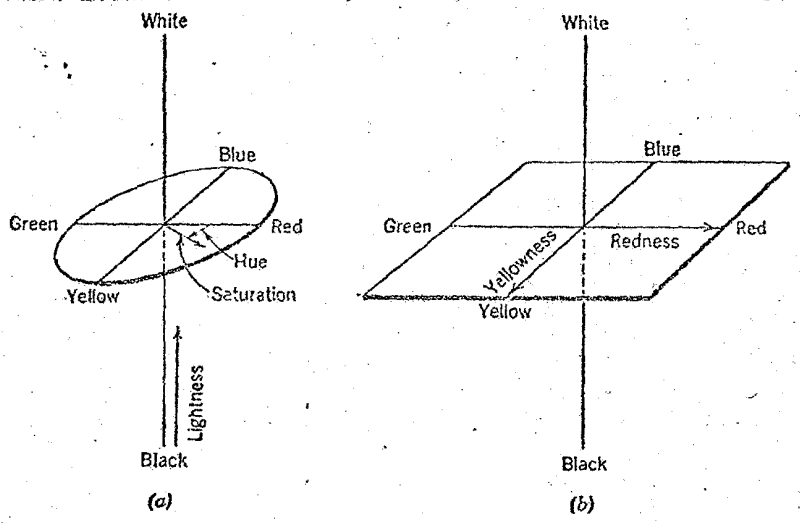


FIG. 1.11. Organizations of color-perception space: (*a*) cylindrical coordinates arising from the ideas of hue, lightness, and saturation, and (*b*) Cartesian coordinates arising from the ideas of black-white, red-green, and yellow-blue.

FIG. 8-5

From Judd and Wyszecki - Loc. cit.

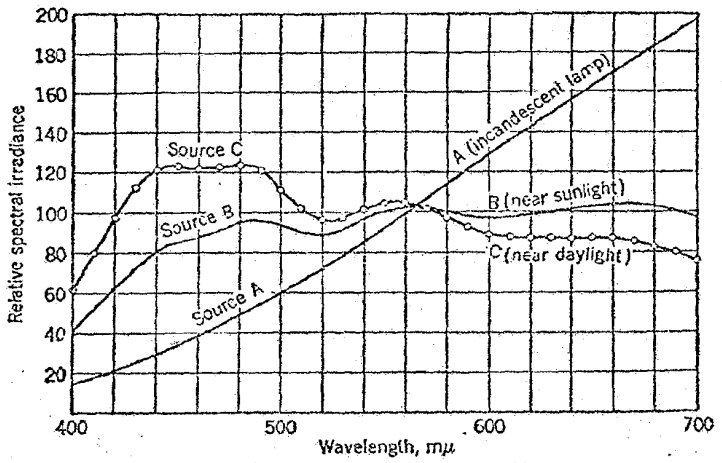
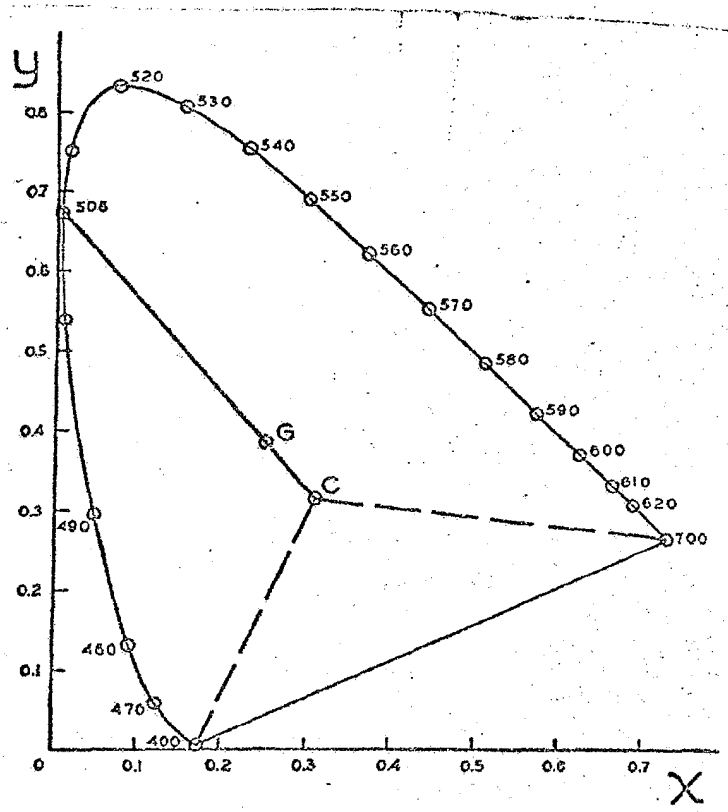


FIG. 2.4. Relative spectral irradiances from standard sources A, B, and C. Source A is typical of the gas-filled incandescent lamp; source B, of noon sunlight; and source C, of average daylight.

FIG. 8-6

From Judd and Wyszecki, Loc. cit.

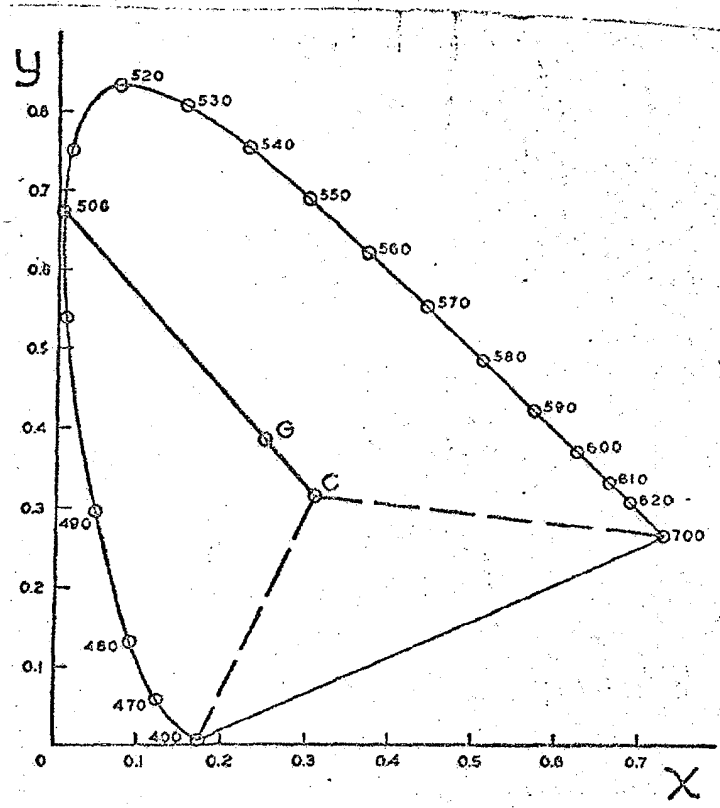


~~FIG. 13~~

Chromaticity diagram showing that the green (G) may be regarded as a mixture of Illuminant C and a spectrum color having a wavelength of 506 millimicrons.

FIG. 8-7

From Hardy-Handbook of Colorimetry -
Technology Press M.I.T.
Cambridge, Mass. (1936)



~~FIG. 13~~

Chromaticity diagram showing that the green (G) may be regarded as a mixture of Illuminant C and a spectrum color having a wavelength of 506 millimicrons.

FIG. 8-7

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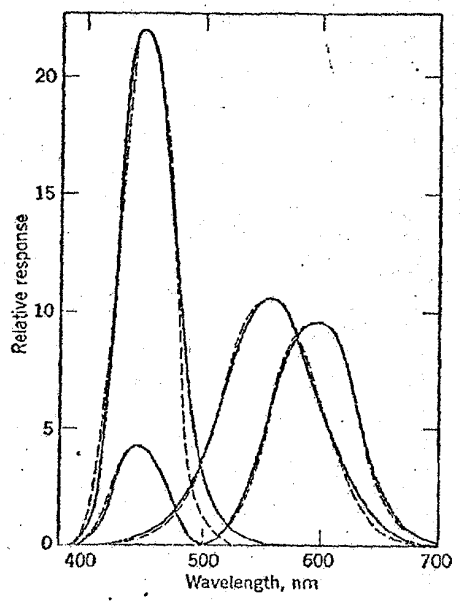
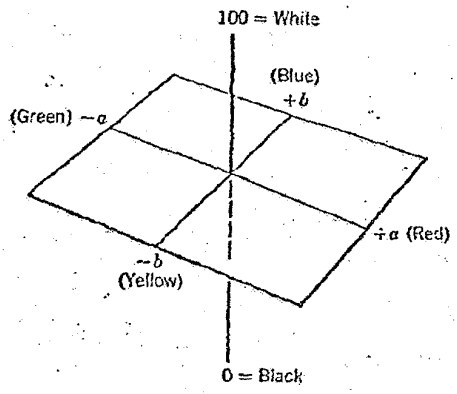
Technology Press M.I.T.
Cambridge, Mass. (1936)



This figure shows how well the CIE color-matching functions (solid lines) are duplicated (dashed lines) in one colorimeter (IDL Signature model Color-Eye) specially calibrated for close conformance to the CIE system (compare with the figures on page 68).

FIG. 8-8

From Billmeyer and Saltzman -
Principles of Color Technology
Interscience, New York (1966)



Hunter's L, a, and b coordinates are a common set of colorimeter readings corresponding approximately to equal visual perception. Their arrangement in three dimensions is shown above, and their relation to G, A (or R), and B is given in the equations below.

$$L = 10\,G^{1/2}$$

$$a = 70\,G^{1/2} \times \frac{A - G}{A + 2G + B}$$

$$b = 28\,G^{1/2} \times \frac{G - B}{A + 2G + B}$$

FIG. 8-9

From Billmeyer and Saltzman, Loc. cit.

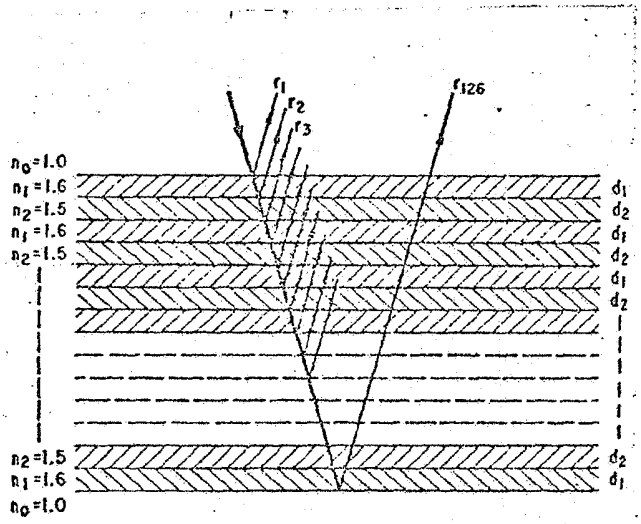


Fig. 1. Reflection of light from multilayer films.

FIG. 8-10

From Alfrey Gurnee & Schrenk - Phys. Optics of Iridescent Multilayered Plastic Films. Polymer Eng. & Sci. 9 400 (1969)

RHEOLOGY OF COATINGS IN THE FLUID STATE

CHAPTER 9

The response of liquid coating compositions to shear forces determines how the coatings can be applied, how smooth they will look after application, how uniform the thickness will be, and how fast the pigment will settle out. The flow response of the materials to shear during manufacture determines how they are mixed and how they are ground. Rheology is the discipline that deals with the flow of fluids in response to shear.

9-1 LAMINAR FLOW AND VISCOSITY

Consider two large plane solid surfaces placed parallel to each other and in relative motion parallel to the surfaces as in Fig. (9-1).

The part of the fluid which is in contact with a solid surface does not move appreciably with respect to the surface; therefore, the fluid in contact with the upper surface will move with velocity v , and that in contact with the lower surface will not move. If the velocity of the upper plane is not too great, and if certain other conditions are met, the fluid will exhibit laminar flow.

The fluid will at all points move with velocity between zero and v and always parallel to the direction of v . Furthermore, the velocity of the fluid will increase linearly with the distance from the stationary plane. The force that must be exerted on each square centimeter of the moving plane, or the shear stress, s, will be proportional to the velocity v and inversely proportional to the distance d between the two plates. Thus,

$$s = \frac{F}{A} = \eta \frac{v}{d}$$ Eq. 9-1

s = Shear stress (in dynes/cm^2)

η = Viscosity - a constant for the fluid (in poise)

d = distance of separation of the two planes in cm./sec.

$\frac{F}{A}$ = force per unit area in dynes/cm^2.

$\frac{v}{d}$ = shear rate in $sec.^{-1}$

The viscosity η is determined by measuring in theory the force per unit area required to move two infinitely large parallel plates past each other in laminar flow, using equation 9-1 to solve for η. In practice it is more convenient to use other configurations and to compute the results with appropriate corrections as though they were infinitely large parallel plates.

Each layer of liquid in motion in laminar flow acts like a moving plane exerting the force F on adjoining layers but decreasing in velocity as distance to the stationary surface decreases.

Eq. 9-1 will apply strictly in cases where the flow is in fact laminar. It tells us that the shear stress is the same everywhere between the plates (v/d is constant independent of d) - really a restatement of Newton's 3rd Law - for every action there is an equal and opposite reaction.

For many fluids the shear stress is proportional to the shear rate over a large range of shear rate provided the temperature and pressure are constant. The viscosity is therefore independent of shear. Such fluids are said to be Newtonian. Gases, pure liquids up to molecular weights of a few thousand, polymer solutions (provided polymer molecular weight is not too high), and certain suspensions of solids are Newtonian in behavior over a considerable range of shear rates.

Fluids tend to have low viscosity when their molecules can glide past each other with minimum deformations of the molecules and minimum cooperative motion of other molecules. Small molecular size favors low viscosity; large molecules cannot move past each other as readily under the crowded conditions without the cooperative motions of the other molecules.

9-2 TURBULENT FLOW

Equation 9-1 will not apply for conditions where flow occurs as eddies or turbulence. Low viscosity, large separations between the plates, high density, and high velocity favor the development of turbulent flow in pipes.

The Reynolds number Re is given by Eq. 9-2

$$Re = \frac{Dv\rho}{\eta}$$

where D is diameter (cm.)

V is velocity (cm./sec.)

ρ is density (g/cm.)

η is viscosity in poise (g/cm. sec.)

When the Reynold's number exceeds a critical value (near 2000 for pipes) flow becomes turbulent. See Figure 9-2.

During laminar flow the shear force and the energy dissipated are proportional to viscosity and independent of density. In turbulent flow, as turbulence increases, density becomes more important and viscosity less so in determining the shear stress at a given rate of shear.

9-3 THEORY OF VISCOSITY

The viscosity of a liquid is explained as due to the restriction of motion by the crowding of molecules which are in constant random motion with elastic collisions. The intensity of random motion is reflected in the temperature. The liquid is viewed as containing holes or small volumes of relatively low molecular concentration into which molecules can move when the holes are large enough. Increasing the temperature increases the probability of holes. Increasing the pressure reduces the probability of holes. During viscous flow the non-random motion (flow) of a liquid is converted to the random motion of the molecules; that is kinetic energy is converted to heat.

