Driers

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THE subject of driers relates so closely to the matter covered in previous lectures in this series that there is bound to be a certain amount of overlapping and duplication which will be avoided so far as possible in covering this particular subject. The chemistry of drier action is a subject concerning which surprisingly little is known. This is remarkable in view of the importance of driers to an industry as large as that of the paint, ink, and linoleum trade. Without paint driers the industry couldn't have attained its present-day magnitude, and yet practically no attention has been paid to any fundamental consideration as to how driers actually function.

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It is assumed that everyone appreciates that the term "drying" of paint is a misnomer. Drying of an orthodox paint is not due primarily to evaporation of the solvent to leave a solid film. It is rather a solidification of a liquid film into solid form. That solidification of a liquid oil film is doubtless due to polymerization and condensation, often induced by a preliminary oxidation of the liquid constituents of the film. The complete mechanism of film formation is today imperfectly understood, but a constantly increasing fund of knowledge is becoming available in this field. Other lectures of this course are covering this subject so completely that there is little point to repeating any more of it than has a bearing on what is known of the influence of driers on those actions.

There are two common and convenient ways of considering and discussing the drying of oils and varnishes and alkyds. These two schemes of consideration are rather closely related, and something is known of the influence of driers on the separate stages in each theoretical consideration.

The first and oldest way of looking at the drying of oils is to consider film formation primarily in the light of its relation to oxygen absorption as related to the state of the film. The second and more modern way of considering drying oil formation is to regard it as a branch of high polymer chemistry.

As a preliminary to discussion of either of these ways of looking at the drying oil film, the constitution of drying oils themselves should be considered. The whole paint and varnish industry is built on the use of these drying oils, whether of vegetable or animal or synthetic derivation. As a group, the drying oils are glyceride or other esters of straight chain fatty acids with even numbers of carbon atoms in the fatty acid chains. The drying oils are distinguished by their relatively high content of unsaturated fatty acids. Acids with two, three, and four or more double bonds per molecule are characteristic of the drying oils.

The multiple unsaturation of the fatty acids in drying oils is responsible for their typical capacity to absorb atmospheric oxygen and to form solid films through polymerization and other mechanisms.

The unsaturated fatty acid glycerides, particularly those of the conjugated di-enoic and tri-enoic fatty acids appear to account for the most pronounced drying tendencies of oils. Conjugate unsaturation at alternate carbon atoms favors more rapid oxygen absorption and polymerization as compared to multiple unsaturation at widely separated intervals in the fatty acid chain.

The paint, varnish, ink, and linoleum industries depend upon these characteristics of the drying oils, whether they be used as such or chemically compounded in the form of oleoresinous varnishes or in alkyd resins. Therefore, for purposes of this discussion, we can consider the action of metallic driers as being similar in all paint liquids based on drying oils.

BEFORE going on with the discussion of driers, it probably would be advisable to define the term. In the strictest sense, it may be stated that a drier for paint is any material of any description whatever, which, in a minor proportion, will induce or speed up the setting or drying or solidification of a liquid oil film. This is a broad and general definition of what a paint drier is or should be.

Today paint driers are, for all practical purposes, limited to oil soluble soaps or salts of certain metals with appropriate organic acids. There is reason to hope that eventually there may become available other materials for the purpose, but as of now the paint driers are largely limited to organic compounds of lead, cobalt, manganese, iron, calcium, and zinc.

Now to revert to consideration of the influence of driers on film formation and the two common ways of considering the drying phenomena.

For decades it has been recognized that the course of drying of an oil film proceeded according to a series of steps having a fairly definite relation to the amount of oxygen absorbed from the air or to the gain in weight accompanying this oxygen absorption. The course of these steps is fairly readily traceable with simple equipment, and the experimental evidence to cover this aspect of drying is monumental.

The first phase of drying of an oil is the induction period. When an oil film is applied to an impervious surface and exposed to the air, there will be a period of time when it shows no measurable increase in weight attributable to the absorption of oxygen from the air. This is the induction period. The presence of metallic driers in an oil film will shorten or altogether eliminate this induction period. The shortening of the induction period will be variable with the composition of the oil, the conditions under which the film is dried, and the amount and kind of drier.

