

Preparation of Modified Resins by the Use of Fatty Derivatives*

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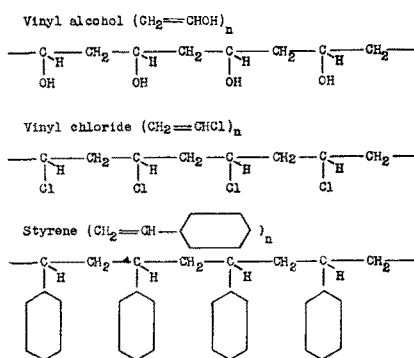
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BEFORE discussing the use of fatty acid derivatives in plastics let us review briefly a few of the theories of resin formation. Synthetic resins are non-crystalline compounds of high molecular weight which are formed either by the condensation or polymerization of relatively simple compounds. In a number of instances resins are formed by a condensation followed by polymerization of the condensed molecules. Polymerization is defined as the union of two or more like molecules to form a larger molecule, of similar empirical formula, whereas condensation is defined as the combination of two or more unlike molecules. An example of a resin formed by polymerization is polystyrene and of resins formed by condensation, the glyptals.

In order to attain the resinous state it is necessary that the initial condensation or polymerization does not preclude the possibility of the occurrence of further condensation or polymerization. Thus, for example, glycerol and benzoic acid will not condense into a resin because each esterification of a hydroxyl group reduces the possibility of further esterification, and this possibility is reduced to zero when all the hydroxyl groups are esterified. Glycerol and phthalic acid, on the other hand, condense to a resin because the initial esterification increases the possibility for further esterification with the result that molecules of extremely high molecular weight are formed.

For the purposes of this discussion I have divided the synthetic resins into three general groups based upon their supposed manner of formation. These groups are: first, those formed by simple polymerization, second, those formed by condensation, and third, those which result from condensation followed by polymerization.

The vinyl resins or the coumarone and indene polymers are examples of the first group. The vinyl resins result from the polymerization of compounds of the general formula $CH_2=CHX$. Resins formed from vinyl alcohols, vinyl



Structures of Vinyl Polymers
Figure 1

chloride or styrene have the structures shown in Fig. 1.

The formula for the polystyrene was first ascribed to this resin by Staudinger (1).

It will be noted that resins of this type are formed by the simple polymerization of the parent substance. These linear polymers attain extremely high molecular weights, and resins prepared from vinyl acetate have been known to have molecular weights of over 80,000.

Another example of resins formed by straight polymerization is those prepared from coumarone or indene. The parent substances, coumarone or indene, are obtained from coal tar naphthas. Both of these substances undergo polymerization upon heating or in the presence of catalysts such as sulfuric acid or aluminum chloride. The resulting products are dimers, trimers, tetramers or higher polymers. The structure of these polymers which is favored by Carmody, Sheehan and Kelly (2) is shown

in Fig. 2.

The molecular weight determinations indicate that under the usual conditions of polymerization substantial proportions of tetramers are formed.

Indene forms polymers in a manner similar to coumarone. The products are dimers, trimers, tetramers or higher polymers. The structure of these polymers has been determined by Whitby and Katz (3) and is shown in Fig. 3.

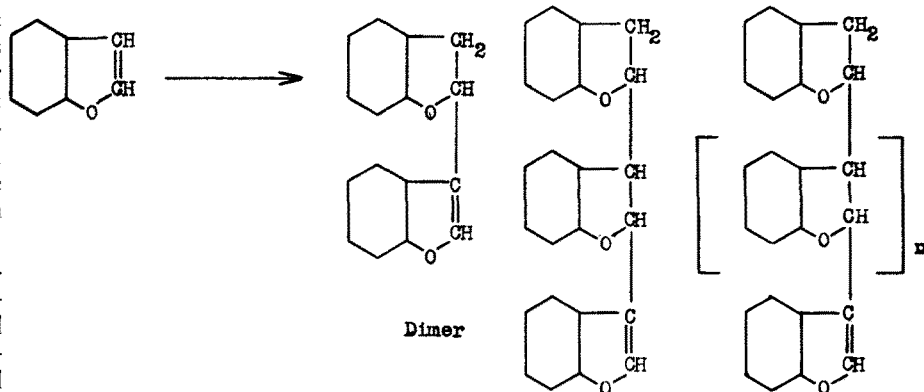
In the case of both the coumarone and indene the degree of polymerization is somewhat dependent upon the strength of the acids used as catalysts. The characteristics of resins obtained from coumarone or indene are a function of the manner of polymerization.