The motion of small molecules of common liquids occurs one molecule at a time. The motion of long-chains occurs in segments of about thirty atoms at a time.

The viscosity of a liquid depends on temperature as in Eq. 9-3.

$$\eta = Ae^{B/RT} \quad \text{or} \quad \log_e \eta = \log_e A + B/RT \qquad 9\text{-}3$$

indicating that a plot of $\log\eta$ against $1/T$ is a straight line. B is interpreted as the activation energy for viscous flow. B is related also to the latent energy of evaporation, L_e . For molecules with nearly spherical fields of force (CCl_4 , C_6H_6 etc.) Le/B is about 3, for unsymmetrical molecules about 4, for liquid metals 8 to 25. For hydrogen-bonded liquids B changes rapidly with temperature because at increased temperature the number of bonds decreases, allowing smaller holes to be effective. A is calculated from theory of absolute rates and is about 0.5×10^{-3} for non-associated liquids.

For long-chain molecules the viscosity does not follow Eq. 9-3. Instead it follows Eq. 9-4.

$$\log_e = a + \frac{b}{T} + cZ^{1/2} \qquad (b = f(Z)\ 0<Z<30) \qquad 9\text{-}4$$

a is a constant for a homologous series at constant pressure.

b is the energy of activation for viscous flow divided by R, the molar gas constant

Z is the number of atoms in a chain

For polymeric liquids of chain length exceeding 30 atoms the value of the energy of activation becomes nearly constant at 8 k cal/mol. The approach to constancy is explained as due to the length of the kinetic unit of flow being about 30 atoms in length.

The logarithm of the viscosity of long chain compounds is dependent on the square root of chain length.

9-4 THE VISCOSITY OF POLYMER SOLUTIONS

9-4-1 Low Concentrations

Solutions of polymers in liquids constitute the vehicle for many common lacquers and enamels. The polymers increase the viscosity of the solvent by large factors.

Polymer solutions usually exhibit Newtonian flow over a large range of shear stress and shear rate - their viscosity is not dependent on shear. (However, if the molecular weight is too high, or the concentration is too high, or the shear rate is too high, deviations from Newtonian flow exist).

For low concentrations of polymer the viscosity depends on the polymer's molecular weight and on the solvent-polymer interaction. Solvents which are strongly attracted to the polymer tend to uncoil and straighten out the polymer molecules resulting in larger structures which move less readily into "holes" in the solvent.

The viscosity of a polymer solution increases with increasing polymer concentration as in Fig. 9-3.

At the limit of low concentrations the specific viscosity $\frac{\eta}{\eta_o} - 1$ increases linearly with concentration. Experimental values of $\frac{\eta}{\eta_o} - 1$ can be extrapolated to zero concentration to yield the intrinsic viscosity usually given as (See Fig. 9-4).

$$[\eta] = \lim_{c \to 0} \left(\frac{\eta}{\eta_o} - 1 \right) / c \qquad \text{Eq. 9-5}$$

The intrinsic viscosity $[\eta]$ increases with molecular weight M according to the Mark-Houwink equation:

$$[\eta] = K\bar{M}^{\alpha} \qquad \text{Eq. 9-6}$$

where K and α depend on the nature of the solvent. K and α are related to each other and to solubility parameters (Chap. 10).

The viscosity of a dilute solution as expressed in the form of intrinsic viscosity or in the form of an actual viscosity at very low concentration depends on the choice of solvent and on the molecular weight and choice of the polymer. The viscosity increases as the net attractive forces between polymer and solvent increase. Strong attraction for the solvent is reflected in extended swollen molecules of polymer, which however, in sufficiently dilute solution, do not interfere with each other.

For up to about 5% by weight

$$\eta_{sp} = [\eta] c + k_H [\eta]^2 c^2 \qquad \text{Eq. 9-7}$$

The Huggins constant k_H is related to α in Eq. 9-6 by the approximation

$$k_H = 1.1 - \alpha \qquad \text{Eq. 9-8}$$

9-4-2 Viscosity of Concentrated Solutions (c=) 5% by weight)

The viscosity is related to the molecular weight. Log η at zero shear is related to log M by a curve like Fig. 9-5.

A relationship Eq. 9-9 between viscosity and concentration was prepared and tested sketchily. It was presented as working over the whole concentration range:

$$\log_e\left(\frac{\eta_{sp}}{c[\eta]}\right) = \frac{k_H[\eta]c}{1 - bc} \qquad \text{(b is a constant)} \qquad \text{Eq. 9-9}$$

In concentrated solutions the solvents with strong net attractive forces for the polymer yield more fluid solutions than those with weak net attractive forces. An explanation of this behavior is that chain entanglements increase with decreasing solvency.

Polymer solutions, like polymers in bulk, do not respond as merely viscous liquids, they possess elastic properties as well. The degree of elasticity increases with concentration and molecular weight. Viscoelastic response is demonstrated by normal force in a rotational viscosimeter, or by the shape of the meniscus in a liquid stirred by a rotating impeller.

9-5 THE VISCOSITY OF SUSPENSIONS

A suspension of rigid particles in a liquid displays higher viscosity than the liquid itself, even if the particles do not interfere with each other but especially when they do interfere with each other's motion.

9-5-1 Dilute Suspensions - No Interparticle Interference

The increase of viscosity is explained on the basis that a rigid particle must rotate in a fluid undergoing shear. The rotating particle carries some fluid with it in directions having components perpendicular to the direction of flow. When the rigid particle is spherical the additional motion causes an increase in the observed viscosity according to Einsteins's Law.

$$\eta = \eta_o (1 + 2.5 \phi) \qquad \text{Eq. 9-10}$$

η = viscosity of suspension

η_o = viscosity of fluid medium

ϕ = volume fraction of rigid spheres

Einstein's Law holds for dilute suspensions of spheres. A modified law holds for slightly higher concentrations of spheres

$$\eta = \eta_o (1 + 2.5 \phi + 14.1 \phi^2) \qquad \text{Eq. 9-11}$$

For non-spherical particles the factor 2.5 in Einstein's Law Eq. 9-10 must be increased. The viscosity for non-spherical particles decreases with increasing shear however, because of increasing alignment of the particles as the shear rate increases.

9-5-2 More Concentrated Suspensions - Interference Between Particles

The suspensions encountered in surface coating technology are usually concentrated enough to result in particle-particle interference; they frequently involve polymer solutions that are themselves non-Newtonian (high molecular weight, bridging between particles, bridging between polymer molecules, electrical forces between particles);and they often involve acicular or plate-like (as opposed to spherical) pigments. As a result, the prediction of viscosity from fundamental data is rarely, if ever, accomplished.

Suspensions of pigments in solvents (or water) and in the presence of wetting agents display certain typical rheological curves. Examples are given in Figure 9-6.

The data of Figure 9-6 can be plotted in the form of viscosity as a function of shear rate. The slopes of the curves of Figure 9-5 represent viscosity. The curves of Figure 9-7 are therefore the curves of the first derivatives of the functions of Figure 9-6.

Most surface coatings have a yield value. The yield value represents that force which is necessary to break down weak but solid structures built up by particle to particle contact between pigment particles.

Most of the practical pigmented coatings have non-Newtonian flow, but in addition to the variation of viscosity with shear rate their viscosities at a fixed shear rate are also time-dependent. Such systems are said to be thixotropic. It is usual for the viscosity of a thixotropic system to reach an equilibrium value, in due course, after being sheared constantly at any given shear rate. The rate of approach to equilibrium may vary between thixotropic systems. The most common situation is for a decrease of viscosity with time to an equilibrium value, but the equilibrium value decreases with increasing shear rate. See Figure 9-8.

There is evidence in the case of many thixotropic systems of the formation of loose structures between the particles (particles flocculate or contact each other spontaneously), and these structures are broken by forces of shear. The higher the shear the smaller the flocculates and the lower their effect on the viscosity of the suspending liquid. The spontaneous flocculation and the effect of the shear explain the existence of time-dependent effects. The flocculation requires diffusion and convection of particles, and their favorable disposition relative to each other. The shearing forces require time for the attainment of favorable positions of the particles for shearing and for attainment of distance between the sheared particles. Not all the flocculates are broken at one instant. See Fig. 9-9.

A simple equation which is reputed to apply to the viscosity of pigmented paints is:

$$\frac{\eta}{\eta_o} = 1 - \frac{kv_2}{1 - Sv_2} \qquad \text{Eq. 9-12}$$

η = viscosity of suspension

η_o = viscosity of fluid phase

v_2 = volume fraction of suspended solid

S = sedimented volume per unit of volume of suspended phase

k = a constant

In equation 9-12 the quantity S reflects the structure-building tendency of the pigment in the liquid - the larger S the greater the attraction between particles and the more voluminous the settled pigment.

Equation 9-12 obviously cannot define the flow properties of a suspension which is non-Newtonian and many surface-coating compositions are strongly non-Newtonian.

9-6 FLOW IN COATINGS AFTER APPLICATION

9-6-1 Sagging

A film of liquid on a vertical substrate is subjected everywhere to a shearing force due to gravitation. The liquid will tend to flow, but the force on each layer parallel to the substrate is that exerted by the mass of paint outside that layer. The shear force therefore increases from zero at the outer surface to a maximum at the interface between the paint and the substrate.

The force of gravity F_g (in dynes) on a layer of A cm^2 lying parallel to the substrate and x cm from the outer surface is given by Eq. 9-13.

$$F_g = A\rho gx \qquad \text{Eq. 9-13}$$

A = area (cm^2)

ρ = Density (g/cm^3)

g = acceleration of gravity (980 dynes/g)

x = distance from outer surface (cm)

The coating responds by flowing except in contact with the substrate. The flow rate increases with the distance from the substrate. It is calculated by equating the shear force F_g at a distance x from the surface due to gravity to the viscous resistance F_η of the sheared film at that point.

$$F_\eta = A\eta \frac{dv}{dx} = F_g = A\rho gx \qquad \text{Eq. 9-14}$$

η = viscosity (poise)

v = velocity

Solving for v as a function of x, and noting that the velocity is zero at the substrate (where x = X, the film thickness) the velocity profile is given by Eq. 9-15.

$$v = \frac{\rho g}{2\eta}(X^2 - x^2) \qquad \text{Eq. 9-15}$$

X = Film Thickness

The volume V flowing past any given level per cm. of width of the film is calculated (Eq. 9-16) as a function of film thickness X, density ρ, time t, viscosity η.

$$V = \frac{X^3 \rho g t}{3\eta} \qquad \text{Eq. 9-16}$$

(g = acceleration of gravity 980 dynes/gram)

The pronounced effect of film thickness on sagging is reflected by the exponent of X, the film thickness. Doubling the film thickness in a particular area would result in a sag rate of 8X that of the rest.

9-6-2 Effect of Yield Value on Sagging - Slumping

The effect of a yield value is to produce no sagging flow when the shear stress induced by gravitation is less than the yield value.

If the film is thick enough, the shear stress near the substrate will be high enough to exceed the yield value. There will be insufficient shear in the shallow layers of the film where the stress does not exceed the yield value. Therefore, the film will sag at the substrate but will move as a unit at some point further from the surface. Such behavior is called slumping.

9-6-3 Effect of Evaporation, Increasing Temperature, on Sagging

In general evaporation of a component of a surface coating results in increased viscosity, increased yield value and decreased film thickness, each of which reduces sagging rate. However, the evaporation of certain materials (e.g. ammonia from a neutralized carboxylic latex paint) can result in reduced viscosity and increased tendency to sag. Increase of temperature usually results in reduction of viscosity. Sagging occurs therefore when some coatings are exposed to baking temperatures.

9-6-4 Levelling - Newtonian Flow

Immediately after brushing, the surface of a paint film will generally contain pronounced striations parallel to the motion of the brush. Surface-tension forces will tend to cause the striations to disappear. An analysis of the flow treats a cross-section of the surface as a complex wave whose shape is analyzed as the sum of a series of sine curves with different amplitudes and different wave-lengths.

Given a paint film of Newtonian viscosity η and average thickness X, with striations of wave-length λ and amplitude Z_o, and with surface tension σ it will level in time t so that the amplitude will be Z_t. The value of t is given in Eq. 9-17 and Eq. 9-18.

$$t = \frac{G\eta}{\sigma X^3} \qquad \text{Eq. 9-17}$$

where

$$G = 0.036 \lambda^4 \log \frac{Z_o}{Zt} \qquad \text{Eq. 9-18}$$

Comparing two films of different thickness having the same initial wave-length and amplitude, the times to arrive at the same appearance (i.e. the same value of Z_o/Zt) will be inversely proportional to the cube of the thickness. Reduction of wave-length of striations in half will result in reduction in time to achieve equal reduction in amplitude by a factor of 16 (i.e. λ^4).

9-6- 5 Effect of Yield Value on Levelling

In levelling the surface tension produces the stresses which result in flow to produce levelling. During the levelling process the stress diminishes When a paint has a yield value, that is, a stress below which no perceptible flow occurs, the levelling will not proceed beyond the point where the maximum stress equals the yield value. The maximum stress γ is given by Eq. 9-19.

$$\gamma = \frac{8\pi^3 \sigma ZX}{\lambda^3}$$ Eq. 9-19

9-6-6 Practical Observations of Flow and Levelling

The usual compositions are thixotropic. The viscosity changes with time, with the magnitude and history of applied stress (during storage, brushing or rolling for example), with evaporation of solvent or water, with wicking of ingredients into the substrate.

The surface tension is not constant but tends to decrease after new surface is created and surface-active diffuse to it. The surface tension may also change by wicking and evaporation during the processes of levelling.

As a result, the equations for levelling can hardly be expected to apply to give precisely reproducible results. They do however provide a useful guide to changes that must be made in formulations to produce desired changes in flow and levelling. Reduction in yield value, reduction in rate of development of structure (producing a yield value), increase in applied film thickness, increase in surface tension, shorter striation wave-length will all produce more levelling.