The second phase of drying of an oil film is the period of active oxygen absorption. When the induction period terminates, the oil film starts to absorb oxygen and to gain in weight. Gain in weight plotted against time results in a curve characteristic of the particular oil film under specific drying conditions. With no drier present, the gain in weight curve will have a certain slope. With metallic driers present, the slope of the curve will be steeper, indicating a more rapid gain in weight or rate of oxygen absorption.

The third phase of drying as related to oxygen absorption is the solidification of the film. After an oil film has absorbed a certain amount of oxygen, it will start to solidify by first increasing in viscosity and then setting to a gel, finally passing into a solid state. With a given oil, this solidification of the film will normally occur at a fairly fixed figure for oxygen absorption or increase in weight. The inclusion of metallic driers results in film formation or solidification at a lower oxygen absorption figure. Thus an oil film without drier might solidify when it has gained 9% in weight through oxygen absorption, but in the presence of some cobalt drier it can very well solidify at only a 7% gain in weight by oxygen absorption.

The fourth easily recognizable factor relating oxygen absorption to drying of an oil film is the ultimate oxygen absorption value. In the course of a reasonably long time an oil film of given thickness without any drier being present will have absorbed some characteristic quantity of oxygen. The presence of paint drier will cut down the total oxygen absorption by the oil in the same extended period of time.

These foregoing stages of drying as related to oxygen absorption or gain in weight are easily demonstrable, and they have for many years afforded a basis for discussing the action of paint driers. They have made it convenient to consider the paint driers to be primarily promoters of oxidation and to give a fairly glib means of explaining in a practical way why paint driers are used. It appears that this over-simplified way of considering the action of paint driers is no longer adequate and that sooner or later it will be necessary to find a much sounder set of theories to account for the observed activity of our present or future driers.

This is not hopeless, but it must be recognized at this point that knowledge is certainly inadequate and that it will be essential to look more and more to the experience in other fields of high polymer chemistry to help understand what metallic driers actually accomplish. This seems to be the necessary preliminary to any thought of replacing metallic driers with purely organic substances to accomplish the same end.

THE second and currently more acceptable way of considering drying of oils involves a relation between chemical reactions and physical phenomena including condensations and polymerizations. Current concepts and experimental evidence strongly support the view that air drying of oil films is a polymerization mechanism initiated by oxidation. The picture as to this concept is as yet incomplete, but experimental evidence is building up to give us an idea of what happens along these lines.

Paul Powers in a fairly recent paper has pointed out that the drying of an oil film may conveniently be considered as embracing five steps in the oxidation process. These may be outlined as follows:

The first stage is easily recognized as the induction period or that interval of time elapsing before oxygen absorption begins.

Peroxide formation is the second stage or really the first evidence of chemical reaction. There seems to be substantial agreement that oxygen absorbed enters into the oil molecule first and predominantly by formation of peroxides at the double bonds of the fatty acid chains. Opinion as to the exact configuration of these peroxides differs, and there is also a lack of agreement as to where they form. There is little doubt that conjugation of double bonds favors speedier oxygen absorption, and it also appears likely that decomposition or rearrangements of these peroxides shifts double bonds along the fatty acid chain to ultimately increase conjugation. This gives support to the theory that drying is a self-initiated chain reaction.

Peroxide decomposition is the third stage in drying. Agreement is general that peroxides initially formed largely disappear, but there is no certainty as to the predominant reaction involved in this change. The peroxides initially formed theoretically could: a) rupture, breaking the chain, forming lower acids, b) rearrange to form hydroxyl and carbonyl groups, c) be reduced, liberating oxygen, and d) dehydrate with formation of water.

Possibly all these peroxide reactions take place in some measure since low molecular weight acids are formed in small amounts, hydroxyl value does develop, water is commonly liberated in drying, and any evolved oxygen would be immediately reconsumed.

Formation and decomposition of peroxides are not sharply differentiated stages. In a drying oil film the two probably occur simultaneously, peroxides forming at some double bonds while others, already existing, decompose. The two stages are simply those where the one reaction is plainly dominant over the other.