The resins prepared by the reaction of polyhydroxy alcohols, such as glycerol with polycarboxylic acids, such as phthalic acid or sebacic acid, are typical of those formed by straight condensation.

Resins formed from glycol and phthalic acid may be used as an example of a type of resin formed by "polyesterification." This reaction tends towards the formation of linear polymers of high molecular weight. The reactions and structure are shown in Fig. 4.

As seen by the example resins of this type have a linear structure. Resinification does not lead to the formation of an infusible product.

When glycerol is substituted for glycol a much more complex resin results. Resins of this nature were



Coumarone Polymers Trimer
Figure 2

Polymer

*An address before the May 1939 meeting of the A.O.C.S.

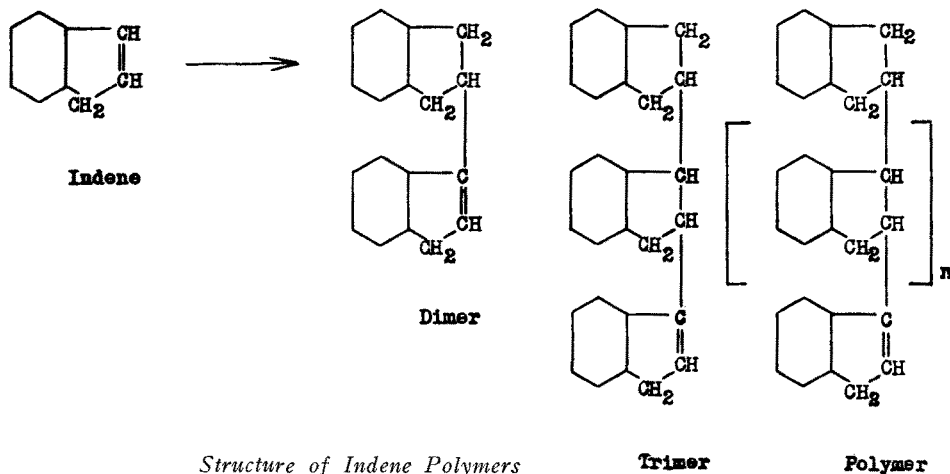


Figure 3

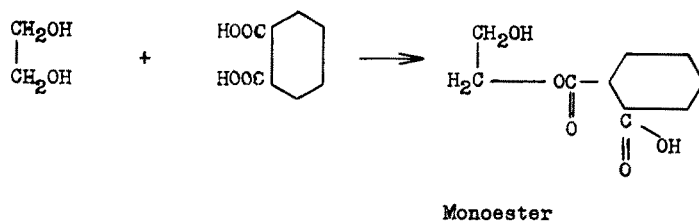


Figure 4

discovered by Smith (⁴) in 1901. Because of the fact that esterification of the glycerol by phthalic acid gives a phthalic monoglyceride which contains two unesterified hydroxyl groups these resins have a branched condensed structure.

The initial reaction and probable structure of the resins are shown in Fig. 5.

Other dicarboxylic acids may be substituted for the phthalic acid. Azelaic acid, a straight chain aliphatic dicarboxylic acid having nine carbon atoms, is often used. Resins formed by the reaction of glycerol and azelaic acid were first described in British Patent 377,265.

It will be noted that the formation of resins by condensation depends entirely upon the fact that the initial reaction results in the formation of a molecule which can react with a like molecule or with either of the initial reactants. The reaction between glycerol and benzoic acid does not result, therefore, in a resinous product because it

does not fulfill the above requirements.

Resins formed by the action of phenols and formaldehyde are the classical examples of resins resulting from both condensation and polymerization. As early as 1872