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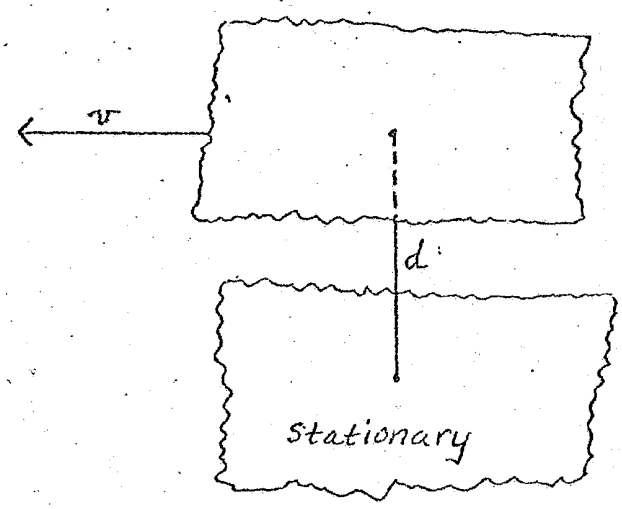


FIG 9-1 - RELATIVE MOTION OF INFINITE PARALLEL PLANES

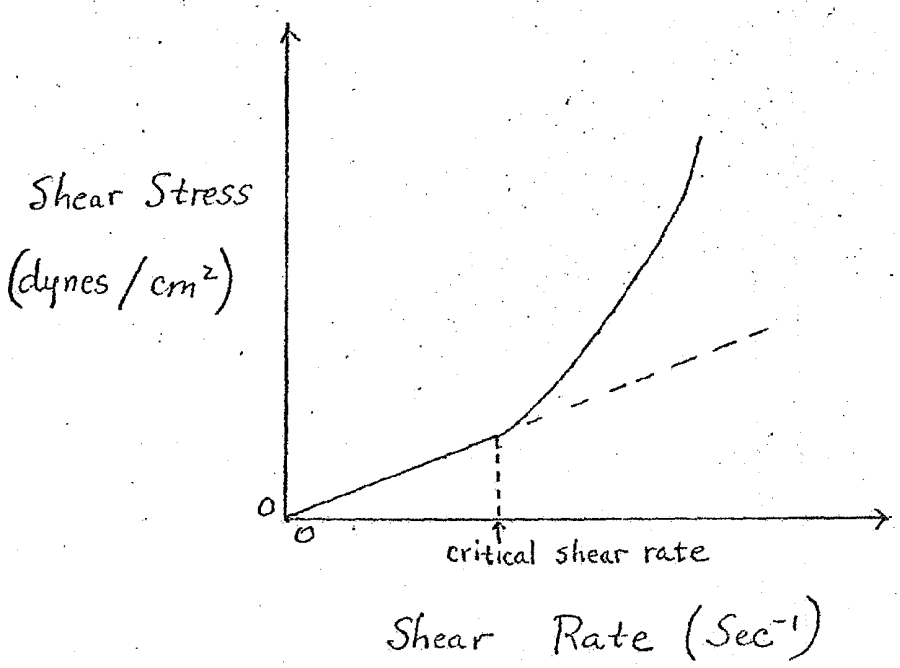
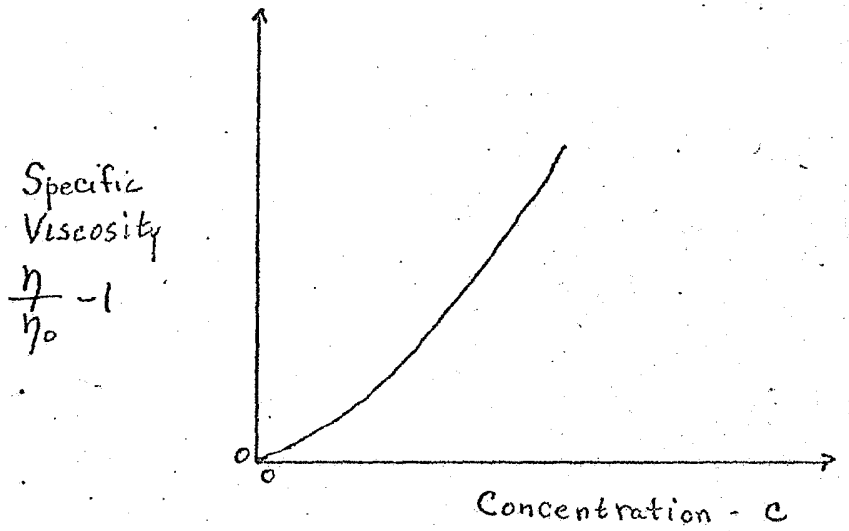


FIG 9-2 - DEVELOPMENT OF TURBULENT FLOW IN A NEWTONIAN FLUID



η = viscosity at concentration c
η_0 = viscosity of solvent
c = concentration of polymer in solvent

FIG 9-3 - SPECIFIC VISCOSITY as a FUNCTION OF CONCENTRATION AT LOW CONCENTRATION

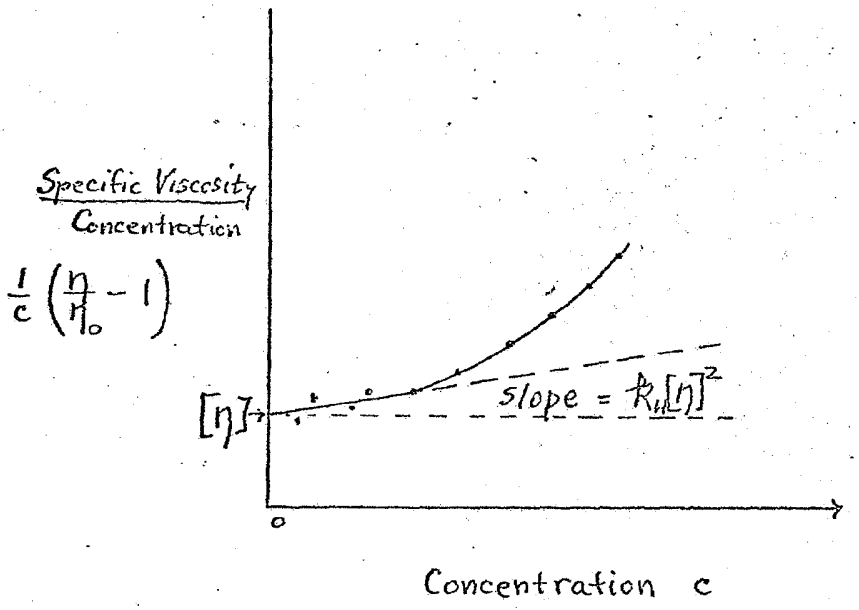


FIG 9-4 - TREATMENT OF DATA for VISCOSITY VS. CONCENTRATION TO DETERMINE INTRINSIC VISCOSITY.

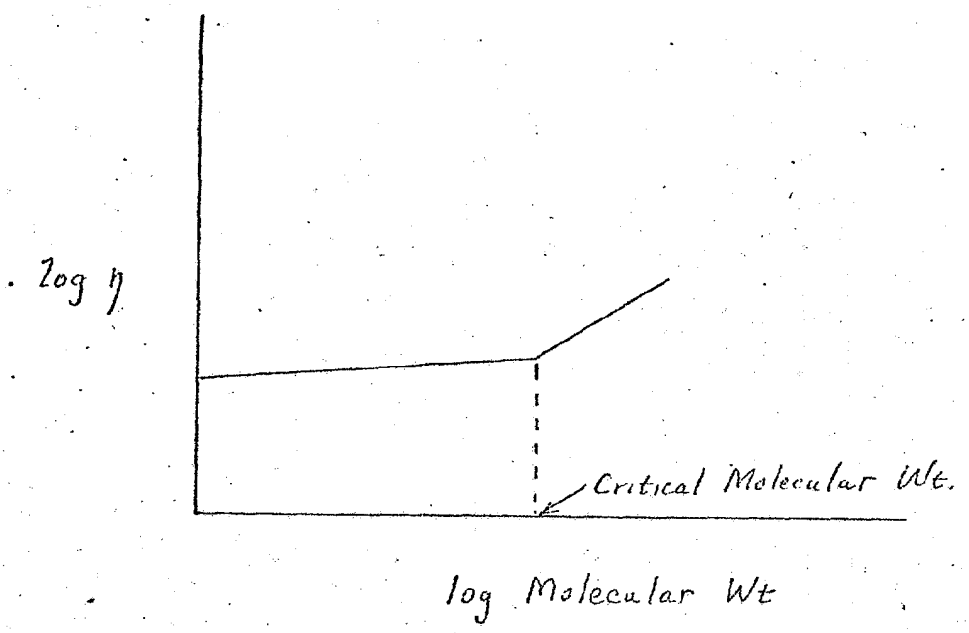


FIG. 9-5 - VISCOSITY VS. MOLECULAR WEIGHT FOR CONCENTRATED SOLUTIONS

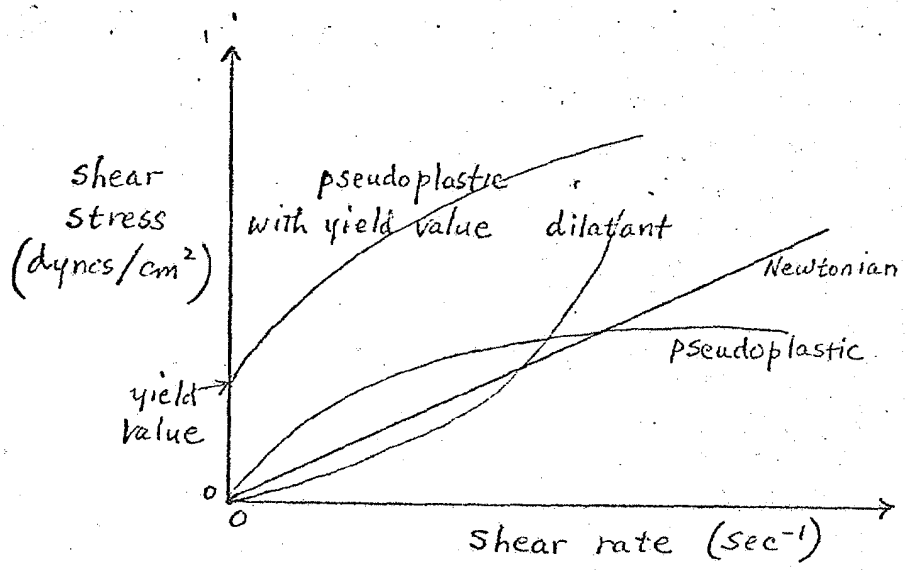


FIG 9-6 - Shear Stress vs Shear Rate for Suspensions

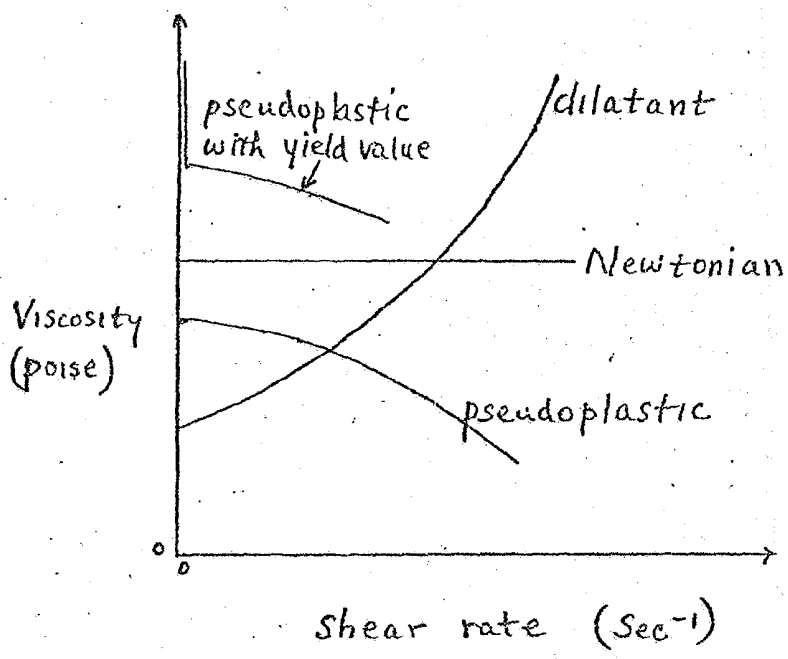


FIG 9-7 · VISCOSITY VS. SHEAR RATE FOR SUSPENSIONS

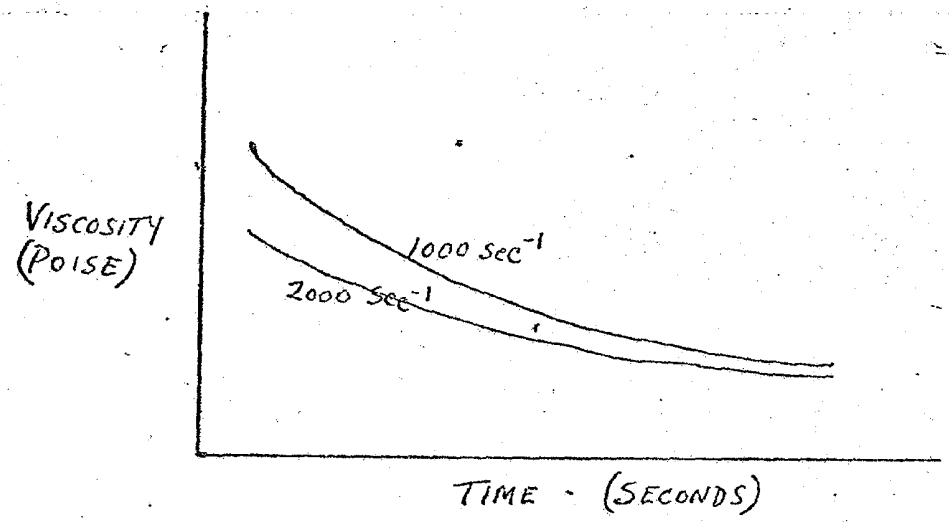
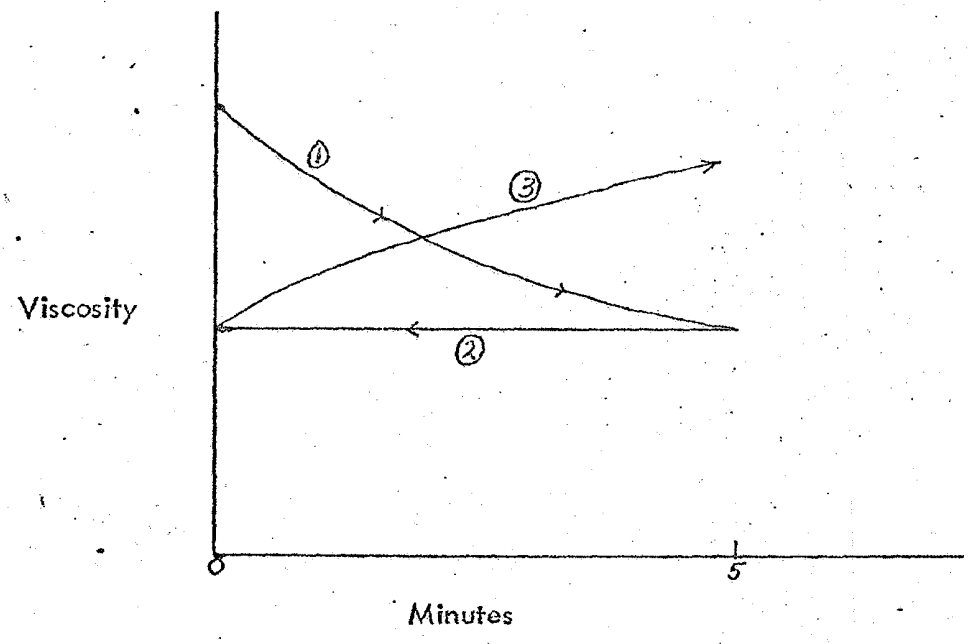


FIG 9-8 · VISCOSITY VS STIRRING TIME FOR A THIXOTROPIC SUSPENSION AT TWO SHEAR RATES.



(1) A paint, after resting 1 day is sheared 5 min. at 1000 sec.$^{-1}$ and its viscosity observed as a function of time.

(2) Shear is stopped momentarily and time clock is re-started.

(3) Viscosity is measured in brief bursts at 1000 sec.$^{-1}$, so stirring is minimal.