Polymerization is the fourth stage in the drying of the oil film. This action is not the only one taking place, but it is the dominant one, with peroxide formation and decomposition still taking place at reduced rates. This is the period when actual solidification takes place, and it is at this point that film formation enters into the field of colloid and high polymer chemistry.

Plausible theories are those which propose cross-linkage and three-dimensional growth through direct carbon to carbon linkage, condensation reactions between peroxide groups or their successors, and association or free valence bonding between molecules.

Degradation is the fifth step in the life of an oil film. It has been pointed out that this phase in the life of an oil film has been explained simply as continued oxidative decomposition, subsequently in colloid terms, and currently in the light of terminal group effects and bridge linkage characteristics. Oxidation certainly plays a role in deterioration either when the damage becomes visible or as a determining factor even while the film is only in the formative stage.

The preceding paragraphs have briefly outlined two ways of considering the drying of an oil film, one with simple relation to gain in weight through oxygen absorption, the other through a little more involved theoretical considerations. There is a definite influence by metallic driers on the course of the oxygen absorption phenomena, and the metallic driers also presumably influence the stages outlined in the more modern concepts. There is at this point no absolute knowledge as to how paint driers function in the drying of oils. Anything mentioned in this connection is almost purely speculation because so little work has been done with the theoretical aspects of metallic driers.

The oldest and most convenient way of surmising drier activity is to assume that the metallic compounds function in a purely catalytic manner to promote oxygen absorption by the oil without the drier itself entering into the reaction or being affected in any manner. This again appears to be over-simplification and not supportable by experiment.

There has been speculation that the drier metals may actually enter into chemical combination with the oil molecules at double bonds. This is a possibility as yet unproven. Just how such metallic complexes would enter into oxidation mechanisms or cross-linkage polymerization has not been properly explained. Metallic complexes at double bonds may introduce highly polar groups, encouraging association growth as the oil polymerizes.

Any such expediting of polymerization by metallic complex formation would have to be remarkably potent if, as Dr. Long points out, ½% of lead metal based on linseed oil amounts to only one atom of lead to 50 molecules of oil or perhaps one atom of lead to 300 double bonds. Such figures make evident this activity of metallic driers as truly remarkable, and it is regrettable that enough is not known about the way they perform their job to present any coherent picture of their true activity.

It is abundantly proven experimentally that the presence of metallic paint driers does speed up oxygen absorption to accelerate the rate of peroxide formation and all the other stages in film formation. In contrast to this established experimental set of facts is the interesting observation that most of the common metallic paint driers are powerful reducing agents extremely destructive to peroxides. To reconcile this increase of peroxide formation with the destructivity of the driers on peroxides seems an interesting project. The balance of this lecture will be devoted to what may be considered a strictly practical discussion of paint driers as they are known today. To that end the following should be pertinent.

As mentioned before, paint driers currently are almost exclusively metallic salts or soaps. This class of compounds is about the only one which exhibits the solubility characteristics required to accomplish the desired end. Linoleates, the metallic salts of the fatty acids present in linseed oil, are a well known group. For many years they were the only driers known. Resinates, or the metal soaps of rosin fatty acids, are still widely used, and probably some of you make them yourselves in cooking litharge and manganese dioxide or cobalt acetate into mixtures of rosin and oil in a varnish kettle. Metallic naphthenates are almost universally used today because of their superior solubility and advantageous price and their storage stability. Finally, there are the metallic soaps or salts of such synthetic acids as octoic acid. It is quite probable that, as time passes, other synthetic acids may be used as a basis for driers.

IT IS probably worthwhile to spend a few minutes discussing the virtues or the defects of some of these various classes of metal soaps as regards their utility as paint driers. Years ago every varnish plant made its own driers in varnish kettles by cooking into oils and resin mixtures such metallic compounds as litharge, manganese dioxide, cobalt acetate, zinc oxide, and lime. The result was the formation of metallic soaps or complex compounds joining the metal elements with the fatty acids and resin acids to make oil soluble soaps. Essentially, the same sort of metallic compounds are formed in the deliberate manufacture of metallic soaps of linseed oil fatty acids or in making resinate driers. Both retain the fatty acid component of the oil or the abietic acid of the rosin as a major portion of the drier soap molecule.

