These results indicate that, although the taste of the extracted yeast immediately after extraction is preferable to the unextracted yeast, upon storage some change occurs in the extracted yeast which makes it undesirable from a taste standpoint.

Taste tests on the yeast from the vertical extractor runs indicated that even immediately after extraction the taste of the extracted yeast was unsatisfactory. This can be explained by: a) only about one-half of the fat was removed from the yeast, and b) the yeast was toasted in the drying process.

Conclusions

The pilot studies performed on the extraction of fat from yeast indicate that it is possible commercially to extract yeast to .05% residual fat or less, using finely pulverized yeast in a continuous countercurrent horizontal extractor and Skellysolve B for the solvent.

The yeast obtained by this extraction is lighter in color and, when fresh, has a blander taste than similar unextracted yeast, provided that it is dried under carefully controlled conditions so that all the solvent is removed and yet the yeast is not toasted. However after several months' aging, the extracted yeast does not compare favorably with fresh unextracted yeast on a taste basis.

The fat extracted has a a high phosphatide and high unsaponifiable fraction and will vary considerably in composition, depending on species of yeast, environment during growth, and method of extraction. Because of its composition it cannot be conveniently refined and therefore would not compete favorably with vegetable oils for bulk industrial use.

Acknowledgments

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Advances in Protective Coating Chemistry: Fatty Acids, Polymerization, End Products[1]

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ONE cannot discuss advances in protective coating chemistry without pointing out that the technology involved is very old. In ancient times men were already aware of the desirability of protecting wood or metal surfaces with a film of some sort of material that would resist scratching and abrasion. Some of these ancient coatings are still extant today, and the scientific investigation of these allows the imagination to call forth a picture of an ancient Egyptian who has come upon some soft, naturally occurring resins. Today these might be called amber, sandarac, or mastic. He also had available to him certain oils which probably were not too remote from linseed oil. The Egyptian heated the resin and the oil together so that there resulted a sort of varnish which he could apply, while it was still warm, with his finger or with a knife. Today in various museums there are mummy cases coated with the varnish prepared by that ancient Egyptian four to five thousand years ago. And the Egyptian paint technologist would have ample reason to be very proud of his work for the varnish is frequently still bright and its surface undamaged and unmarred.

Considerably more is known about the composition of the protective coatings of the Middle Ages. Although many of these very early formulations were shrouded in secrecy, some have been preserved. And it is perhaps with some amusement that we note one technologist of some centuries previous who recommended that a certain type of varnish be cooked by allowing the oil to burn at the mouth of the kettle for a period of time sufficient for the recitation of three Pater Nosters.

These facets of protective coating history are offered here only to show that the protection and decoration of surfaces has been the concern of man since the dawn of civilization. In this paper will be discussed protective coatings which dry by polymerization; that is, coatings which, when spread out on a surface, polymerize—under the influence of air, light, heat, or chemicals—to yield solid, resistant, continuous films. Such coatings are based largely on compounds formed from unsaturated fatty acids which, as we shall see, provide the functionality necessary for polymerization and subsequent film formation. The second large class of coatings, which are not to be discussed here, are those based on cellulose and other polymers. These are already sufficiently highly polymerized so that they provide films as soon as they are applied to a surface.

As already indicated, fatty acids are the basic building blocks of polymerizable protective coatings.

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Accordingly it is necessary to gain some insight, first of all, into the chemistry of the fatty acids themselves. Secondly it is important to see how these fatty acids undergo the process of polymerization. Finally it is of interest to inspect the protective coatings which are based on the chemistry of fatty acids and on their ability to polymerize. These three objectives, then, form the basis for this review. The discussion is intended to be exemplary rather than all-inclusive.

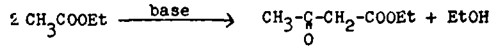
Fatty Acid Chemistry

The chemistry of fatty acids (15, 16) goes back to Chevreul, the famous French fat chemist who lived to be 103 years old and who, in 1815, discovered that fats and oils are fatty acid esters of glycerol. Fatty acid chemistry subsequently was not remote from every-day living for the soap our ancestors made as one of their routine chores was the sodium salt of fatty acids, and the candles which provided their one source of illumination were stearic acid candles.