FIG. 9-9 - DECAY AND REBUILDING OF THIXOTROPIC STRUCTURE

INTERMOLECULAR FORCES AND THEIR INFLUENCE ON OBSERVED SURFACE AND INTERFACIAL PROPERTIES:

CHAPTER 10

In connection with the properties of polymer molecules, attraction of the molecules or segments of them to other molecules or segments was related to crystallinity and the restriction of mobility in masses of large molecules.

Intermolecular forces operate of course also in the case of small molecules and are regarded as responsible for a variety of observations. The Van der Waal's equation of state relating pressure and temperature of gases, the condensation of gases to liquids, and crystallization are examples.

In this chapter, the connection between intermolecular forces and surface tension, interfacial tension, capillary action, wetting, stability of dispersions, foams and solubility will be discussed.

Forces between organic molecules were seen to be mainly classified as a) London dispersion forces, b) polar forces and c) the forces associated with hydrogen bonds; others, usually of less importance in connection with organic chemicals, are the forces related to the free electrons in metals and the electrostatic forces between ions.

10-1 SURFACE TENSION OF PURE LIQUIDS

The surface tensions vary between pure liquids according to the magnitude of the cohesive forces. Thus hydrocarbons, with only weak dispersion forces, are low, and water, with weak dispersion, but strong polar and hydrogen bonding forces, is high in surface tension. The surface tension of a liquid decreases with increasing temperature to the critical temperature, where it becomes zero and the surface vanishes.

10-2 SURFACE TENSION OF SOLUTIONS; SURFACE-ACTIVE AGENTS

The surface tension of a solution is less than that of the pure component of highest surface tension. Thus, a small quantity of dissolved butanol reduces the surface tension of water. The component of lowest surface tension concentrates in the surface. The energy liberated by reduction of the surface tension provides the energy required to concentrate the component in the surface from its less concentrated bulk.

Surface active agents consist of molecules which tend particularly to concentrate in the surface. Usually they consist of large molecules (compared with solvents or water) having one part with strong attraction to the medium and another with relatively weak attraction to the medium.

10-2-1 Dynamic Surface Tension

The increase of concentration of solutes in the surface of a liquid when they lower the surface tension is not an instantaneous process. It is controlled by rates of diffusion. Measurements of the surface tension of new surfaces which are made rapidly compared with diffusion rates will therefore yield high values that diminish to equilibrium values as the surface stabilizes

in concentration. The distinction between dynamic and static (or equilibrium) surface tension becomes more important as diffusion rates are reduced (high viscosity, large molecules).

10-3 SURFACE TENSION OF DISPERSIONS

Dispersions of pigments or other large particles in water which are wet by water show no change of surface tension compared with pure water. However, when such dispersions are made in solutions of surface active agents they can produce an increase in surface tension by absorbing surface active material from the solution and consequently reducing this concentration at the surface.

Pigments or other solid particles which are not readily wet by a liquid will often collect at the surface. If present in sufficient quantity the particles will cover the entire surface and will in effect form a solid though porous film. This phenomenon occurs with certain leafing aluminum pigments and with polymer latices made with a severe deficiency in surface-active agent.

10-4 SURFACES AND INTERFACES - MOLECULAR PICTURE

10-4-1 Surfaces of Pure Liquids

The molecules in the bulk of a liquid are in constant motion. They are separated from each other by small spaces. While thermal vibrations tend to separate the molecules from each other, they have forces of mutual attraction, operating over distances of several molecules, which tend to keep the molecules at some equilibrium distance depending on temperature. The surface is considered as a region extending for several atoms in depth or a depth sufficient to achieve equilibrium distances characteristic of the bulk. While the intermolecular attraction acts in all directions deep in the bulk of the liquid the attractive forces near the surfaces are reduced because of the absence of attractive forces from above. Accordingly the surface layers are deficient in molecular concentration as though they were stretched from the equilibrium concentration in the bulk. The creation of such extended or stretched volumes requires work which is restored when the surface is reduced.

The reduction in molecular concentration is regarded as the cause of surface tension, a measurable quantity. Naturally the surface tension depends on the intermolecular forces (e.g. London dispersion, hydrogen bonding, polarity, metallic bonds).

10-4-2 Molecular Picture of Interfaces Between Pure Liquids

The picture here is modified by the presence of intermolecular forces operating across the boundary areas of both liquids. Again, there is a reduction in molecular concentration in the boundary region giving rise to an interfacial tension. The forces of mutual attraction are of the same types as operate for single pure liquids but when two phases are in contact the interfacial layer is stretched less in each phase compared with the stretch of each surface of the pure materials.

In the measurement of surface tension of liquids the gas phase is usually ignored when the molecular concentration in the vapor (or vapor pressure) is low. Strictly speaking, what is measured is an interfacial tension between two phases. At high pressures, as near the critical temperature, the observed

surface tension becomes quite small. The gas phase above a liquid can be considered as dilute liquid and is ignored as a practical matter.

10-4-3 Molecular Picture of Surfaces of Solids

The surfaces of crystalline solids are composed of regular arrangements of atoms which have vibrational, but no substantial translational, motion. Non-crystalline or amorphous solids are structured like liquids of extra high viscosity. The attractive forces in solids are of the same types as are found in liquids and a tension must therefore exist in the surface of solids as it does in liquids. However the surface tension of solids is not subject to direct measurement. It is subject to indirect estimate by measurement of contact angle with liquids.

10-5 CONTACT ANGLE - IMMISCIBLE LIQUIDS

When a droplet of oil floats on water without spreading, Fig. (10-1), the forces of surface tension and interfacial tension at the intersection of the air, oil and water interfaces are in equilibrium and can be represented by three vectors which add to zero. If the oil is selected differently the droplet shape may be flatter, and the angle in the oil phase sharper. If the oil spreads on the water indefinitely the contact angle will be zero.

10-6 RELATIONSHIP BETWEEN SURFACE TENSION AND INTERFACIAL TENSION

The surface tension of a pure liquid can be regarded as the sum of component surface tensions due to the different types of forces which operate. Operation across interfaces by London dispersion forces is universal because they are of sufficiently long range and common to all materials. They are additive. On the other hand the forces of metallic bonds in mercury would not operate across a boundary with a hydrocarbon, nor would the hydrogen-bonding forces of water operate significantly across a boundary with a hydrocarbon.

According to Fowkes the interfacial tension γ_{12} between two liquids, subscripts 1 and 2 respectively, when only London forces operate across the boundary, is related to the individual surface tensions γ_1 and γ_2 by the equation:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d \gamma_2^d} \qquad \text{Eq. 10-1}$$

In equation 10-1 γ_1^d is the portion of γ_1 attributable to the London dispersion forces in liquid subscript 1, γ_2^d is the corresponding quantity for the other liquid.

The equation is obtained by assuming that the magnitude of the dispersion force operating across a boundary is the geometric mean of the dispersion force in the separate phases, an approximation which becomes less valid as the volume elements which interact across the boundary diverge in size.

A value for the dispersion force component of the surface tension can be derived from measurements of interfacial tensions with a hydrocarbon and the surface tension of the pure hydrocarbon using equation 10-1 and assuming that in hydrocarbons only the dispersion forces operate. Thus the interfacial tension of mercury (surface tension $\gamma_1 = 484$ dynes/cm.) against n-hexane, surface tension $\gamma_2 = \gamma_2^d = 18.4$ dynes/cm., is measured as 378 dynes/cm.

Using eq. 10-1, and solving for γ_1^d , one obtains the dispersion force component of the surface tension of mercury.

One can use the value of γ_1^d , to calculate the interfacial tension between mercury and another hydrocarbon whose surface tension is known.

The value for the interfacial tension between water and mercury calculated from values for the respective dispersion force components of surface tension is in agreement with measurements, indicating that the forces between dipoles in water and free electrons in mercury can be neglected in comparison with the London dispersion force.

10-7 SPREADING COEFFICIENT

The spreading of oil over water results in an increase of the interface, creation of an oil surface, and a corresponding decrease in the water surface. The spreading coefficient S is given by eq. 10-2 and represents the energy liberated in the spreading process in terms of ergs/sq. cm.

$$S = \gamma_w - (\gamma_o - \gamma_{ow}) \qquad \text{Eq. 10-2}$$

The interfacial tension γ_{ow} is predicted from eq. 10-1 and yields a value for S as in eq. 10-3:

$$S = 2\sqrt{\gamma_o \gamma_w^d} - 2\gamma_o \qquad \text{Eq. 10-3}$$

10-8 CONTACT ANGLE OF LIQUIDS ON PLANE SURFACES OF SOLIDS

When solids are contacted by liquids there is generally an angle of contact (Fig. 10-2). When the liquid spreads spontaneously and completely the contact angle is zero. When the liquid balls up, the contact angle approaches 180°. The angle of contact θ can be related to the surface tension of the liquid γ_L , the surface tension of the solid γ_s and the interfacial tension between solid and liquid γ_{Ls} by eq. 10-4.

$$\gamma_L \cos\theta = \gamma_s - \gamma_{Ls} - \pi_e \qquad \text{Eq. 10-4}$$

π_e = equilibrium film pressure of absorbed vapor on solid. γ_{Ls} not readily determined independently, can be calculated from Eq. 10-1 and substituted into Eq. 10-4 yielding Eq. 10-5.

$$\gamma_L \cos\theta = -\gamma_L + 2\sqrt{\gamma_L^d \gamma_s^d} - \pi_e \qquad \text{Eq. 10-5}$$

For situations where $\gamma_L > \gamma_s$, π_e is zero, and

$$\cos\theta = -1 + 2\sqrt{\gamma_s^d}\,\frac{\sqrt{\gamma_L^d}}{\gamma_L} \qquad \text{Eq. 10-6}$$

a plot of cos θ vs. $\sqrt{\gamma_L^d} / \gamma_L$ yields a straight line with slope of $2\sqrt{\gamma_s^d}$ and passing through the point cos θ = -1, $\sqrt{\gamma_L^d} / \gamma_L = 0$.

10-8-1 Advancing and Receding Contact Angles

The observed contact angle between solids and liquids is often dependent on whether the liquid contacts a fresh solid surface or one previously wet. The angle measured as the liquid advances over the solid is usually greater than the receding angle. The difference is explained as due to roughness in the solid surface and as due to changes in the solid surface by contact with the liquid. The changes can be due for example to compounds selectively absorbed from an impure liquid. Averaged values of advancing and receding angles are often used as the equilibrium angle.

10-9 CRITICAL SURFACE TENSION OF SOLIDS

In general in a series of solid surfaces of low energy, for example, hydrocarbons, fluorocarbons, silicones, those of lower surface energy yield larger contact angles with liquids than solid surfaces of higher energy. When a series of liquids differing in surface tension are applied to a low energy surface, those liquids having a surface tension below some critical value are found to spread with contact angle zero on the surface. That value is described as the critical surface tension of the solid. If the liquids used have only dispersion forces, the surface tension of that liquid for which cos θ just departs from zero can be taken to mean the surface tension of the solid.

10-10 CAPILLARY ACTION

The spreading of liquids on solids combined with surface tension results in the penetration of liquids into pores or capillaries. Flow in a capillary is resisted by viscous forces. The viscous resistance depends on pigmentation and on the viscosity. If capillaries are small enough absorption of large molecules such as surface active agents or polymers can have large effects on flow.

10-11 STABILITY OF DISPERSIONS

In organic coatings finely divided solids or liquids are usually dispersed in other liquids for use. Two stabilizing mechanisms are actually employed: (1) ionic and (2) entropic.

10-11-1 Ionic Stabilization

Charges are present on the particles. All the particles are charged with similar sign. Counterions are present in the medium. This method of stabilization is used for aqueous dispersions of hydrophobic materials. The mobility of the particles in an electric field is used to calculate the zeta potential, a property which is used as a quantitative measure of stability of ionically-stabilized dispersions.

Negative (anionic) charge stabilization of polymer particles is often achieved by incorporation of carboxylic acid groups attached to the polymer chains. When the polymer particles are suspended in water and depending on pH, the particles become charged negatively. Amines are often used to adjust the pH because they can be evaporated after application. Negative (anionic)

charge stabilization is also achieved by addition of soap, or other anionic active agent which can be absorbed on the particles.

Positively charged (cationic) dispersions are made by incorporating an amine as part of the polymer and neutralizing with an acid, or absorbing a cationic surface-active agent on the particles.

10-11-2 Entropic Stabilization

Dispersion of pigments or of resins in non-aqueous media is accomplished by coating the particles with a non-ionic surface active agent which has a portion soluble in the non-aqueous medium. These coated particles repel each other because solvent forces its way into the regions of high concentration of the coating, exerting osmotic pressure between two closely-spaced coated particles, and separates the particles.

10-11-3 Destabilization of Ionic Dispersions

Increase of salt concentration, particularly these salts containing multivalent ions opposite to that of particles, results in a decrease of electric repulsion between particles and consequent flocculation. During the course of evaporation of a polymer latex the concentration of soluble salts increases to this level. The tolerance of an ionically stabilized dispersion to the addition of salts is one indicator of effective formulation. Other indicators are mechanical stability and freeze-thaw stability. The addition of solvents of low dielectric constant - e.g. alcohols or acetone - to ionically stabilized dispersions has a similar effect to the addition of salts. The low dielectric constant forces the counterions closer to the particles and thereby reduces their repulsive effect on each other. Thermal forces then become sufficient to drive them close enough for the dispersion and polar forces to operate and flocculation occurs.

10-11-4 Destabilization of Entropically Stabilized Dispersions

This is usually achieved by addition of a large-molecular-component which attaches preferentially to the particles if they are not completely coated or by providing a system in which the entropic surface active agent becomes insoluble - change of pH, change of temperature, addition of non-solvents.

10-12 FOAMS

Foams are dispersions of gas in liquid. Usually the gas is air in the form of spheres. If the gas volume is high enough, the spherical bubbles are deformed and look more like a beehive in structure. Foams are always unstable because the pressure inside a bubble is smaller in a large bubble and still smaller on the surface and because gases will diffuse from small to large bubbles and from large bubbles to outside air.

If the time of observation is short compared with diffusion time a foam may be quite stable. That is, particles of air will not grow by the breakage of the boundary layers of liquid. The surface of a sphere of air is an interface between the liquid and air. At this surface, surface-active agents collect and are oriented in direction. Between two such bubbles therefore there will be two layers of surface active agent directed oppositely. If these absorbed layers repel each other sufficiently they prevent the surfaces of the spheres from approaching each other. The breaking of foams usually involves interfering with the repulsion of the stabilizing layers.

10-13 SURFACE VISCOSITY

The surface of a liquid is obviously different from the bulk due to absorption of surface-active material, and due to the formation of close-packed layers. It is expected that the viscosity in the surface layer will be different from the viscosity in the bulk. Though viscosity increase can be demonstrated, the measurements are open to question. The viscosity in a surface film can be Newtonian or even pseudoplastic with a yield value.

10-14 THE CONCEPT OF SOLUBILITY

Practically all surface coatings are made of mixtures of chemicals. A mixture may consist of particles dispersed as units of one molecule which retain their identity on standing or mild stirring; in that case the mixture will be called a solution. It may consist of particles containing a plurality of molecules; in that case the mixture is called a suspension.