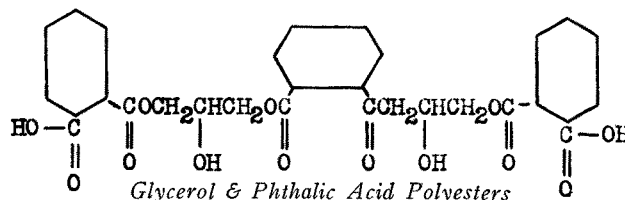
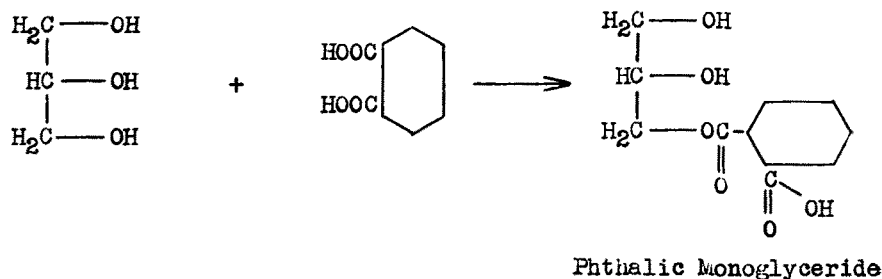


Figure 5

Baeyer (⁵) announced that phenols and aldehydes react to yield resinous products. One of the simple condensation products of phenol and formaldehyde is hydroxybenzyl alcohol which is formed by the action of phenol and formaldehyde in alkaline solution. Among the first to prepare this compound may be mentioned Lederer (⁶) and Manasse (⁷). The compound is crystalline and melts at 82°. Condensation in acid solution produces as an initial product diphenylolmethanes which were first isolated by Baeyer (⁸). These initial condensations probably proceed as shown in Fig. 6.

Compounds of this type can be looked upon as the parent substances of phenol-formaldehyde resins. Their dehydration and the subsequent polymerization of the resulting products is responsible for resins of this nature. Hydroxybenzyl alcohols may be dehydrated by heat alone but the reaction is hastened by catalysts such as acids, etc. Baekeland (⁹) was among the first to realize the possibilities of this reaction.

The resinification of formaldehyde and phenol proceeds in three steps:

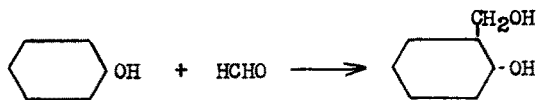
1. The formation of an initial condensation product (A) such as the above described hydroxybenzyl alcohol.

2. The formation of an intermediate product (B) which probably results from the dehydration of the initial product.

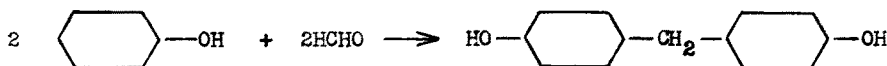
3. The final stage C which results from a polymerization of stage B with additional formaldehyde.

The various stages can be represented as shown in Fig. 7.

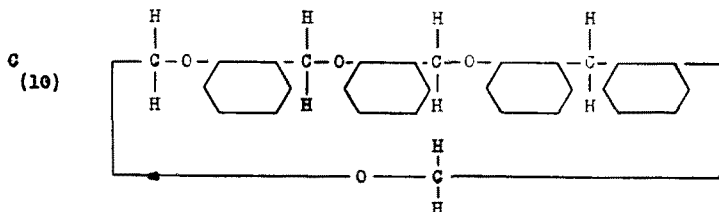
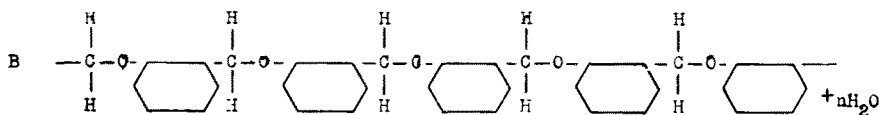
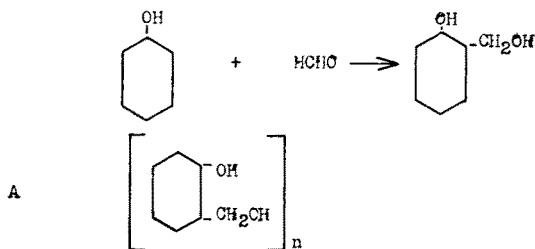
Alkaline



Acid



Initial Reactions of Phenol & Formaldehyde
Figure 6



Stages in the formation of Phenol-Formaldehyde Resins
Figure 7

This is only one of the many explanations for the formation of resins of this type. Ammonia, acids, etc. modify the nature of the products formed and in the former case probably enter into the reaction. It can be seen that stages A and B represent condensations and that the final infusible resin is formed by polymerization of these products.