Although fatty acid investigation began in the early days of chemistry, it has not through the years attracted many workers. Like their close relatives, the sterols, fats and fatty acids are difficult to obtain pure. They have an affinity for one another which makes mixtures difficult to separate without elaborate techniques which are only now becoming available to the chemist and technologist. To be sure, a fairly voluminous literature has accumulated. But, in perusing this literature, one is impressed not only with the lack of organization in fatty acid research but also with the fact that much of the work must be discounted since it has been done on impure or inadequately characterized materials. Thus early workers in the field were hampered in the first place by the lack of pure starting materials which were for them museum pieces. In the second place they often did not grasp the fact that a higher fatty acid differed from a lower one, such as acetic acid, only in degree and not in kind. It was very difficult to introduce into the literature the concept that the bland, wax-like stearic acid which could be formulated into soap and candles is a full-fledged chemical brother of the corrosive liquid acetic acid and that these should be able to undergo the same chemical reactions. And the analogy assumes still greater importance in the field of unsaturated acids for it has been shown conclusively that the two double bonds in linoleic acid are very much like the double bonds in any simpler analog such as 1,4-hexadiene. Thus the two compounds undergo polymerization practically in the same way; the products differ physically only because one molecule is more complex than the other. This will be discussed in greater detail later.

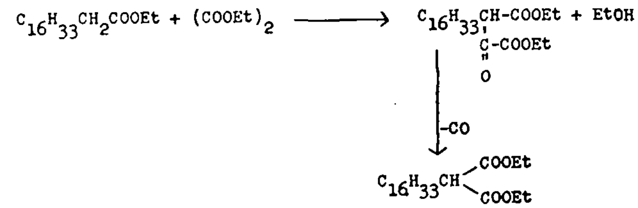
Accordingly the modern worker in the field of fatty acids is equipped with two important tools. The first of these is the availability of pure starting material, and the second is the knowledge that research in this field, as in most fields, is best accomplished by realizing that one must go always from the simple to the complex. That is, that there exists a real analogy between the higher fatty acids, whose chemistry is somewhat obscure, and the lower fatty acids whose chemistry has been elaborately detailed. Thus it may be said almost categorically that any reaction which can be applied to a lower fatty acid may be applied to a higher one if the conditions are discovered which the more complex physical state of the higher fatty acid demands.

An excellent example of the use of this principle of analogy may be derived from the application of the Claisen reaction to higher fatty acids. One of the commonest condensations which acetic acid (in the form of its ester) undergoes is the Claisen reaction to yield ethyl acetoacetate.



$$2\ CH_3COOEt \xrightarrow{\text{base}} CH_3\text{-}\underset{\displaystyle O}{\overset{\|}{C}}\text{-}CH_2\text{-}COOEt + EtOH$$

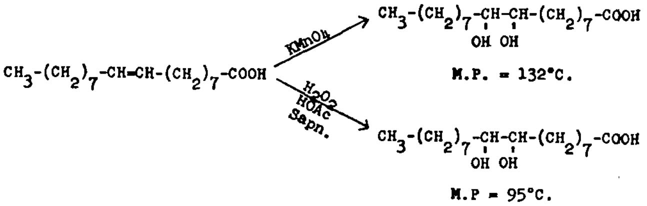
Analogously Floyd and Miller (10) found it possible to carry out a mixed Claisen condensation between higher fatty acids and ethyl oxalate to obtain a 90% or higher yield of the oxalo esters.



This was accomplished by recognizing first of all that an analogous reaction should take place, and second by recognizing that the proper conditions must be found in order to make the complex molecule behave like the simpler one.

The product, incidentally, once it has been decarbonylated, is a dibasic acid with a substituting group which may be derived from a mixture of the unsaturated acids found in oils such as soybean or linseed. It is immediately obvious that such a material may have very interesting ramifications in the formulation of protective coatings.

The double bonds of higher fatty acids differ from the double bond of ethylene only so far as the large substituting groups might affect their reactivity, again a difference of degree and not of kind. As an interesting example of this similarity may be cited the reaction in which two hydroxyl groups are added to the double bond of oleic acid to yield 9,10-dihydroxystearic acid. It is possible to obtain two forms of the glycol acid, and the form actually isolated depends on the hydroxylating agent used.