The molecules are associated with other molecules with forces that depend on the chemistry of the particles. In solutions, associations between the unlike molecules are favored over associations between like molecules so that momentary clumps of molecules of one kind are spontaneously broken up by diffusion of the other molecules to achieve homogeneity.

In the case of large organic molecules (such as polymers) dispersed in poor solvents segments of a large molecule associate with other segments of a similar type rather that with molecules of the solvent, and tend to aggregate and exclude the solvent. If the concentration of large molecules is low enough, each large molecule will not encounter another. The aggregation will contain the segments of a single molecule and will tend to be contracted and spherical. At higher concentrations the aggregations will contain many molecules and will form a separate macroscopic phase.

In good solvents the large molecules are extended rather than spherical, and are held apart by solvent molecules which are associated by attractive forces to the polymer molecule.

10-15 SOLUBILITY PARAMETERS

At one time the principle which governed the selection of solvents for the polymers used in surface coatings or, in fact, for the compatibility of any two substances, was that the chemical natures of the substances should be similar. Present-day methods for the selection of solvents are more precise in their definitions of similarity and they emphasize intermolecular forces between solvent and polymer.

Gases are all infinitely soluble in each other. The cohesive forces which are represented by the attractive force constant in Van Der Waals equation, and which act to hold the molecules of a gas to each other, are smaller than the thermal forces which shake them apart. In the case of liquids and solids the cohesive forces are obviously greater than the thermal forces. In the case of two soluble substances the free energy of the mixture must be less than the total free energy of the individual components at the same temperature.

For two non-polar liquids the heat and mixing may be expressed by the equation:

$$\Delta H_m \approx \Delta E_m = \phi_1 \phi_2 \ (x_1 V_1 + x_2 V_2)(\delta_1^2 - \delta_2^2) \qquad \text{Eq. 10-7}$$

where x_i = mol fraction of liquid i

ΔH_m = heat of mixing

ΔE_m = internal energy of mixing

ϕ_i = volume fraction of liquid i

V_i = molar volume of liquid i

δ_i^2 = cohesive energy density of liquid i

The δ_i is defined by

$$i = \sqrt{\frac{\Delta E_{vi}}{V_i}} \qquad \text{Eq. 10-8}$$

where ΔE_{vi} = molar energy of evaporation of liquid i

and $\frac{\Delta E_{vi}}{V_i}$ = cohesive energy density

(δ_i is given in $cal^{1/2} cm^{-3/2}$ or in hildebrands)

The free energy of mixing, which must be negative for mixing to occur, is given by $\Delta F_m = \Delta H_m - T \Delta S_m$ where T is the absolute temperature ΔF_m and ΔS_m are the free energy and entropy of mixing respectively. For spontaneous mixing ΔS_m is assumed positive, and to make ΔF_m negative the value of ΔH_m must be made small. ΔH_m approaches zero as δ_1 approaches δ_2.

10-15-1 Hansen's Modification

This approach was modified for application to polar and metallic liquids using several different schemes which differ in detail but not in the general idea. One of these is Hansen's approach and it will be described further.

The cohesive energy ΔE, is assumed to consist of the added contributions of London dispersion forces ΔE_d (estimated from the cohesive energy of a hydrocarbon similar in structure), hydrogen bonding forces ΔE_h and the interaction of permanent dipoles with other dipoles ΔE_p.

Accordingly, $\delta^2 = \frac{\Delta E_m}{V}$, is assumed to be the sum of δ_d^2, δ_h^2, and δ_p^2.

Permanent dipole - permanent dipole forces are small compared with others and are lumped with hydrogen bonding forces as are other forms of association - e.g. π bond, quadrupole interactions.

Typical values assigned to certain solvents are given in Table 10-1.

TABLE 10-1

TYPICAL VALUES OF THE COMPONENTS OF THE SOLUBILITY PARAMETER

COMPOUND	Vcm^3/mol	d	p	h
n butane	101.4	6.9	0	0
n hexadecane	294.1	8.0	0	0
benzene	89.4	9.0	0	1.0
styrene	115.6	9.1	0.5	2.0
p diethyl benzene	156.9	8.8	0	0.3
methyl chloride	55.4	7.5	3.0	1.9
methylene dichloride	63.9	8.9	3.1	3.0
chloroform	80.7	8.7	1.5	2.8
carbon tetrachloride	97.1	8.7	0	0.3
ethyl bromide	76.9	8.1	3.9	2.5
acetone	74.0	7.6	5.1	3.4
cyclohexanone	104.0	8.7	3.1	2.5
ethylene carbonate	66.0	9.5	10.6	2.5
methyl acetate	79.7	7.6	3.5	3.7
propylene carbonate	85.0	9.8	8.8	2.0
2 ethoxyethyl acetate	136.2	7.8	2.3	5.2
dimethyl phthalate	163	9.1	5.3	2.4
n - butyl benzyl phthalate	306	9.3	5.5	1.5

10-15-2 Determination of δ_d, δ_p and δ_h

δ_d is estimated from the value of δ_d for a hydrocarbon of similar structure.

For the determination of δ_p from measured quantities sensitive to polar structure Hansen and Beerbower use Eq. 10-9.

$$\delta_p^2 = \frac{12,108}{V^2} \frac{\epsilon - 1}{2\epsilon + n_D^2} (n_D^2 + 2)\mu^2 \qquad \text{Eq. 10-9}$$

V = molar volume

ϵ = dielectric constant

n_D = refractive index (for yellow line sodium spectrum)

μ = dipole moment in Debye units (10^{-18} e.s.u. cm.)

δ_h is determined from δ and previous determination of δ_d and δ_p as in Eq. 10-10.

$$\delta_h^2 = \delta^2 - \delta_p^2 - \delta_d^2 \qquad \text{Eq. 10-10}$$

δ_h should be consistent with the observation of the contribution of an OH group to the heat of vaporization.

$$\Delta H_v = V\delta_h^2 = 4650 \text{ cal/mol of OH}$$

δ_h and δ_p are also calculable from the molecular formula using group contributions to δ_h and δ_p. In the case of δ_p the contributions to $V\delta_p$ are additive for the different groups. For the δ_h calculation the values of $V\delta_h^2$ are additive. See Table 10-2.

TABLE 10-2

GROUP CONTRIBUTIONS TO PARTIAL SOLUBILITY PARAMETERS

FUNCTIONAL GROUP	POLAR PARAMETER $V\delta_p$ (cal $cm^3)^{1/2}$/mol	H. BOND PARAMETER $V\delta_H^2$ cal/mol	
		Aliphatic	Aromatic
-Br	300 ± 25	500 ± 100	500 ± 100
-NH	300 ± 25	1350 ± 200	2250 ± 200
-OH	250 ± 30	4650 ± 400	4650 ± 500
-COOH	220 ± 10	2750 ± 250	2250 ± 250

Calculations of δ_p and δ_h for complex compounds may be useful, but many exceptions are noted.

10-15-3 Solubility of Polymers

Polymers are soluble in a solvent which is similar in δ_d, δ_p and δ_h. See Fig. 10-3. The region of solubility is represented by the ball in space and the projection of the ball on the planes bounded by δ_d, δ_p and δ_h axes. The size of the ball is reduced as the molecular weight increases and the intrinsic viscosity in the center of ball is greatest. The viscosity of a polymer in concentrated solution will in general be least near the center.

Graft and block polymers of two types of long sequence will in general show two regions of solubility which may or may not overlap.

10-15-4 Surface Free Energies: Relation to Solubility Parameter

The surface free energy or surface tension is related to the solubility parameters by the equation of Beerbower.

$$= 0.0715\ V^{1/3}\left[\delta_d^2 + 0.632\ (\delta_p^2 + \delta_h^2)\right] \qquad \text{Eq. 10-11}$$

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ENVIRONMENTAL PROBLEMS

RECENT ECONOMIC DEVELOPMENTS IN SHORTAGES OF PETROLEUM PRODUCTS AND RECENT LEGISLATION

CHAPTER 11

11-1 RELATIONSHIP OF APPLICATION COSTS TO FUEL COSTS

The cost of applying coatings has risen recently because of sharp increases in the prices of fuel.

In industrial application of coatings by spray large volumes of air are evacuated into the open. This air is usually at the plant's ambient temperature and for a large part of the year is heated. Certain types of spray equipment use more air than other types and the costs of heating the air affect these accordingly.

The requirement of heat for evaporation of water or solvents from coatings and the need for achieving high temperatures for crosslinking results in a substantial use of fuel. The substrates must generally be heated to the same temperature as the coating.

Generally, ovens must carry a large supply of air to keep the evaporated solvents below their explosive limits, and this air must be heated. Typically in existing installations there is poor conservation of heat because heat has been relatively cheap.

The allocation of fuels to users necessarily means that at each plant where coatings are applied hard decisions must be made about how the short supply will be used.

Accordingly, coating compositions and methods of application which require less heat become more attractive. Reduced temperatures for cross-linking, reduced quantities of solvents and water and reduced quantities of heated air are taking on new importance.

11-2 ULTRA VIOLET CURE

Finishes which are applied without inert solvents and which are converted from liquid to solid form by exposure to ultra-violet radiation are receiving attention.

11-2-1 U.V. Cure Using Vinyl Monomers

The most prominent U.V. curing coatings are those involving a vehicle of acrylate, methacrylate, or styrene monomers, which typically include polyfunctional acrylates of low volatility like trimethylolpropane triacrylate and other, more volatile, monomers. Polymers of low molecular weight such as unsaturated polyesters and pigments are included with the polymerizable compounds. Generally, a sensitizer, such as benzoin methyl ether or benzophenone is used which increases the rate of initiation of polymer molecules by absorbing longer wave-length ultra-violet light and

converting it to free-radical production. Curing time can be as short as 2 seconds in practical equipment. The incorporation of waxes, which crystallize on the surface on evaporation of a fraction of the monomer, reduces the diffusion rate of oxygen into the film and of monomers out of the film. (Oxygen inhibits free radical reactions). When waxes are used, they crystallize, and rough surfaces result.

11-2-2 U.V. Cure by Production of Acidic Substances

The formation of strong acids by exposure to ultra-violet can also be used for polymerization. Thus the U.V. light decomposes an azo compound $R-N=N-BF_4$ to form the strong acid BF_3 which polymerizes epoxides.

11-3 ELECTROCURE OR ELECTRON-BEAM CURE

A beam of electrons of about 200-500 milliamperes is accelerated in a vacuum by a 200-500 kv potential drop. It is directed through a thin rectangular metal window to an inert atmosphere (nitrogen) and to the wet surface coating on a moving sheet of substrate. Before leaving the window the electron beam is shifted back and very rapidly by a scanning mechanism as in a TV picture tube. The purpose of scanning is to produce a wide area of exposure to electrons.

The electron beam produces high speed electrons. Some of these electrons produce penetrating X-rays on striking atoms of the window, at the expense of their speed. On striking molecules of gas or liquids the electrons ionize them, releasing more electrons, still at high velocity. Beyond a few inches from the accelerator are many electrons and ions and their direction is somewhat diffused by the collisions. On penetrating the wet coating the electrons continue to ionize atoms and to produce free-radicals. Nitrogen is often used between the accelerator and the coating.

The single primary electron emitted from the accelerator may have an energy of 200 kev on issuing from the machine or 13,000 x the energy required to remove an electron at low velocity in most materials. As a result many electrons and ions are formed successively from a single primary electron in the course of the collisions of that electron and the others released by it. The flux of electrons and free-radicals is maximum at some distance from the accelerator, and the production of radicals inside the wet coating, usually about 1 mil thick, is fairly uniform. An absorption of 1 - 10 megarads is usually required for conversion (1 rad = 100 ergs/g. of absorber).

11-4 LIMITATIONS OF U.V. AND ELECTRON CURE

Rapid polymerizations employing large concentrations of initiating free-radicals would necessarily favor low molecular weight in each kinetic chain process. High molecular weight is obtained by the use of polyfunctional monomers in substantial quantity. These polyfunctional monomers are more expensive than the monofunctional ones.

Inhibition by air, by extracts from wood, or by pigments complicates the application process and the formulation of finishes. The requirement for sensitizers in U.V. cure involves a cost penalty and an extra ingredient that can hasten degradation on exposure.

The electron-beam cure is accompanied by many side-reactions. The action of a fast-moving electron is non-specific with regard to the location of attack. It will attack polymers as well as monomers producing chain scission, cross-linking, or free-radicals which absorb oxygen, for example.

The X-rays produced by voltages greater than 25,000 volts penetrate deeply into materials and are dangerous. Heavy concrete shields (20 inches thick) are needed for electron-beam apparatus.

11-4 SOLVENT EMISSIONS

The use of solvents in coatings is limited by legislative and administrative rules. The Federal Environmental Protection Agency sets standards for air quality and the local governments apply their own rules. These rules are in a state of flux.

In general solvents vary in the severity of the effects they produce - visible smog, and atmospheric irritants in particular. Aromatic and olefinic hydrocarbons are among the worst offenders. Los Angeles Rule 66 is typical of regulations in effect.

11-4-1 Overcoming the Effect of Solvent Shortages and Legislation

Many commercial products have been formulated with solvents that do not conform to legislative standards. For that reason, and also because particular solvents can be in short supply, it becomes necessary to reformulate the solvent-composition. The use of the partial solubility parameters (Chapter 10) permits one to choose mixtures of permissible solvents that provide approximately the same solvency as the current, non-conforming or non-available solvent mixture. Generally there will be a large number of possible solutions to the problem which will vary in cost and evaporation rate and other properties. Computer techniques allow one to make the necessary calculations for minimum cost while fitting the rest of the requirements best.

11-5 EXEMPTIONS FROM RULE 66

Exemptions from Rule 66 are provided which have encouraged R&D to develop industrial coatings based largely on water or of low volatile content.

11-5-1 Water-based Finishes

Architectural Finishes are based on dispersions of aqueous polymer latices containing dispersed pigments, glycols, extenders, polymeric thickeners and surface-active agents. The latices are usually carboxyl-containing polymers that are stabilized against flocculation be neutralizing the carboxyl groups. The latices have glass-transition temperatures near the lower temperatures of application to ensure coalescence. For interior use they are of high enough pigment content to get the added effect of included air on hiding. Exterior finishes usually contain less pigment. Virtually all the architectural products consist of polymers sufficiently high in molecular weight to require no further polymerization. The films are soft (low Tg), tough (high mol. wt.), soluble, swollen by water (high hydrophilic content).

To meet their special requirements the industrial water-based finishes are generally of low molecular weight and cross-linked in an oven after application. The cross-linking agent is usually a melamine-formaldehyde resin and the polymer may be a suitable combination of styrene, methacrylates, acrylates or other vinyl monomers including some containing hydroxyl groups and carboxyl groups (e.g. hydroxyethyl acrylate and acrylic acid). Modified drying oils containing maleic anhydride adducts are another example of a popular type of industrial water-based coating.

Industrial water-based coatings are applied by spray roller-coating, or electrocoating. (Chapter 12).