One of the very common defects of many synthetic resins is brittleness. For almost every conceivable industrial use it is necessary that the resin possess some degree of flexibility. It is not surprising, therefore, that the problem of plasticity and the development of plasticizing agents has gone hand in hand with the development of the resins themselves. It is not the purpose of this paper to discuss in detail

the many substances which have been added to modify resins.

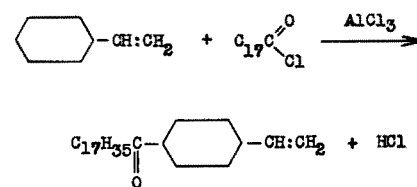
Most plasticizing agents, with some notable exceptions such as the modified glyptal resins, are substances which dissolve in the resin and impart desirable properties thereto. In order to be effective for this purpose the substance must be completely compatible with the resin, it should be as stable as the resin and resistant to the same substances. In addition, it should not impart any undesirable characteristics such as cloudiness, tackiness, light sensitivity, etc. Time will not permit of a detailed discussion of many of the substances which have been proposed. Glycerol, dibutyl phthalic, phenyl stearate, o-cresyl phosphate, and animal and vegetable fats and oils are among the products often used. The proper

plasticizing agent depends, of course, upon the resin in question and it cannot be stated that there is any universal plasticizing agent.

We have now discussed in a very brief and sketchy manner the theory or resin formation and we have seen how various resins result by the polymerization, condensation or a combination of polymerization and condensation of simple molecules. During the remainder of this paper it is proposed to show how various fatty acid derivatives can be employed for the preparation of resins which possess distinctive properties chiefly among which is flexibility. Resin-forming compounds such as styrene, coumarone, indene, phenol, etc. can be reacted with high molecular weight fatty acid chlorides in the presence of aluminum chloride or other Friedel-Crafts catalysts to produce acylated compounds which can then be polymerized by heat or catalysts to give resins. These resins possess a variety of properties dependent upon the degree of acylation and the type of acyl group which is introduced. They may be illustrated by examples as follows:

Styrene Resins:

Styrene may be acylated with high molecular weight aliphatic acid chlorides in the presence of aluminum chloride or other Friedel-Crafts catalysts to give products which can then be polymerized to flexible transparent resins. Using stearoyl chloride as the acid chloride the equation for this acylation is as shown in Fig. 8.

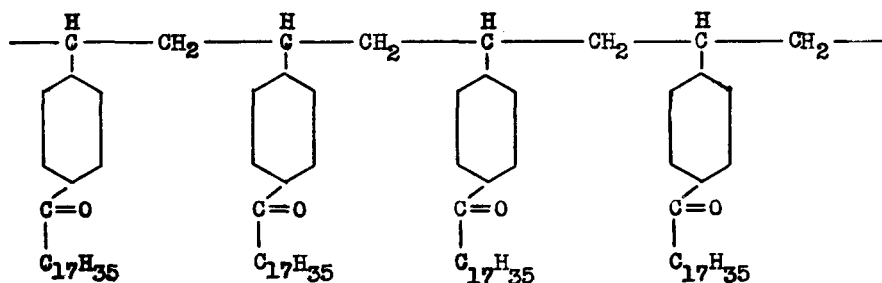


Acylation of Styrene
Figure 8

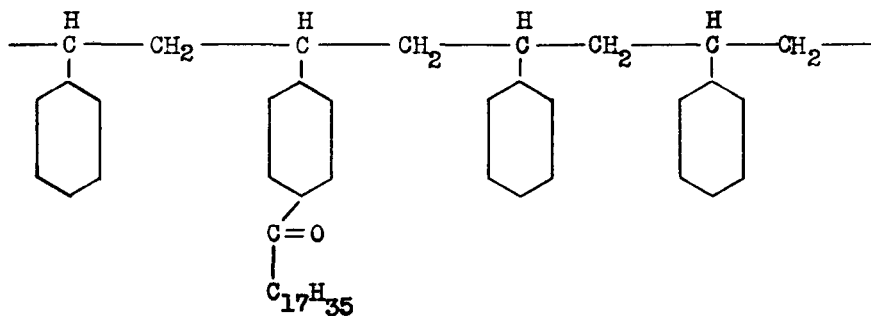
This compound can be polymerized to give resins which probably have the structure shown in Fig. 9.

It is of course possible to prepare a series of resins in which the proportion of acylated group varies over wide ranges. Thus, when unmodified styrene is resinified with the p-stearoyl styrene a resin of the structure shown in Fig. 10 is obtained.