One of these hydroxylating agents is a normal one, that is, it inserts hydroxyl groups on the same side of the double bond or at the points previously united in the double bond. The other hydroxylating agent is an abnormal one, which is to say, it inserts hydroxyl groups on the opposite sides of the double bond. Some years ago Atherton and Hilditch (4) arrived at the conclusion that permanganate hydroxylates oleic acid (*cis* double bond) abnormally, inserting hydroxyl groups on the opposite sides of the double bond. This would not be expected if one reasons from analogy, for it is well-known (11) that with the much simpler maleic acid, which like oleic acid possesses a *cis* double bond, permanganate inserts hydroxyl groups on the same side of the double bond. Subsequent investigation (5, 20, 21) has shown that permanganate and osmium tetroxide actually hydroxylate oleic acid normally whereas peracetic acid and silver iodobenzoate hydroxylate it abnormally.

It is of interest, again bearing analogy in mind, to determine what happens mechanistically when the double bond of oleic acid is hydroxylated. In the first instance (Fig. I, Step I), the hydroxyls are inserted on the same side to yield a compound in which R groups are also on the same side. But the R groups repel each other with a great force, and thus one-half of the molecule swings around (Fig. I, Step II) so that the R groups are as far apart as possible. Concurrently the hydroxyl groups are placed in positions where they are no longer proximal even though they were inserted on the same side. When abnormal hydroxylation takes place, the hydroxyls enter on opposite sides (Fig. I, Step Ia). But the repulsive effect of the R groups still is dominant, causing one-half of the molecule to swing around (Fig. I, Step IIa). The R groups have again reached their preferred position and in so doing have forced the hydroxyls into a proximal position. The point must be stressed that the free rotation ordinarily associated with a single bond has here been reduced, because of the repulsive effects of the R groups, to a sort of oscillation within a very restricted area.

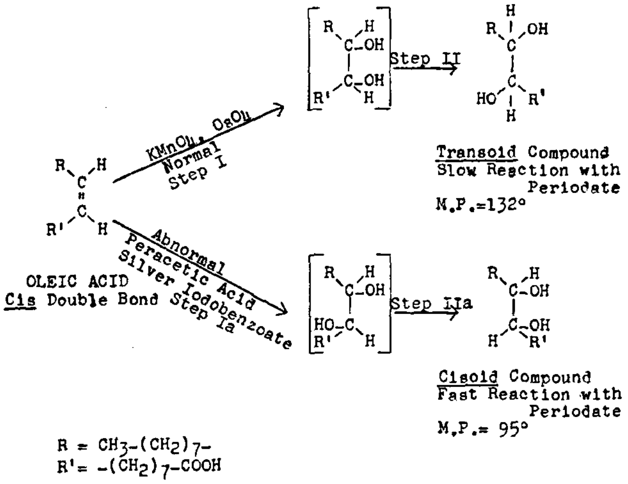


FIG. I

This was proved chemically by oxidation experiments with periodic acid (21), which actually showed that the hydroxyl groups in the low-melting form of 9,10-dihydroxystearic acid are closer together than those in the high-melting form.

It may be seen that the repulsive effect of the R groups is dominant over the repulsive effect of the hydroxyl groups. This is the case not only where the R groups are large as they are in oleic acid but also where the R groups are methyls, as in the 2,3-butylene glycols. For with the 2,3-butylene glycols it may be shown that hydroxyl groups are more distant in space in the *meso* form which results from the normal hydroxylation of the *cis* butylene (14). And this is once again evidence that the chemistry of the higher fatty acids is analogous to that of their much shorter chain analogs.

Dihydroxystearic acid, incidentally, also may have ramifications in the field of protective coatings. For if it were dehydrated twice over, there would result a compound with two double bonds. What is more, these double bonds would be conjugated, a highly desirable situation for rapid polymerization as will be seen later.