Water-based coatings can be of a lacquer type i.e. the binder is of final high molecular weight as packaged. In such a case considerable amounts of water are needed if the polymer is in solution. If the polymer is a latex, high gloss will be hard to attain.

11-5-2 High Solids Finishes

Some of the earliest drying oil-based finishes would qualify as high solids finishes exempt from Rule 66. Recent high-solids finishes are mixtures of low molecular weight polymers that are reactive with each other, for example hydroxyl-terminated polyester and methylated melamine-formaldehyde resins. Application of high-solids finishes is usually by spray, electrostatic or conventional.

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APPLICATION OF COATINGS

CHAPTER 12

Organic Coatings are applied to substrates by a variety of processes. The rheology of a liquid coating is important in determining how fast, how thick, and by what processes a paint can be applied, but they also determine how fast it smoothes out or roughens in response to surface tension, how fast and to what degree it sags on a vertical surface. The different methods of application require different rheological characteristics.

12-1 SHEAR RATES CHARACTERISTIC OF VARIOUS APPLICATION METHODS OF LIQUID FINISHES

The different application methods differ in their characteristic shear rates. Since the viscosity of coatings usually varies with shear rate, the rheology must be adjusted at the appropriate shear rate ranges for the particular mode of application intended. See Table 12-1.

TABLE 12-1

APPROPRIATE SHEAR RATES FOR VARIOUS PROCESSES OF APPLICATION

Process	Shear Rate (sec^{-1})
Doctor Knife	2000 - 10,000
Brushing	5000 - 20,000
Spraying	1000 - 40,000
Roller Coating	3000 - 40,000
Dipping	10 - 100
Flow Coating	10 - 100

The shear rates during application are considerably higher than those pertinent to settling of pigment in storage or to sagging and levelling after application, i.e. 0.01 - 0.10 sec^{-1}.

12-2 METHODS OF APPLICATION OF COATINGS

12-2-1 Straight Edged Doctor Knife or Doctor Blade

A puddle of liquid on a plane substrate surface is smoothed out by drawing a straight edged tool across the puddle at a fixed clearance from it. The thickness of the wet applied film is less than the tool's clearance but the thickness depends on the shape of the tool as well as the clearance.

Doctor-blades used in the laboratory usually leave a wet film about half as thick as the clearance. The film usually shrinks further on drying.

When the flow of liquid and its wetting qualities are such that it flows to the back of the doctor-blade, ridges occur in the deposited film parallel to the motion of the blade and with a spacing which depends on film thickness.

12-2-2 Industrial Roller Coating

Large steel rollers are used for coating paper, cloth, or sheet metal surfaces, usually on a continuous basis. Various kinds of configuration are available for the machinery. The selection of type of coating machine is based on the rheology of the coating to be applied. Conversely the rheological properties of the fluid coating are adjusted for particular machines and coating speeds. The shear rate in a roller coating is apt to be high and it is sheared in one direction. Color and gloss deviations resulting from shear will become evident as patterns of lines, and are likely to be objectionable. Accordingly, the pigments must be highly dispersed and well broken down.

Roller-applied coatings often have special mechanical requirements after drying. Usually the sheets, after they are coated and the paint has hardened, are rolled up into multi-layered cylinders for shipping and storage. The paint must not be marred by contacting surfaces in the roll even under hot storage conditions. Soft, fine pigments and hard,roughened, elastic, lubricated films are routes to these properties.

At least two important flow defects can arise during rolling in addition to the gloss and color defects that might arise from pigment - vehicle interactions.

1. Ridging - At evenly spaced distances stripes are developed with frequency dependent on film thickness.

2. Spattering - Where the roller leaves the painted surface, liquid strings develop in the paint film which stretch as the roller rotates and its surface recedes from the painted strip. The strings break causing a spray of large drops.

12-2-3 Napped Rollers

For hand-painting walls and ceilings in homes, napped rollers have become the preferred method of application. The roller is a cylinder covered with a soft mat of material - like a high-piled synthetic fiber fabric, for example. Such a cylinder holds paint by capillary action. The deeper the pile the more paint will be held and the more suitable for rough and porous surfaces. The amount of coating picked up increases with increasing viscosity as measured at about 100 sec^{-1}.

As the roller is being used and as the roller surface leaves the substrate, the paint film divides between the roller and the paint surface. If the roller is without hairs the breakage occurs smoothly with some ridges, and in the form of strings at still higher speeds. Strings are accentuated by the hairs on the rollers. When the strings break they collapse back on the coated surface and form a stipple because they do not flow back to a uniform surface (yield value and thixotropy).

12-2-4 Brushing

Generally the shear rate is about 10,000 sec^{-1} . The higher the viscosity at 10,000 sec^{-1} . the thicker the film applied, and the harder the painter must work to brush the coating out uniformly.

Paints of dissolved polymers and low volumes of pigment approach Newtonian behavior. A typical example would be a high gloss alkyd solution paint. Generally, to have easy-brushing properties, such finishes with Newtonian behavior must have low viscosities at all shear rates (viscosity independent of shear rate) and they will therefore tend to sag unless applied quite thin. To prevent sagging a thixotropic or pseudoplastic character is built in, so that the viscosity builds up rapidly after brushing. To help with rapid increase of viscosity there can also be fast evaporation of some solvent.

Water-based trade-sales products, usually applied by roller and brush, have pronounced pseudoplastic and thixotropic behavior. They resist sagging and can be brushed with minimal effort. Typical brushing viscosities for these are 0.6 to 3.0 poise at 10,000 sec^{-1} with much higher viscosity at lower shear rates and a yield value. The levelling of such coatings necessarily suffers.

Typical brush marks are probably partly due to the same mechanism as ridging behind doctor knives. They may also be partly due to clumping of the bristles, an effect of surface tension forces.

The amount of paint picked up by a brush is determined by the viscosity at about 15 - 25 sec^{-1} . Whether or not it will drip off the brush or a substrate will depend on a yield value or on a viscosity at still lower shear rates. Generally, a large pick-up of paint by the brush, a low force for brushing out, a rapid and complete levelling and freedom from settling in containers are mutually opposing requirements for which compromises are worked out depending on the manufacturers perception of the consumers preferences.

12-2-5 Dipping and Flow Coating

Complex parts are often dipped in large vats of paint and removed gradually so that excess paint runs off. Obviously, the rheology helps determine the amount of paint left on the surface. The withdrawal rate determines the uniformity of the deposit, more rapid withdrawal resulting in heavier films with greater difference between top and bottom. Viscosity, surface tension, density, play their parts. Viscosities are typically 0.4 - 0.5 poise.

An alternative to dipping is flow-coating which does not require as large a container. The liquid coating is flowed over the surface.

Proper rheology is required at about 10 - 100 sec^{-1} representing the dipping and flow-coating shear rates and at 0.01 - 0.1 sec^{-1} representing sagging conditions.

12-2-6 Spraying by Shearing with Gas

Fine droplets of paint are made by various kinds of devices. In all of these fine strings or thin sheets of liquid are caused to form first. Each of these collapses into a series of droplets which are air-borne to the substrate.

The theory of spraying is poorly developed, probably due in part to the difficulty of measuring the particle sizes of liquid droplets, the complexity of particle-size statistics and the complex response of liquids to the high and variable shear rates usually used when sprays are created.

a) Compressed-air spray guns: A stream of liquid is directed into a more rapid stream of air. The velocity of the air approaches that of sound. The air elongates the stream of liquid into thin threads or sheets. These break spontaneously into droplets by the action of surface tension. The elongation and subsequent break-up are resisted by viscosity. They are also affected by elastic forces if the liquid contains dissolved polymeric substances.

In any given compressed-air spray gun, the particle-size increases with decreasing air pressure (air velocity), with increased flow rate of liquid. Usually the weight of air pumped through a spray gun is about equal to that of the liquid. The volume of air is much larger, of course.

The atomization occurs within a centimeter or so from the spray gun. The shear rates are so great at this point and the particles are so fine that rapid equilibration of solvent-concentrations and temperatures occurs between gas and liquid. If the particles are fine the velocities of air and particle also tend to equilibrate rapidly. The momentum of air and liquid leaving the gun is transferred to the relatively motionless ambient air, and a turbulent mixture results. The mixture has an overall component of velocity in the original direction of spray but it falls off rapidly in forward velocity and carries more and more air as distance from the gun increases. The scale of turbulence grows steadily larger and the velocity of turbulence decreases as distance from the gun increases.

Spray guns often have auxiliary nozzles which shape the dimensions of the cone of spray. The auxiliary nozzles must have little effect on the dimensions of the particles.

b) Airless Spray: A thin jet of fluid under high pressure is forced into the air. The jet breaks up into droplets. The velocity difference between liquid and gas is generally smaller than in compressed-air sprays and the particles are larger.

c) Hot Spray: Liquid finishes are sprayed at high temperatures to reduce their viscosities during application. The temperature falls rapidly and the liquid coating increases rapidly in viscosity as it cools. As a result, the effect on the spraying, sagging and levelling of increasing the temperature is like that of adding a particularly volatile solvent, but at lower cost.

d) Aerosol Bomb: In its simplest form, a mixture of a liquid to be sprayed and a propellent confined in a can under pressure is allowed to flow through a narrow tube to the open air. The propellent is a liquid like dimethyl ether, propane, dichlorodifluoromethane (Freon 12) or other liquid which boils considerably below room temperature. A manually controlled valve is usually added so that the spray can be stopped and started at will. If the liquid to be sprayed is pigmented, a pebble or some steel shot help to make it easier to redisperse settled pigment. The nozzle outlet of the tube can be shaped to alter the dimensions of the cone of spray.

The aerosol bomb acts by forcing a mixture of gas and liquid, intimately mixed, through a fine tube or small orifice. The mixture of gas and liquid is developed from the original liquid as a result of the drop of pressure in the narrow tube (or other restricted passage through which the paint flows toward the outside).

The volume of gas developed is a function of the temperature, the heat of vaporization of the propellent, the molecular weight of the vaporized gas, the solubility of the gas in the liquid and the degree to which equilibrium is approached (nucleation may sometimes be important) during passage through the narrow tube.

12-2-6-1 Molecular Weight and Spraying

The ability of a spray mechanism to produce fine droplets depends on the rheological characteristics at high shear rates. The viscosity and elastic modulus rise with increasing concentration of dissolved polymers. Accordingly, as the concentration of dissolved polymer is increased, the droplets become larger. As the particle size increases, the loss of volatile solvents from the particle by diffusion from the inside and evaporation from its surface decreases. The large particles therefore arrive at the substrate with a high content of volatile solvent and a low viscosity. Such coatings tend to sag readily. Therefore, it is often desirable to increase the concentration on the substrate. Because of the cost of solvents, however, and because of air-pollution and other considerations, higher concentrations of the polymer are often sprayed but with reduced molecular weight.

The limiting concentration for spraying is usually given in the form of a viscosity at some shear rate easily obtained on common viscosimeters. Such viscosity limits tell only part of the story. When high molecular weight polymers are sprayed, the viscosity limits are reduced sharply. Traces of dissolved high molecular weight polymers yield large droplets.

12-2-6-2 Deposition From Ordinary Sprays

Objects in the path of a moving air stream carrying a spray of particles are coated by the spray, but the fraction deposited on the surface depends on the velocity of the air, spray particle diameter, and the shape of the surface being coated. The remaining fraction is deviated around the object being painted and is, practically speaking, largely wasted. (In industrial spraying the overspray is recovered and reconstituted into new coating material where practical).

For purposes of estimating the fraction deposited, the amount of spray intercepted geometrically by the object is regarded as the theoretical maximum. Implicit in this idea is that the path of the spray particles is not affected by the presence of the object. In fact, however, the presence of the object causes the air, and with it the particles, to deviate.

For any given shaped object the fraction of spray deposited changes directly with the velocity and the square of the particle diameter and inversely with a dimensional parameter of the object (e. g. diameter of a disc). The amount deposited can be calculated from the assumption that the particles tend to follow the air stream-lines around the object, but at the same time tend to follow their original directions according to their momenta. The deviation

from a stream-line is equivalent to a velocity difference between the air and the particle. The force due to this velocity difference comes from the rate of change of momentum of the spray particle. Such calculations have been made for various shapes and velocities. (Sell) The larger particles deviate less than the smaller ones. (See fig. 12-1).

Obviously, decreasing the distance from gun to surface (thus increasing air velocity at the point of deposition) and increasing the particle size (by spraying at higher viscosity, for example) will increase the efficiency of deposit of particles. These steps to increase efficiency of deposit result in other effects, too, some of which may be troublesome (i.e. too much solvent remains in the particle when it reaches the surface , tending to result in sagging, poor appearance of metallics). Large droplets produce splashes and rapid air flow produces wave patterns. The overall effect, including appearance and efficiency, must be balanced.

Spray efficiency in painting objects like an automobile may be as low as 40 to 50%, the remainder being deviated around the substrate.

12-2-7 Electrostatic Spraying

If a fine-wire or point high voltage electrode is placed near a stream of liquid the liquid is broken down into fine droplets. The droplets are electrically charged with the same polarity as the fine-wire or point.

In the electrostatic spraying of coatings the liquid coating is usually fed out to the edge of a rotating disc-like or bell-like surface placed near a high voltage point electrode.

A sufficiently fast rotation will produce a spray by the shearing of liquid by air, the same mechanisms as in the case of usual spray guns. However, in the presence of an electric field slow rotation is sufficient. The purpose of the rotation in this case is merely distribution of the coating at an even thickness.

12-3 ELECTROSTATIC APPLICATION OF SURFACE COATINGS

Spray particles can be directed to an object by an electric field terminating on the object if the spray particles are suitably electrically charged. Suitably used, the loss of spray particles by their missing the substrate can be made negligible. In practical electrostatic application the charge on each spray particle must be high and the electric field must be strong to overcome the competing effects of air currents. Furthermore all the spray particles must have charges of the same sign in order to avoid coalescence in the air and in order to be directed to the work by the electric field.

The particles are all charged negatively by passing them through ionized air produced in a high voltage discharge from a negative sharp point or wire electrode. The objects to be coated made the positive and grounded terminal of a strong electric field. The negative terminal can be the sharp wire or auxiliary electrodes.

The electrostatic precipitation of dusts and fumes by an essentially similar process is about 150 years old. The application of surface coatings by electrostatic precipitation is only about 30 years old. The electrostatic production of spray particles is still newer and is usually combined with electrostatic application.

12-3-1 The Production of Electrically Charged Particles Without the Deliberate Use of Electricity

During the usual non-electrical spraying processes, droplets are often found to be charged and the spraying device is charged oppositely. Usually, however, the charge transferred per particle is small and not suitable for practical electrostatic application.

The collection by particles of ions from the air, initially produced by cosmic rays, electron emission from hot objects, etc. results in small values of charge - some particles positive, others negative, but most neutral.

12-3-2-1 The Production of Ionized Air by Corona Discharge

When an ion or electron is placed in an electrostatic field it moves with an acceleration that depends on the electric field strength.

