SYNTHETIC RESIN CHEMISTRY

SYNTHETIC RESIN CHEMISTRY

FOR STUDENTS

by

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AUTHOR'S PREFACE

Many excellent books have already been written on synthetic resins, by Carleton Ellis, and Morrell and his collaborators, but, with the exception of the Penguin *Plastics*, all have been advanced textbooks, above the comprehension of the average laboratory assistant or resin chargehand. The Penguin *Plastics* was the first attempt to interest people other than chemists and skilled technicians in resins and plastics, but it dealt mainly with applications of resins.

No one who has had any experience with resins will doubt that there is quite an art in handling these materials. Their manufacture is an intricate process, and their properties quite unlike those normally encountered in the field of chemistry ; and in every resin, paint or plastics laboratory there are young men and women handling these new materials every day, and frequently carrying out only routine work with no idea of the reasons underlying the work. These young people, ranging in age from 16 upwards, all hope to improve their position by study, usually in the evenings or weekends, or by making themselves masters of their craft. Many go to Polytechnics and Technical Schools, either to take external degrees, or to attend specialised courses. There are many courses on Paint or Plastics Technology, but these are not enough, and it is hoped that in the near future there will be many more courses on Synthetic Resins and similar subjects so that those who are keen can familiarise themselves not only with the materials they handle every day but also with other materials closely allied to them.

This book is intended primarily to assist such people. They may use it as a text book in their evening studies or as a primer in their laboratories. It has been assumed that readers have studied chemistry to School Certificate standard and it is hoped that the majority have an elementary knowledge of organic chemistry ; but the first chapter is devoted to a brief survey of the various classes of organic chemicals met with in the resin industry. The other chapters are divided essentially into two parts, the first theoretical and the second practical, giving experiments which have actually been carried out but which are well worth repeating.

This book, too, will be of use to the qualified chemist by relieving him of a great deal of training and explanation which sooner or later he will have to give to his assistants.

May I also recommend it to those who come straight from universities to enter the resin industry; they, too, might find the experiments useful and interesting.

I have never forgotten the sage remarks made to me by a very eminent resin chemist at the commencement of my studies in Germany in 1934–1935. "You must have a sound knowledge of chemistry," he said, "but you must be prepared to keep it in the background. Until now you have been concerned with getting good yields of crystalline compounds or clean, easily distilled liquids, and resinous materials and gummy residues have been thrown away. Our products must not crystallise and we want the resinous gums. You will find that our products will not melt sharply. Above all you will soon realise how difficult it is to repeat the same experiment and get identical products, but in time you will find it possible. And, lastly, when you are experienced, if you are very good you will control these products more by instinct than by chemical tests, but don't let your instinct make you forget too much of your chemical training."

In conclusion, the author wishes to thank his many friends in the industry and the directors of A. Holden & Sons, Ltd., for their encouragement in the preparation of this book. In particular, thanks are due to Mr. E. A. Bevan and Mr. R. S. Robinson for their very helpful advice and criticism. My former colleague, Mr. H. T. Richardson, very kindly prepared the drawings and my wife assisted in the preparation and reading of the manuscript. My thanks are also due to Mr. G. Copping for his work in preparing the manuscript for the press, and to Mr. C. J. A. Taylor for reading the proofs. Table 1 and diagram 1 are reprinted from *Paint Manufacture*, by permission of Leonard Hill, Ltd.

S.R.W.M.

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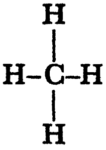
CHAPTER I

ELEMENTARY ORGANIC CHEMISTRY

Except for a few special cases, *e.g.*, silicon resins, all synthetic resins are organic chemicals, and organic chemistry is essentially the chemistry of carbon compounds, of which some hundreds of thousands exist. The large majority of organic chemicals are made up of the elements carbon and hydrogen, often in combination with oxygen, nitrogen, sulphur, phosphorus or halides and only rarely are other elements found. Because of the enormous number of compounds to be dealt with they are generally grouped in series having similar formulæ and properties, although of course a good deal of overlapping occurs, and also many anomalies.

A peculiarity of organic chemistry, as compared with inorganic chemistry, is that in many cases several quite different compounds with the same atomic composition exist. Ethyl alcohol and dimethyl ether both have, for example, the same empirical formula, C_2H_6O, yet they are extremely unlike one another. For instance, the former is very soluble in water whereas the latter is practically insoluble. These differences are explained by structural formulæ. Thus, two substances may have the same empirical formula, but the various atoms in the molecules are linked together in different ways.