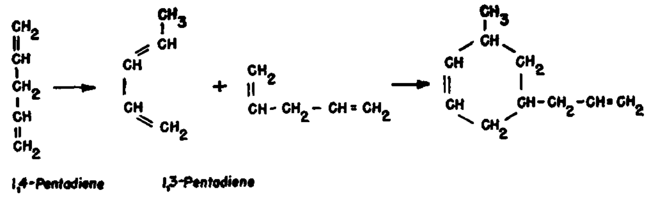
These examples of fatty acid chemistry have been singled out from the hundreds which are available, simply because they illustrate well the guiding principle of analogy between the chemistry of the lower and the higher fatty acids.

Polymerization

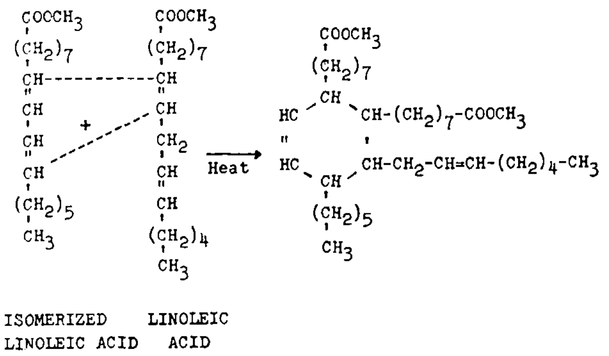
A discussion of the chemistry of unsaturated fatty acids leads directly to a consideration of polymerization phenomenon, the basic reaction which gives rise to protective coatings. Polymerization has been likened to the process whereby laths, which ordinarily may be dumped freely from a truck, are combined in a disorderly crisscross fashion by the random insertion of nails. The resulting network may be considered the polymerized oil film, and the nails may be considered the polymerizing agents such as heat or oxygen.

One of the earliest bits of technology which the oil chemist learned in order to improve his product was bodying, that is, heating oil at high temperatures for long periods of time to make it viscous. Thus the polymerization process was given a good start before the oil was applied as a protective coating. The ultimate result of heating was, of course, conversion to the gel or solid state. But if one should stop short of this stage, a highly viscous oil of excellent drying properties resulted.

Eventually the chemist asked himself what might be in this viscous material that was not in the original drying oil. In 1940 Ahmad and Farmer (2) provided a clue to the answer. They showed that the heat polymerization of 1,4-pentadiene yielded a dimer of a structure which would result from the Diels-Alder condensation of the conjugated 1,3-pentadiene with the unconjugated 1,4-diene. In other words, heat had caused one molecule of the di-unsaturate to seek its more stable or conjugated form, and this had condensed with the unchanged material to yield a dimer.



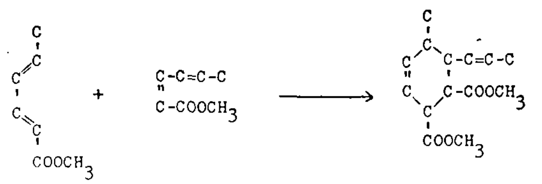
This relatively simple situation offered a clue to the more complex ones of fatty acid and drying oil polymerization. Thus in 1941, a year later, Bradley and Johnstone (6) actually isolated by fractional molecular distillation a pure dimer from methyl linoleate. Linoleic acid, it will be recalled, is a non-conjugated, di-unsaturated C_{18} acid and thus, except for its size and lack of symmetry, is analogous to the simpler 1,4-pentadiene.



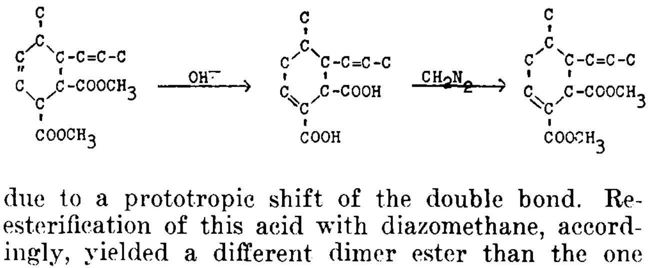
The dimer it yields is similar to the one from 1,4-pentadiene save that it has more "tails" due to the greater complexity of the starting material. This so-called pure dimer of Bradley's was pure only in that it was free from monomer and higher polymers for one is impressed immediately with the fact that a myriad of things can result.