At low gas pressure, an electron is unlikely to collide with a molecule of gas for a considerable distance. When it finally collides with a gas molecule it will have achieved a large enough velocity to produce additional ionization of the molecule. With successive collisions the number of positive ions and electrons increases steadily. Under such conditions, the gas becomes a good conductor of electricity. Incidentally, it emits light because of the recombination of electrons with ions.

At atmospheric pressure, the collisions are more frequent. As the pressure is increased, higher values of electric field strength are needed to accelerate electrons between collisions to velocities sufficiently high to produce additional ionization.

Conditions for achieving a stable supply of ionized air without castastrophic discharges are obtained by using a fine wire or point as one electrode, a flat plate or other object of low curvature as the other electrode at an appropriate distance and connecting them to a source of high voltage 10,000 to 100,000 volts.

The electrostatic field intensity near a wire or point increases as the dimensions of the point decrease. The ion production is therefore at a maximum near the wire or point and diminishes rapidly at a distance.

Consider a negatively charged point and a positive electrode. An electron near the point is accelerated and collides with a molecule of gas resulting in an additional electron and a positive charged ion. The positive ion is accelerated toward the point and the two electrons are accelerated toward the large electrode. Since most of the space will have too low a voltage gradient to produce ionization between collisions the space beyond some short distance from the point will have only electrons or negative ions. A similar situation exists for a positively charged point which produces only positive ions over most of the air space. (In the case of positively charged point, it is mainly electrons accelerated to the point that produce the ionization rather than protons or positive ions which leave it).

12-3-2-2 Attachment of Electrons to Molecules

While electrons moving rapidly enough cause ionization of molecules with which they collide, they may also, at lower velocities, be captured by

neutral gas molecules to form negative ions. Oxygen, water, sulfur dioxide and halogen-containing molecules are particularly effective in capturing electrons while nitrogen is not.

The carriers of electric current at large distances from a negative corona electrode are therefore mainly negative ions.

12-3-2-3 Attachment of Charges to Particles

Neutral particles pick up electric charges from the ionized gas until their repulsion for the charges becomes large enough. The amount of charge depends on the particle diameter, the dielectric constant, the conductivity. The pick-up of charges is described as due to both (1) field charging and (2) molecular motion. In field charging, the particle concentrates the field around it by virtue of its dielectric constant; charged particles follow the field to the particle. In charging by molecular motion there is diffusion of ions to the particle. For very fine particles 0.2 nm. dia. the number of charges per particle is influenced largely by molecular motion and in turn by the concentration of ions, directly proportional to the current density of the fine wire or point electrode. For large particles, 20 nm., the maximum number of charges depends on the electric field intensity and is proportional to the cross-sectional area.

A negative corona is slightly more efficient than a positive corona at the same voltage.

12-3-2-4 Deposition of Charged Particles on Surfaces

The charged particles are directed by the electric field along electric lines of force toward the surface but they move air with them. This air is diverted around the object and tends to divert the motion of succeeding particles away.

When particles are fine enough so that their initial momentum is lost and when there is little motion of air around the object the particles will be directed most nearly in accordance with the electric field. Back surfaces of the objects will be coated according to the electric field in the back. The term "wrap-around" is indicative of this type of situation.

However, the electric field does not penetrate effectively into recesses. It concentrates in areas of high convex curvature like outside edges and points. To insure that spray particles are deposited in recesses the spray gun may be helped with auxiliary air flows which cause particles to deposit by impingement. Much of the commercial electrostatic application is therefore a compromise between impingement and electrostatic deposition.

12-3-2-5 Ozone

A negative corona produces about 8 times as much ozone as a positive corona. In both cases the ozone concentration is proportional to the ionizing current. Devices for electrostatic purification of air for ventilation use a positive corona to reduce the ozone level at equal ionization current; Industrially, for electrostatic application of coatings, a negative corona is used in spite of higher ozone concentration.

12-3-2-6 The Effects of Electrical Conductivity in Electrostatic Spraying and Application

As each spray particle arrives at the substrate, the conductivity of the particle allows its charge to leak off to the substrate. If the coating conducts poorly enough its outer surface will retain its charge and act to reduce the electric field intensity that directs additional particles to it. Furthermore large electric field intensities are produced within the applied coating and electrical breakdown can result. (sparks, burning)

The conductivity of organic liquids and solids is usually by ionic mechanisms, and is the product of ionic mobility and concentration. The ionic mobility is a function of viscosity. The concentration of ions is a function of initial charge and spontaneous ionization of carboxyl, hydroxyl, etc.

High conductivity and high dielectric constant yield both increased charge per particle and satisfactory application on the substrate. A resistivity of 10^{10} ohm cm is generally required. However, high conductivity can lead to poor electrostatic spraying (as opposed to deposition) and to leaks of high voltage electricity across insulators and through pipes conducting paint to the spray equipment.

If it is desired to recoat, by an electrostatic mechanism, an article that has been coated, the conductivity of the dry coating must be raised to an acceptable minimum level.

12-4 POWDER COATINGS

The application of organic coatings in the form of powders which are sintered by heating is considered as potentially economical and, of all the current methods of application, least likely to result in air-pollution or water-pollution. The low cost derives from the absence of organic solvents and the relative absence of volatile materials during shipping.

12-4-1 Composition of Powder Coatings

Powder coatings can be made of either thermoplastic or thermoset binders. If thermoplastic, the molecular weight of the binder must be relatively high to provide the needed mechanical strength in the sintered coating and the softening point must be high enough to prevent sintering during shipment of the powder. If thermoset, the powder can be of low molecular weight but the softening point must be high enough to prevent sintering in shipment.

In either case, the components of the binder, including catalysts in the case of thermoset powders and all the pigments needed to provide color must be mixed uniformly in each particle because thorough mixing of different powders to achieve uniformity is difficult.

For subsequent application properties particles of about 20 - 40 microns are desired. This particle diameter is comparable with usual paint film thickness. As a result, films from powders tend to be rougher than those from liquids.

The pertinent shear rates for flow out of powder finishes in the oven are low - say .001 sec^{-1} and there should be low viscosity at that shear rate. In the usual liquid finishes, impurities which may be introduced inadvertantly tend to mix and become equalized through the mass. Impurities introduced into a powder tend to remain where introduced. An impurity which is relatively low in surface tension will result in flow of the polymer away from the area of the impurity and a substantial defect in appearance.

12-4-2 Manufacture of Powdered Coatings

The powders are made by spray-drying of a conventional finish or by extruding a dispersion of pigment in the molten vehicle, cooling, and grinding. Spray-drying does not release all the solvent. Spray drying results in round particles while grinding results in jagged ones which pack differently in the container and on the substrate after application. Since the powders of thermoset materials contain the reactive ingredients, extrusion must be fast to avoid excessive increase in molecular weight.

Flow agents are added to prevent caking of powders - the formation of relatively large clumps which do not flow readily.

In making liquid coatings, adjustments for color, or viscosity properties, or additions of catalysts are often performed as the last step in manufacture. In making powders, adjustments are made in the liquid state and subsequent operations may result in some changes. Thus control of color and reaction rate is more difficult to achieve with powders than with liquids.

12-4-3 Application of Powder Coatings

Powder coatings are applied mainly by a) fluidized bed or b) electrostatic spray or c) electrostatic fluid beds.

In the fluidized bed technique, a mass of powder paint is kept moving by air flowing upwards through it at such a rate that particles are suspended. The substrate, previously heated above the softening point of the powder is immersed in the fluidized powder and is withdrawn, taking with it adhered sintered powder coating. The thickness depends on the mass of hot substrate, its temperature, and its heat conductivity.

12-4-4 Application of Powders by Electrostatic Spray

The powder is sprayed through a strong electric field with corona, and the powder particles are directed to the substrate by the field and by air-currents. The particles adhere to each other and the substrate, which is then heated. Insulating powders deposit to a limiting thickness.

12-4-4-1 Special Problems with Powders Applied by Electrostatic Spray

Various problems are inherent in the spraying of powders. The degree of clumping and sticking to walls of equipment varies with time, temperature history, particle size, and the flow of the powder into the spray guns varies accordingly. Powdered binders generally have high resistivity and the resistivity must be adjusted to below about 10^{10} ohms to obtain high electric charge per particle and to prevent the deposited powder from repelling additional powder unduly. Too low a resistivity results in undesirable leakage on insulating components and to generally undesirable physical properties depending on the mechanism chosen to produce low resistivity.

12-4-5 Electrostatic Fluid Bed

A fluidized bed of powder is subjected to corona. The charged fluidized particles in the form of a cloud are driven to the substrate in an electric field. The substrate is removed from the cloud and heated to coalesce the particles.

12-4-6 Film Formation from the Applied Powder

The applied powder contains a considerable amount of air between the particles. On heating the particles are sintered together and larger air pockets are formed. In sufficient time, and provided that a yield value is negligible, the film would flow out smooth. In practice, there often is an appreciable yield value, particularly in pigmented products. The flow-out to form smooth surfaces is simultaneous with gradually increasing viscosity (and cross-linking) for thermoset powders.

12-5 ELECTROCOATING

12-5-1 Description of an Anodic Electrocoating Process

An aqueous dispersion of a coating in which the polymer particles carry a negative charge is contained in a tank. The counterions (or cations, in this case) are usually ammonium (or substitute ammonium), sodium or potassium. Typically the polymer might be a carboxyl-terminated polymer, which is soluble or strongly hydrophilic in its ionized form, less so in its acid form.

The substrate is a conductor (typically metallic - iron, aluminum, etc. with or without a previous metal treatment). The substrate is attached to the positive terminal and the tank or a separate electrode is attached to the negative terminal of a D.C. source typically of 400 volts.

The current starts high and falls off to essentially zero as relatively non-conductive polymer is deposited on and insulates the substrate. The substrate is withdrawn from the bath after a few seconds carrying with it a viscous film of 0.5 to 2.0 mils thickness and a fluid run-off, most of which drains back into the electrocoat tank. A separate water-rinse washes away the remainder of the fluid electrocoating material. The substrate, carrying the viscous film, is then baked and hardened.

The deposit of the viscous paint is self-limiting. Those areas of the substrate subjected initially to highest current density are coated most rapidly, and as the current density falls in those areas due to insulation by deposited paint it increases automatically in the uncoated areas. A relatively uniform deposit therefore occurs. Complicated shapes, even recessed areas, are easily coated uniformly. The ability to apply the coating in a recessed area is measured by throwing power.

If the deposit of polymer is not coalesced in the electrocoating bath it will not limit the flow of electricity to a low value. The film thickness will continue to grow and the throwing-power will be relatively poor. To insure that coalescence occurs, solvents which plasticize the polymeric vehicle are added in relatively small amount.

The electrocoating system differs from a conventional dipping system in a number of important ways.

1. The viscosity of the conventional dipping system is high enough so that the desired film thickness will be left on the substrate. Because the run-off determines the amount left on the work, the bottoms of the substrate are left with thicker coatings than the tops. Heavy beads of paint are often obtained at those points last drained. Sag marks and other evidence of substantial flow are often obtained on the face of the substrate. The electrodeposited film is much higher in viscosity than a dip coating so that little flow occurs in it. The adhered fluid bath material is low in solids, very fluid and is mainly washed off.

2. A conventional dipping system will usually contain a substantial amount of a high-boiling solvent that is removed in an oven. The solvent may be a pollution hazard. In recessed areas, removal of the solvent is slower, and as temperature increases and the paint becomes more fluid it tends to drain away. Furthermore solvents evaporated from hotter surfaces condense on cooler ones and wash off the coating. Accordingly, recessed areas tend to be coated thin when conventional dipping processes are used.

3. In an anodic electrocoating bath (the most prevalent) the substrate is not inert. Acids formed at the anode dissolve some of the protective oxide conversion coatings and tend to reduce their protective power. In a conventional dip-coating the substrate is mainly inert.

The electrolyte in an electrocoating bath consists of a polymer in the form of charged particles with their associated counterions. Pigments, plasticizers, reactive but unionized polymers, and other additives also carry absorbed charged polymers and are thereby charged similarly.

If the polymer is negatively charged it is usually a carboxylate and the counterions may be positively charged ammonium, substituted ammonium, sodium or potassium.

The current carriers in the electrolyte are not only those charged polymer particles and their counterions but hydrogen and hydroxyl ions necessarily present in water, and other ions which originate from attack of the bath on the substrates being coated and from the residues of cleaning baths preceeding the electrocoating bath.

The mobility of ions (including the charged polymer particles) in an electric field determines the amount of current carried by the ions. The amount carried by the charged paint particles can be relatively small. The charged particles are directed toward the anode where some are deposited. The major fraction deposited comes from coagulation of the electrocoat bath by acids and metallic ions formed at the anode from the more mobile ions during the electrolysis. The acids and metallic ions, which diffuse into the bath from the electrodes, cause the polymer particles to become less repellent to each other, and they therefore contact each other whenever the acidity or metallic ion concentration exceeds a critical amount.

In an electroplating bath, like a copper-plating bath for example, metals are deposited at the cathode, but the deposits of metal atoms occur only in intimate contact with the previously deposited conductive metallic particle. In electrocoating baths the deposit occurs for a substantial distance from the

conducting substrate through the coagulating action. The coagulated particles are carried out of the bath with the substrate. Some uncoagulated material on the surface of the coagulated material is flowed back into the electrocoating tank. Because the coagulation occurs at a critical concentration there will always be a finite volume of bath next to the deposited polymer which contains a finite but less than critical amount of the coagulation-causing ions and these will cause a gradual change of the conductivity of the bath and its performance even if no adventitions foreign material were carried in with the substrate.

Carbon dioxide from the air is gradually absorbed into alkaline baths changing the electrical conductivity and the acidity, thereby also affecting the coating action.

The formation of a continuous film from the particulate deposit is not an instantaneous process. The deposited film must start spongy with an aqueous continuous phase. The individual paint particles must coalesce and flow into each other while water and water-soluble ions are exuded. The aqueous phase eventually becomes discontinuous, some water must be retained temporarily as globules and some must be dissolved in the paint (which will still be chemically partly acid and partly salt).

The potential across the electrodeposited film when the current has reached its minimum value is almost the full potential applied, i.e. 400 volts. The film therefore carries the large potential gradient of about 400,000 volts/in or 150,000 volts/cm, and correspondingly lower gradients while the film is being coalesced. The flow of electric current through the film helps to remove water by electroosmosis.

The electrode potential required to produce chemical reactions at the electrode is of the order of one or two volts and the need for several hundred volts with the accompanying hazards can well be questioned. In some cases reduction of the electrocoat voltage would require a corresponding increase in conductivity of the bath and chiefly by the addition of non-paint ions. Such ionic material trapped in the paint film can be the cause of later osmotic and corrosive failure.

Paints applied by electrodeposition contain defects due to formation of oxygen gas bubbles, dielectric breakdown, etc. A certain amount of flow is needed in such paint to heal these defects. The deposited paint must therefore be viscous enough to prevent flow due to gravity forces when the substrate is removed from the bath, but fluid enough at that time or in subsequent baking to allow the healing of surface defects. This requirement means that the claim for perfect edge coverage is strictly met only during the brief moments of electrodeposition. The very surface tension forces which would cause healing of surface defects cause flow away from edges. Furthermore, the requirement that the electrocoated polymer be fluid means that a hardening mechanism is needed. This can be accomplished by conventional chemical reactions accelerated with heat, by evaporation of solvents contained in the electrodeposited film, by radiation etc.