These fatty acids and rosin acids are the building blocks of the paint industry because their chemical nature permits them to become oxidized and so to polymerize to form insoluble solid films. Very much the same characteristics are inherited by metallic soaps made from those fatty acids. The organic acid radical in the metallic soap retains its high degree of unsaturation and is still capable of oxygen absorption at the double bonds. The soaps do take up oxygen from the air and when they do, the same thing happens to those soaps as does to a paint film itself. As the soaps oxidize, they become increasingly insoluble in solvents and oils. For that reason, the linoleates and resinates and tallates tend toward instability and to precipitate out and to become less compatible with oils and varnishes. Thus it was that years ago it was necessary to store driers and varnishes containing them for extended periods of time to let all the sludge and precipitate settle out. What varnish makers used to do was to cook in an unknown amount of metal and then let the mess stand in tanks till a major proportion of it precipitated out. Then they ended up with a composition of unknown value.

That was a very uneconomic procedure and productive of all sorts of inconvenience so it was natural to attempt to develop compounds better suited to the purpose to mitigate these inherent drawbacks of the linoleates and resinates. About 1926 the Germans first commercially marketed as paint driers the metallic naphthenates. The naphthenic acid used in these early naphthenate driers was derived from Roumanian crude petroleum, and the United States imported these driers for a time. It soon became apparent that these naphthenate driers were so advantageous technically and would be used in such quantities that importing could not be continued. Manufacture was started in this country, and today the United States leads the world so far as production of paint driers is concerned.

To digress for a moment naphthenic acids as such might be discussed. They are, it is believed, oxidation products of the hydrocarbons present in naphthenic base crude petroleum oils. Structurally, naphthenic acids are 5-carbon ring structures with one to three side chains on the ring with only one acid group at the end of one of the chains. The number of carbon atoms in the side chains governs the molecular weight of the naphthenic acids.

Naphthenic acids of commerce are never pure compounds but are always mixtures of naphthenic acids of varying structure and molecular weight. Naphthenic acids are sold on a basis of acid number, and the combining weight is calculated from the average acid number value.

Naphthenic acids occur in petroleum in very small amounts, in the order of one-tenth per cent. The recovery of naphthenic acids from crude oil or from certain distillate fractions is a nice example of gathering a very valuable minor ingredient for a better purpose than burning in a furnace.

THE manufacture of paint driers is a subject concerning which one could talk at length, but this discussion will be limited to the following. There are three primary methods of manufacturing the metallic soaps which are used as paint driers.

First would be the home cooked or the kettle cooked driers, which have been touched on briefly before. The essence of the process is to put into a varnish kettle either linseed or other oils with or without rosin or other acid resins. This represents a mixture of fats or glyceride esters of fatty acids, with a certain amount of free acids in the form of rosin or free acid in the oil. The oil, etc., is heated to a temperature high enough to react with metallic oxides or metallic acetates so that a certain amount of double decomposition takes place to form metallic soaps or other complex oil soluble metallic compounds.

The second principal method of manufacture of paint driers is that which is customarily designated as the fusion method. That term is almost self-explanatory in that it is the simple reaction of free organic acids, not the glycerides, with metallic oxides or metallic salts. The reaction is simply neutralization of an organic acid by a metallic base, or displacement of acetic acid by a less volatile organic acid such as rosin or naphthenic acid. The fusion or neutralization may be made with simple equivalent quantities of metallic oxide and organic acid to produce solid soaps, or the fusion may be carried out in the presence of additional oil or solvent to produce liquid driers.

The third major method of manufacture of metallic soaps is that which is designated as the precipitation method. It is simply double decomposition of equivalent quantities of water-soluble metallic salt with water-soluble sodium soaps of the organic acids. The heavy metal soaps are insoluble in water, and they precipitate and so can be washed and dried and fused and dissolved in solvent to make liquid driers. A specific example would be mixing together equivalent amounts of sodium naphthenate with cobalt sulphate solution, both in water, to precipitate cobalt naphthenate which may be washed free of sodium sulphate and fused to dehydrate it and then dissolved in mineral spirits to form a useful liquid paint drier.