The 9,12-linoleic acid can isomerize either to 9,11- or to 10,12-conjugated structures. Each of these in turn can condense by a Diels-Alder mechanism either with the 9 or the 12 double bond of the unconjugated structure or with either of the 9,11 or 10,12 double bonds of the conjugated structures. Furthermore each of these condensations can occur in two different ways because of the lack of symmetry of the fatty acids.

The resolution of the dimer fraction in the face of this complexity becomes a very difficult task. Wheeler (17), working with the simpler sorbic acid ester, has actually been able to isolate a pure dimer and prove its structure. Sorbic acid provides fewer possibilities for isomeric dimers than linoleic acid because it is already conjugated. But because of its unsymmetrical structure it is one step closer to the true situation for linoleic acid than is the above mentioned 1,4-pentadiene. Thus the following type of dimerization was shown to take place, and the dimer was actually isolated in crystalline form.



An interesting sidelight on this work which is indicative of a few of the difficulties encountered is demonstrated by the fact that saponification of the dimer yielded an acid with a conjugated structure due to a prototropic shift of the double bond. Reesterification of this acid with diazomethane, accordingly, yielded a different dimer ester than the one originally obtained due, of course, to the presence of the conjugated double bond structure.



One can readily see that this dimerization reaction, carried out with glycerides, leads to the formation of very high molecular weight polymeric materials. Obviously the reaction does not stop at dimerization for the dimer structures themselves contain unsaturated bonds which may act as dienophiles in further Diels-Alder reactions. The net result, then, is the formation of insoluble, infusible, cross-linked polymers which are the films that form the basis of protective coatings.

As indicated above, the oil chemist employed this type of polymerization to improve his oils long before he had the vaguest notion of what sort of chemistry was involved. But once he learned something about the chemistry of polymerization, he was immediately prepared to forge ahead and prepare new, useful, and practical materials. Thus it became immediately obvious that soybean and other vegetable oils which contain a large percentage of linoleic acid could be bodied to provide a good yield of linoleic acid dimer. Here was a dibasic acid, which, despite its high molecular weight, ought to be able to undergo all of the reactions which a dibasic acid, such for example as adipic acid, undergoes. And that indeed proved to be the case.

When ethylene diamine was reacted with this new dibasic acid a hard, brittle polyamide resin was obtained (3). Such a polyamide is now being produced commercially in both solid and suspensoid form. It provides a non-edible outlet for vegetable oil produced by the farmer and is a direct result of the so-called useless or academic research engaged in by chemists who wanted to find out what happened when their drying oils became viscous on heating.

So far only one procedure has been discussed for polymerizing drying oils, namely, by the use of heat. Drying oils also polymerize in the presence of air and oxygen. And, here again, the oil technologist was making use of this procedure to improve his drying oils long before etymologists had invented the word polymerization. The technologist merely bubbled air through his oil at moderate temperatures. And he found, after doing this for a certain length of time, that his product yielded tough films much more rapidly. Actually, of course, he was again merely starting the polymerization procedure prior to the application of an oil to a surface.

The theory regarding the type of polymerization which takes place here is at present highly obscure. The present state of knowledge has been ably reviewed by Wheeler (18).

Again, the experiments cited here are not intended to be all-inclusive but are merely exemplary of the large amount of excellent work now underway which will ultimately lead to a complete definition of the phenomenon of polymerization.

Protective Coatings

In the early days of protective coating technology vehicles and formulations were discovered largely by hit or miss procedures. Modern protective coatings, on the other hand, are more and more a result of the application of fundamental chemistry of the type described in the two preceding sections. This last section will concern itself with the compositions of the protective coatings which form the basis for a vast and ever-expanding industry.