If unsaturated acid chlorides



Structure of Acylated Polystyrenes
Figure 9



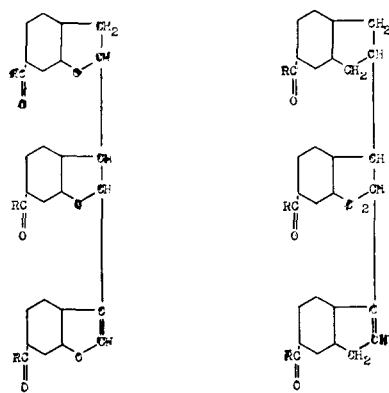
Partially Acylated Polystyrene
Figure 10

such as linoleoyl or linolenoyl chloride are used as acylating agents the products have both the polymerizing properties of styrene together with the drying properties of the highly unsaturated alkyl group. It is, therefore, possible, depending upon the kind and amount of the acylating agent, to prepare resins having a wide range of properties.

Coumarone and Indene Resins:

Coumarone when reacted with high molecular weight fatty acid chlorides in the presence of aluminum chloride or other Friedel-Crafts catalysts undergoes simultaneous acylation and polymerization to yield acylated dimers, trimers, etc. which can be further polymerized to give flexible resins.

Indene and dicyclopentadiene undergo similar reactions. These resins have the following general formulas:



Acylated Coumarone and
Indene Polymers
Figure 11

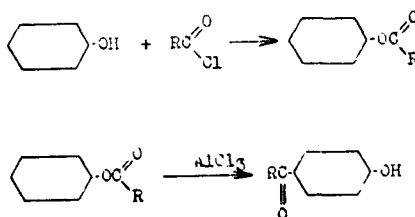
These resins are either formed by the polymerization of acylated coumarone or indene or by acylation of a previously formed polymer. It is, of course, possible to reduce the amount of acid chloride employed and resins have been prepared containing from ten percent to one-hundred percent of a molecular equivalent of acid chloride.

Glyptal Resins:

Oleic acid and stearic acid were suggested by Arsen⁽¹¹⁾ as modifiers for glyptal resins. The use of drying oil acids was suggested by Bradley⁽¹²⁾. Kimle⁽¹³⁾ employed monoglycerides of drying oil acids as modifiers. In these cases the addend becomes a reactant and a modified resin is obtained. The properties of the resins are dependent upon the type of monoglyceride or fatty acid employed.

Phenol-Aldehyde Resins:

Phenol when reacted with fatty acid chlorides in the presence of aluminum chloride first forms an ester which then rearranges to give an acylated phenol. This rearrange-



Acylation of Phenol
Figure 12

ment is known as the Fries Rearrangement. The reactions are as shown in Fig. 12.

The acyl group may be in either the ortho or para position. Since the acylated phenol still contains two reactive positions, either one ortho and one para for the ortho acylated phenol or two ortho for the para substituted phenol, these compounds can be condensed with formaldehyde to form resins. In our experimental work we have made a variety of resins from phenol and formaldehyde containing various molecular proportions of these acylated phenols. When the acyl group is para or ortho the compounds act probably as chain terminating reactants; if the acyl group is in the meta position it would not have as pronounced a modifying effect. A number of formulas could be postulated for modified resins of this character but because of the complexity of even the simple types it does not appear that speculation as to their constitution is warranted. It is known, however, that these acylated phenols react with phenol and formaldehyde to give a series of resins which possess unusual properties.

It is, of course, important that the acylation does not result in a compound which will not subsequently polymerize. This means that the groups or positions necessary for polymerization must not be blocked by the acyl group.

In all of the resin types which have been described the long alkyl group is actually incorporated into the resin structure and the plasticizing agent is an integral part of the resin itself. Whenever these long acyl groups are introduced into a resin formula the resulting product is more flexible than the unmodified resin. Since the need for flexible resins is increasing it is predicted that these products have a future in this field.

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(3) Whitby and Katz, Jour. Am. Chem. Soc. 50, 1160, 1928.

(4) Smith, J. Soc. Chem. Ind. 20, 1075, 1901.

(5) Baeyer, Ber. 5, 25, 1872.

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(8) Baeyer, loc. cit.

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(11) Arsen, U. S. Patents 1,098,776 and 1,098,777.

(12) Bradley, U. S. Patent 1,893,699.

(13) Kimle, U. S. Patent 1,889,923.