The three methods of making paint driers as outlined above sound very simple, and so they are in theory. Of course, there are a great many trade secrets involved in the successful operations of these seemingly simple processes. There have been many real problems however to overcome in order to provide the quality paint driers that are taken today as a matter of course. The quality of paint driers today is something that the majority cannot appreciate because they have never seen what the paint industry was up against as little as 20 years ago.

With this foregoing description of the preparation of driers, it is probably advisable next to consider the characteristics of individual metals and metallic compounds used as paint driers. There is a very significant difference in the performance of various metallic soaps, and a few conclusions can be drawn:

IF SOAPS of any one metal are considered there will be a considerable difference in the characteristics of soaps of various structures. Drying power for paints does not vary tremendously, but the composition of the organic component of the soaps does alter other significant characteristics. They will differ in degree of solubility in oils and solvents. They will vary in their compatibility with oils so that a whole series of homologous lead soaps will exhibit remarkable differences in that regard. The stability of soaps as regards precipitation and clouding depends largely on the acid radical of the soap. Wetting characteristics also are a great variable depending upon soap composition. For purposes of further discussion of the various metals, all these variations attributable to the acid base of the soap are disregarded and the discussion confined just to general effectiveness of the various metals as driers.

Lead driers are first in tonnage consumption by the paint trade. There is more lead drier used than all the other metals put together. This is due to a combination of several factors. Lead driers are ineffective in small amounts and practically always are incorporated to the extent of from one-tenth per cent to 2% lead metal on the vehicle solids. In the second place, lead is relatively inexpensive and so can be afforded in the large quantities necessary. Lead driers generally all have the property or characteristic of promoting what is currently designated as "through drying." Lead soaps in paint are primarily promoters of polymerization without much effect on oxygen absorption. Lead to cause polymerization is always used with an active oxygen-absorbing catalyst, such as cobalt or manganese. The oxidation catalysts promote that function, and then the lead appears to speed polymerization of the partially oxidized oil to gel or solidify the film throughout its depth rather than only on the surface when cobalt alone is used. Lead soaps as a group do not detract water resistance of paint films. Lead soaps are usually relatively tough and plastic in consistency in their own right and so do not detract from film distensibility or flexibility and elongation. This means that lead driers are not detrimental to durability. Lead soaps in general are good pigment wetting agents, especially the lead naphthenates. On the debit side, it must be admitted that lead driers generally are likely to cause more trouble with clouding and precipitation with oil vehicles than any of the other drier soaps. Lead naphthenate presents the minimum of trouble on this score, and today relatively little difficulty is encountered in this way.

Cobalt driers are next to lead in tonnage in the paint industry and probably are the most essential of the whole group. While cobalt soaps are expensive, they are effective in such small amounts that their use involves no economic hardship. As an oxidation catalyst in straight linseed oil, cobalt is perhaps 40 times as effective as an equal amount of lead metal. Cobalt is a powerful oxidation catalyst which will act not only on drying oils but even lubricating oils and paraffin wax or most any other hydrocarbon or fatty material. That is why it is so widely used in the paint industry. The cobalt driers induce oxidation of oils, and oxidation in turn induces polymerization to form solid films. Amounts of cobalt in excess of that required for desired drying speed are not recommended. Cobalt excess is considered to be detrimental to film durability because it keeps right on oxidizing the dried film to cause its ultimate degradation.

Manganese is the third principal drier in use throughout the paint industry. It is limited in its utility by the relatively dark color of its coaps. Manganese driers, regardless of initial color, usually end up imparting a characteristic pinking or browning of white paints into which they are incorporated. This limits the use of manganese where otherwise its characteristics might be very desirable. Cobalt remains essential for use in best white paints because of its lack of discoloring tendency. Manganese is in a sense intermediate between lead and cobalt so far as activity is concerned. It is a powerful oxidation catalyst and at the same time definitely induces polymerization. Manganese generally induces formation of harder and more brittle films than does a combination of lead and cobalt. This is advantageous, for instance, in floor varnishes and detrimental in such finishes as those of oil cloth and such flexible finishes.