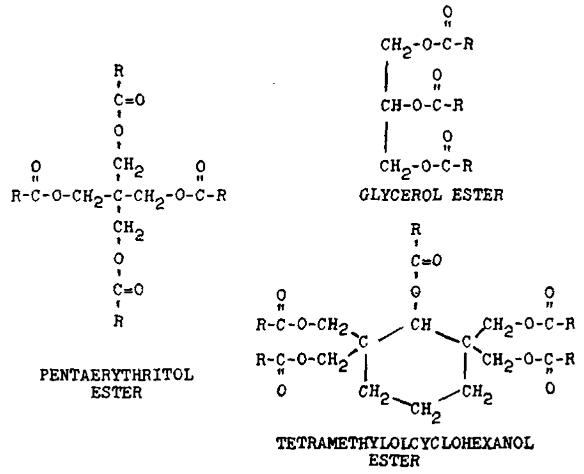
Paint as we know it is a mixture of drying oil, pigment, and drier. The pigment provides the color, and the drier, which consists of salts of lead, cobalt, manganese, or other materials, accelerates the polymerization process. The driers are the hammers which hit the nails in the previous analogy of the laths. The most important constituent is the drying oil for this is what provides the continuous film and gives the protection. But the present day technologist is not content with anything so simple. Our complex civilization does not allow him to be. Modern living requires paints for battleships which brave the arctic cold as well as the equatorial sun. It demands a coating for bomber planes which does not interfere with the speed of the plane as does ordinary paint. And so the paint technologist is continually looking for ways to improve this mixture of oil, pigment, and drier.

Partial polymerization of the oil prior to its use as a vehicle by heat bodying or by "blowing" with air or oxygen were among the first procedures used for improving what nature had provided. These techniques are still widely used at the present time.

In discussing polymerization previously, it was indicated that the first step was probably the conjugation of the double bonds since conjugated double bonds appear to be necessary for dimerization. In this same vein chemists realized that if they could take unconjugated drying oils, such as soybean or linseed oil, and conjugate them, they would have improved oils. Research has revealed certain catalysts including alkali, metals like nickel, or gases like sulfur dioxide which effect the necessary prototropic shift. Thus artificially conjugated oils are now of some commercial interest. Of greater interest is the preparation of a conjugated oil by the dehydration of castor oil.

Castor oil acids contain one hydroxyl group and one double bond in the 9 and 12 positions respectively. If the acids are dehydrated and if the dehydration goes as one would like it to go, there results acids with conjugated double bonds. Actually in the commercial dehydration a mixture of conjugated and unconjugated acids are obtained. But there are sufficient conjugated acids present to make dehydrated castor oil of considerable interest in the protective coating industry.

Still a different method is available for improving drying oils. Natural oils are of course glycerides. If the trihydric glycerol is replaced by an alcohol of greater functionality, that is, by an alcohol with more hydroxyl groups, it is possible to have more fatty acids in the molecule and thus more double bonds. Accordingly there is a resultant improvement in the drying and film properties of the oil. This technology is called reconstitution of oil and is based on the theory of functionality (9, 13). This states that the greater the number of points of attachment within a molecule, and in this instance the points of attachment are double bonds, the more complex will be the resulting polymer. The more complex the polymer, the stronger it is, as is reflected in oils by greater film strength and faster drying time. By substituting pentaerythritol (8), sorbitol (7), or tetramethylolcyclohexanol (19) for glycerol we introduce more functionality, that is, more points of attachment. This technology is of great interest today.



$R = CH_3\text{-}(CH_2)_4\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_7\text{—}$

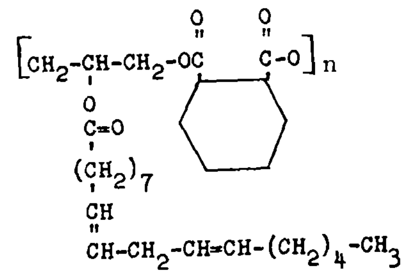
Pentaerythritol is produced by condensing acetaldehyde with formaldehyde whereas tetramethylolcyclohexanol results from the condensation of cyclohexanone and formaldehyde.

Of infinitely great importance in improving drying oils is the formulation of varnish. A varnish is merely a combination of a drying oil and a resin. When properly formulated, the resin imparts strength to the oil film without impairing the ability of the oil to dry or polymerize.