Phenomena during passage of electric current through an aqueous system:

1. Heat is developed. The amount of heat developed in any part of the bath depends on the product of the resistivity and the square of the current density or alternatively on the ratio of the square of the potential gradient to the resistivity. Some new chemicals will be created by the current flow and some non-homogeneities will develop that use a small fraction of the electrical energy provided by the electric current. In total the electrical energy provided is at a rate proportional to the product of the current and the voltage between the electrodes. With the exception of the small amount of chemical energy produced all the electrical energy results in heat. Electrocoating baths must therefore be cooled.

2. During the passage of current hydrogen will be evolved at the cathode and oxygen at the anode. This is one of electrolysis reactions of an aqueous solution. Furthermore, the region of the anode becomes acidic and the region of the cathode becomes basic. Other reactions that can be of consequence are oxidation of a metallic anode to produce positive ions, and a series of other electrochemical oxidations at the anode and reductions at the cathode depending on the chemical ingredients present. These reactions generally result in a gradual increase in conductivity of the bath.

3. In a typical anodic electrodeposition system the polymer will be an ammonium salt of a polymeric acid and will contain the minimal possible quantity of Cl^-, $SO_4^=$, Na^+, etc. At the anode, assumed here made of Fe the polymer will be precipitated richer in acid and poorer in NH_4^+ and richer in Fe^{++} . The electrolyte near the cathode will become more alkaline and will be richer in NH_3 . It will become richer in metal ions like Na+ and K+ as well.

12-5-2 Cathodic Deposition

Positively charged paint particles are deposited on substrates connected at the cathode as a result of increase in basicity. There is no dissolution of metals at the cathode, no attack on phosphate treatments. Therefore, the coatings tend not to be discolored by the metal ions and the metal treatments tend to remain undamaged.

A typical paint polymer system would be a polymeric amine neutralized with an acid, e.g. phosphoric acid or CO_2 .

12-5-3 Bath Maintenance

The electrocoating tank contains pigments, curing agents, solvents etc., in addition to the dispersed ionic polymer. While most of the electrodeposited material is coagulated and therefore tends to deposit without substantial separation there are mechanisms which operate to cause differentials in the deposit.

The vehicle deposited is different from the average vehicle in the bath in solvent content and in details of chemical composition - acid number for example and in pigment content. Thus the paint components must be replenished to compensate for the amounts removed of each component. The build up of ionic contaminants in a bath must also be controlled.

The control of ionic contaminants (of low molecular weight) can be accomplished by dialysis against pure water and reverse osmosis, by isolating the cathode and flushing it with water, or by the use of ultrafiltration. In ultrafiltration fine-pored membranes allow small ions to pass through while

large ions are retained. The solution to be filtered is pressured at 10 - 100 psi against the membrane. Water and small ions are passed thru and are discarded. Deionized water may then be added to the solution to compensate for the removed water if necessary.

12-6 POWDER DISPERSIONS IN WATER

A variant of powder coatings is a dispersion of a powdered coating in water. In this case pigment and vehicle are mixed as a good dispersion before dispersion in water. The powder deposited from water packs more tightly on the substrate than one deposited from air. In theory, smoother coats should be possible. On the other hand, the handling of aqueous materials poses corrosion and freezing problems.

12-7 REFERENCES FOR FURTHER STUDY

Books

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Industrial Electrostatic Precipitation - H. J. White - Addison-Wesley Reading, Mass. (1963). While not directed to electrostatic paint application the book teaches principles of electrostatic deposition which apply to powders and to spray particles. There is a satisfying description of the phenomena near high-voltage sources (corona, fields etc.).

Gaseous Conductors - Theory and Engineering Applications - J. D. Cobine - Dover Publications (1958). A detailed study of corona, space charge, discharges.

Organic Coating Technology - Vol. II - H. F. Payne - Wiley New York (1961) describes electrostatic application, electrostatic spraying, and detearing as well as other older methods. Electrocoating is not discussed.

Chemical Engineers Handbook - J. H. Perry - McGraw Hill (1950) has a short Chapter on Spraying - pp. 1169 - 1175.

Paint Flow and Pigment Dispersion - T. C. Patton - Interscience (1969) has good technical descriptions of brushing, dipping.

Journal Articles

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Electrocoat, Powder Coat, Radiate - Part II - Powder Coat - J. Paint Technology 44 #570 (1972) describes the various materials, methods, shortcomings and advantages of applying coatings as powders.

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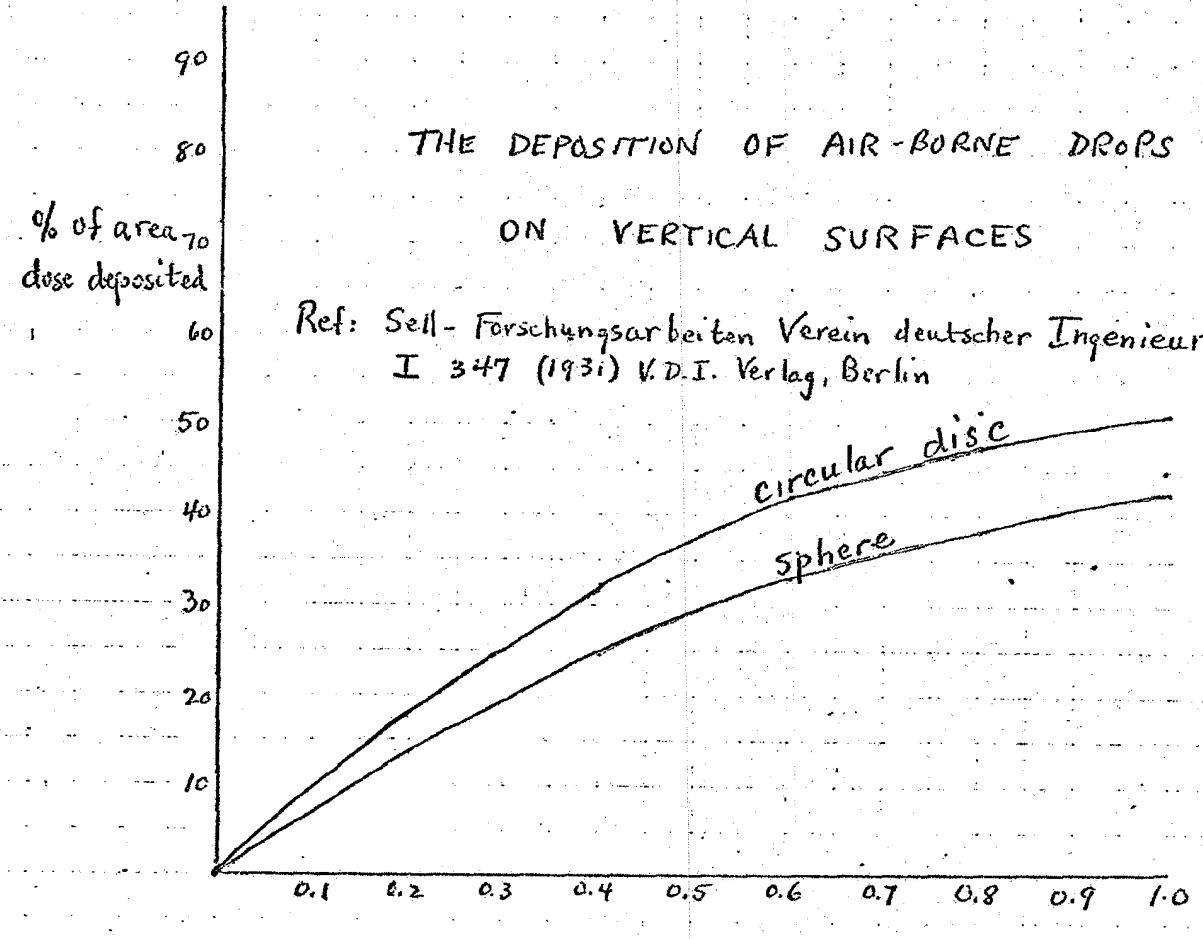

$$P = 317 \frac{\rho u d^2}{\beta}$$

ρ = density
u = wind velocity
d = diameter
β = viscosity of air

FIG 12-1

FORMULATION OF COATINGS

CHAPTER 13

It is often a chemist's job to formulate a coating to meet a set of performance and cost specifications. The specifications may be defined loosely or tightly. The chemist's formulation must be one that then can be applied by the prospective customer at a reasonable cost and will provide him with the values he desires. This chapter will describe what factors a chemist must consider, how he might start, and how he proceeds to formulate a product. In general, he will arrive at a final formulation after some trial unsuccessful formulations and after studying the weaknesses in his formulations.

There are so many decisions to be made, and so little reliable information on the absolute values of properties as a function of formula, that artistry is essential.

13-1 FORMULATE FOR MINIMUM COST TO THE CUSTOMER

1. Cheapest materials - Cost of liquid coating and auxiliary solvents or other additives.

2. Cheapest labor - Minimum requirement of quantity and quality of workers to apply the coating and handle the coated substrate.

3. Lowest capital investment, new or old. The impact of investment on cost depends on bookkeeping methods, tax rates, and interest rates.

4. Lowest hazard to personnel and property. Fire hazard and exposure to poisons are most prominent.

5. Largest tolerance for error - Tolerance for variation in humidity, temperature, contamination of surfaces (mold release agents, grease, for example), inhibitors of drying, foreign spray droplets, oven gases, storage conditions (stability of viscosity, settling, for example).

13-2 CONSIDER NEEDED VALUES OF COATINGS

The chemist should determine what qualities the applied and dried coating is expected to have. Appearance qualities are usually apparent immediately and are therefore of paramount importance.

13-2-1 Decorative Values

1. Color

2. Gloss

3. Filling

4. Special decorative effects - metallics, iridescence, three dimensional effects.

13-2-2 Protective Values

1. Water transport
2. Corrosion inhibition
3. Integrity
4. Adhesion
5. Resistance to damage by chemicals or mechanical stress.

13-2-3 Durability in Service, Ease of Maintenance Values

1. Chalking of exterior finishes
2. Cracking
3. Dirt collection
4. Mildew collection
5. Peeling
6. Blistering
7. Temperatures and temperature cycling
8. Repainting restrictions.

13-2-4 Special Properties Required

13-2-4-1 Electrical conductivity

13-2-4-2 Electrical insulation value - Dielectric strength, dielectric loss

13-2-4-3 Sound deadening

13-2-4-4 Magnetic permeability, coercivity.

13-3 PROPERTIES REQUIRED OF THE COATING MATERIAL IN THE CAN SHOULD BE STUDIED

13-3-1 Storage Stability

1. Settling
2. Freezing
3. Corrosion of containers - particularly water-based finishes
4. Mechanical stability

5. Growth of microorganisms

6. Pigment-floating, color drift

7. Syneresis.

13-3-2 Rheological Properties

1. For removal from containers under probable storage-conditions.

2. For ease of stirring with added solvents, etc., as may be required for application.

13-4 THE PROBABLE SUBSTRATE AND ITS CONDITION SHOULD BE IDENTIFIED

13-4-1 Metals - previously painted, oily? How much distortion in use?

13-4-2 Wood - previously painted? Mildewed?

13-4-3 Plastics - Surface treatment for adhesion allowed? Necessary?
- Mold-release agents present? Distortion in use?

13-5 THE APPLICATION CONDITIONS SHOULD BE SPECIFIED

13-5-1 Open air - temperature, humidity

13-5-2 Factory - temperature, humidity, ventilation

13-5-3 Residential, indoor

13-5-4 Legal restrictions - fire, EPA, OSHA, Union restrictions

13-5-4-1 Industrial uses.

13-5-4-2 Trade Sales uses.

13-6 APPLICATION METHODS ALLOWABLE BY OR AVAILABLE TO THE CUSTOMER SHOULD BE DETERMINED

13-6-1 Industrial Uses:

Spray, dip, roller coating, electrostatic (several types) ovens, baking temperature.

13-6-2 Trade Sales Uses:

Brush, napped rollers.

13-7 DETERMINE THE AVAILABILITY OF MATERIALS AND PROCESSES FOR MANUFACTURE WHICH MIGHT RESTRICT THE CHOICES

13-7-1 What equipment is needed for pigment dispersion?

13-7-2 What equipment is needed for control and testing?

13-7-3 Are the materials needed available at a reasonable cost?

13-8 CONSULT THE LITERATURE

13-8-1 Books on coatings

13-8-2 Suppliers' literature - manufacturers of materials for the coatings industry supply formulas using their products.

13-8-3 Government agencies issue specifications for a product approximating the needed properties. These usually specify ingredients.

13-8-4 Study the available ASTM test methods.

13-8-5 Examine the appropriate journals and read advertisements to obtain late developments.

13-8-6 Talk with experts.

13-9 On the basis of the specification in the literature compare the properties you would expect from the materials with the properties you want in the new coating.

13-10 Make up a composition similar to the specification but making appropriate substitutions on the basis of desired deviations.

13-11 DECISIONS THAT MUST BE MADE

Choice of binder

Choice of pigment or pigments and amounts

Choice of grinding or dispersing methods

Mode of application

Choice of solvents or carriers

Choice of curing or hardening mechanism

Viscosity requirements

Choice of modifying additives.

13-12 MODIFYING ADDITIVES

13-12-1 Driers and activators to adjust the rate and direct the oxidation of drying oils and similar compounds with oxygen.

13-12-2 Antiskinning Agents - These are usually phenols or oximes. They are anti-oxidants and volatile. They complex drier metals. Phenols are reduced in anti-oxidant activity by ortho substitution e.g. as in guaiacol. Phenols are used in baking industrial products but not in trade sales because their low volatility and high activity makes their degree of oxidation inhibition less reliable in variable temperatures of drying. Butyraldoxime, methyl ethyl ketoxime, cyclohexanone oxime form complexes with metals. They often introduce color, and zinc is used to improve color.

13-12-3 Surface Active Agents.

13-12-4 Anti-Foam Agents.

13-12-5 Thickeners - Methyl cellulose, hydroxyethyl cellulose, casein, polyacrylic or polymethacrylic acid - clays help also. The polymers bridge between latex particles and pigment particles with loose bonds.

13-12-6 Anti-settling, Anti-sag Agents - Various proprietary amine-modified clays, hydrogenated castor oil.

13-12-7 Moldewcides - Mercurials, organics, ZnO.

13-12-8 Bactercides - Formaldehyde, proprietary products

13-12-9 Electrical Conductivity is increased by use of quaternary ammonium compounds and polar compounds generally.

13-12-10 U.V. Sensitizers - Usually ketones, benzoin derivatives.

13-12-11 Anti-caking or Flow Agents for Powders - Usually finely divided silica.

13-13 - Test the product and modify the formulation to correct the weaknesses.

14-1 REFERENCES FOR FURTHER STUDY

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Organic Coatings - Properties Selection and Use - A. G. Roberts U.S. Dept. of Commerce, National Bureau of Standards - (1968) Superintendent of Documents, Washington, D.C.

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