Iron driers have been rather neglected by the paint industry for the past two decades. This is probably the fault of drier manufacturers themselves because old time varnish-makers used to use a lot of iron driers made by cooking ochres and umbers and Prussian blue into oils and resins to form Japan varnishes. Iron driers were responsible for the beautiful lustre and toughness of patent leather finishes and the black baking Japans which used to be used on bicycles and industrial hardware. Iron driers are dark in color, but they are phenomenal in their ability to polymerize oils, especially at elevated temperature. Polymerized oils are generally rated as being superior in regard to flexibility and durability so that iron driers in dark finishes are staging a comeback. Iron naphthenate affords a means of putting iron drier in alkyd resin finishes where otherwise it would be practically impossible. Barn paints and aluminum paints benefit from the presence of iron, and commercial literature is available to cover those specific uses.

Calcium driers are so designated with mental reservations on my part. Calcium soaps in the form of limed rosin or gloss oil and in the form of limed oils have been used for a long time as a means of increasing rosin's melting point and to increase oil viscosity. Calcium naphthenate has recently been found to be exceptionally useful wholly or partially to replace lead driers, both for the purpose of preventing precipitation of lead and to formulate lead free non-toxic paint systems. Calcium naphthenate properly made will appear to act as a drier for linseed oil without any other metal being present. This apparent drying very possibly is a gel formation due to the presence of the soap forming a rigid gel in the oxidizing oil. Calcium is widely used together with lead and with cobalt, and it certainly bolsters their action, but there is some evidence that this is due to synergistic action between calcium and cobalt to form a more active complex of the cobalt.

Zinc driers likewise are so called by courtesy. Actually, zinc has little or no drying power, but zinc soaps of one sort or another are exceedingly useful in paint making. Zinc naphthenate is widely used in large quantities in the paint trade as a pigment wetting and dispersing agent. It is probably the most universally useful agent of the sort available. Zinc napthenate is also widely used to reduce the wrinkling tendency of large amounts of cobalt drier, and that use was the first for zinc naphthenate in the trade. The presence of zinc soaps delays gel formation so that it usually slightly slows up film setting time. Oxidation continues during that continued liquid state of the film so that eventually with zinc present a harder film results. Zinc resinates are also widely used as hard resins and as pigment wetting agents.

The other metallic soaps are of only minor utility for very special purposes so far as the paint trade is concerned. Vanadium soaps are powerful driers, but they are extremely expensive and dark in color and difficult to prepare. Chromium naphthenate is used as a catalyst in certain oil processing operations, as is nickel naphthenate. Mercury naphthenate and more complex compounds are used as fungicides and mildew-proofing agents. Copper naphthenate enjoys a relatively large market in the order of thousands of tons as a wood preservative and rot-proofing agent for all sorts of cellulosic products. Thorium naphthenate, currently unavailable, is a good polymerization catalyst for oils but inferior to lead and more expensive. Lithium soaps are good alcoholysis catalysts with penta and oils.

IN CONCLUSION, the question is often raised as to the relative drying efficiency or effectiveness of different drier metals. No positive rating can be assigned because the relative action of given quantities of different metals is a variable depending upon the kind of oil, varnish, or alkyd, upon the manner in which the metals are incorporated, and upon the physical circumstances prevailing during the drying of the test films.

The best generalization is the old and long accepted ranking in raw linseed oil, dried at normal room temperatures. In such cases, the average ratio of activity of a given weight of metal is something like 40:8:1 for cobalt, manganese and lead. In other words, one weight of cobalt metal can be expected to dry about as well as eight weights of manganese or forty weights of lead.

The above figures are deceptive so far as practical usage is concerned because they refer to tests of single metals only, and in linseed oil as the vehicle. In practice, in varnishes and in alkyds, there is nowhere near this difference between cobalt and manganese, which even approach equality in drying effectiveness, especially in cases where mixed driers are used.

From this it is rather obvious that actual use of driers is not exactly susceptible to fixed rules, but is still largely a matter of experimentation and empirical formulation.