Today the technologist can choose from a wide variety of oils and from literally hundreds of resins, both natural and synthetic. He combines these in the varnish kettle, heats them at high temperatures, usually for several hours until he attains the desired viscosity, and finally mixes his product with solvent and drier. If pigment is ground into this mixture, an enamel results.

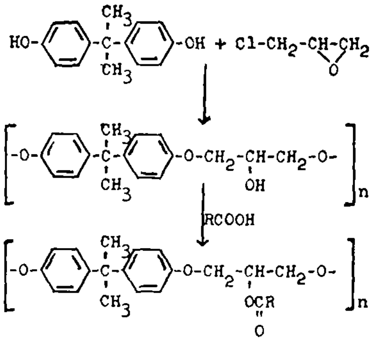
The chemistry of varnish making is very obscure. Little more is known other than that because of the influence of high temperatures the oil and the resin in some way are combined in a highly polymerized composition. But this lack of knowledge did not stop the chemist from wondering about the possibility of combining the resin and the oil in a molecule which in turn will polymerize to hard films. The answer has assumed several ramifications. One of these falls into the category of co-polymerization. If a drying oil is heated with a polymerizable monomer like styrene, co-polymerization takes place between the complicated drying oil molecule and the simple styrene molecule to yield a drying oil which has had imparted to it by the styrene a resinous character. Thus it yields films which are faster drying, harder, and more resistant.

Of great importance as a means of obtaining a chemical combination of resin and oil are the so-called modified alkyd resins. Here a polyhydric alcohol such as glycerol, pentaerythritol, or tetramethylolcyclohexanol is reacted with the correct stoichiometric proportions of a dibasic acid, such as phthalic acid, and an unsaturated monobasic acid, such as the acids obtained from the saponification of soybean oil. The preliminary polymerization is basically a glycol-dibasic acid polyesterification for the monobasic acid reacts with one of the hydroxyl groups leaving in essence the glycol to interact linearly with the dibasic acid. The structure of such an alkyd polymer may be represented without oversimplifying too much as follows.



This facet of protective coating technology is of interest for the fatty acids used in modifying alkyds are frequently those from soybean or cottonseed oil. Ordinarily neither of these oils dry well alone for their fatty acids do not have enough double bonds, that is, they do not have sufficient points of attachment or enough functionality. In alkyds this lack of functionality is compensated for by the resinous structure of the glycerol phthalate.

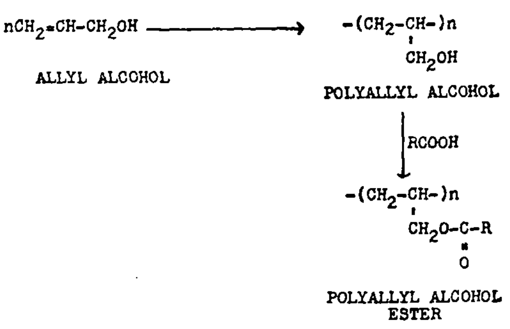
In this same vein the so-called Epon resin (12) is of interest.



$R = CH_3-(CH_2)_4-CH{=}CH-CH_2-CH{=}CH-(CH_2)_7-COOH$

Here a *bis*-phenol is reacted with epichlorohydrin to yield a polymer. In the polymerization process a hydroxyl group is introduced, and this is esterified with a fatty acid. The net result is a composition which, like an alkyd, is a chemical combination of resin and drying oil. In alkyds the resinous portion is a polyester resin whereas in esterified Epon resins the resinous portion is a polyether. Polyethers, capable of esterification also result when glycerol is condensed with glycerol dichlorohydrin (22), and thus these esterified products likewise are chemical combinations of resin and oil.

In the same category, finally, are polyallyl alcohol esters (1). Again we find a chemical combination of resin and oil, save that the resinous portion here is a polyethylene.



$R = CH_3-(CH_2)_4-CH{=}CH-CH_2-CH{=}CH_2-(CH_2)_7-$

Summary

This review has attempted to present somewhat diagrammatically exemplary fundamentals of drying oil chemistry and technology. The point has been stressed that the chemistry of the higher fatty acids is entirely analogous to that of the lower fatty acids. Finally typical protective coatings have been described from the point of view of the fundamental chemistry involved.

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