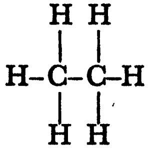
Carbon is tetravalent, *i.e.*, it has four valencies by means of which it can link itself to other atoms. Moreover, these valencies or bonds are equal. The simplest compound of carbon and hydrogen—a hydrocarbon—is therefore CH_4 or methane and accordingly it can be written to the following structural formula (1) :—



$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array} \qquad (1)$$

Other hydrocarbons of the same series can be produced by carbon atoms linking to other carbon atoms. Consequently, compounds such as

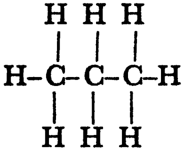
Ethane C_2H_6



$$\begin{array}{c} H\;\;H \\ |\;\;\;| \\ H-C-C-H \\ |\;\;\;| \\ H\;\;H \end{array}$$

(II)

Propane C_3H_8

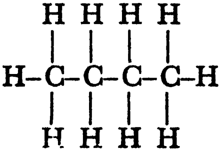


$$\begin{array}{c} H\;\;H\;\;H \\ |\;\;\;|\;\;\;| \\ H-C-C-C-H \\ |\;\;\;|\;\;\;| \\ H\;\;H\;\;H \end{array}$$

(III)

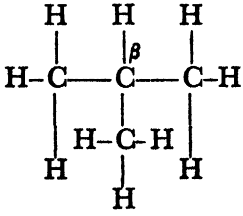
and many other compounds are possible. They vary from gases, when the members have few carbon atoms, to liquids and finally wax-like solids, as the number of carbon atoms increases to 20.

The importance of structural formulæ is illustrated in the next members of the series. Thus, the butanes C_4H_{10} may exist in two forms, represented by formulæ (IV) and (V).



$$\begin{array}{c} H\;\;H\;\;H\;\;H \\ |\;\;\;|\;\;\;|\;\;\;| \\ H-C-C-C-C-H \\ |\;\;\;|\;\;\;|\;\;\;| \\ H\;\;H\;\;H\;\;H \end{array}$$

(IV)



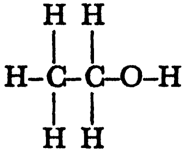
$$\begin{array}{ccccccc} & H & & H & & H & \\ & | & & |\beta & & | & \\ H- & C & — & C & — & C & -H \\ & | & & | & & | & \\ & | & H- & C & -H & | & \\ & H & & | & & H & \\ & & & H & & & \end{array}$$

(V)

That these compounds are different structurally is obvious. Formula IV represents normal butane, and it will be noticed that all the carbon atoms form a chain—a straight chain—and all are linked to at least two hydrogen atoms, whereas in formula (V) one carbon atom, marked β, is linked to only one hydrogen atom and from the other link a fresh branched chain begins. This compound is iso-butane. All these compounds belong to the class of compounds called paraffins and have the general formula C_nH_{2n+2}. When we reach the next member of the series—pentane—C_5H_{12}—this may exist in three different forms. The succeeding members of this series are called hexane, heptane, etc., the hexa, hepta, being the Latin for six, seven, etc., the number of carbon atoms in the molecule, and the suffix -ane indicating that these compounds are saturated hydrocarbons of the paraffin series.

Where several organic compounds exist with the same formulæ they are called isomers, and where the differences can be attributed to the structure they are called structural isomers.

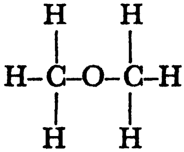
The difference in the formula of ethyl alcohol and dimethyl ether can now be explained. Ethyl alcohol (vi) has the structure



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & O-H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

(vi)

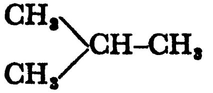
and dimethyl ether (vii) the formula



$$\begin{array}{ccccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & - & C & - & O & - & C & - & H \\ & & | & & & & | & & \\ & & H & & & & H & & \end{array}$$

(vii)

It must be remembered that these formulæ are purely diagrammatic. They are clumsy and can be more simply written as $CH_3.CH_2.OH$ (via) and CH_3OCH_3 (viia), or sometimes as CH_3-CH_2-OH and CH_3-O-CH_3. Similarly, the isomeric butanes already described may be written $CH_3CH_2CH_2CH_3$ (iva) and



$$\begin{array}{l} CH_3\diagdown \\ \qquad\quad CH-CH_3 \\ CH_3\diagup \end{array}$$

or even $(CH_3)_3.CH$ (va)

These isomers, as well as being different in the way they are formulated are also different in physical properties. Thus, normal butane is a gas liquifying at $-1°C.$, and isobutane liquifies at $-10°C.$

The group CH_3- from methane is called methyl, and C_2H_5- or CH_3CH_2- is called ethyl, so isobutane, from formula (va), can also be called trimethylmethane since it is a molecule of methane in which three hydrogen atoms have been replaced by methyl groups. The group $-CH_2-$ (*see* formula (iva)) is called methylene, and is an important group in resin chemistry. Its structural formula is

$\begin{array}{c} H \\ | \\ -C- \\ | \\ H \end{array}$, and as it has two free bonds it can form a bridge between other groups, hence it is sometimes referred to as a methylene bridge.

Oxygen Linkages.

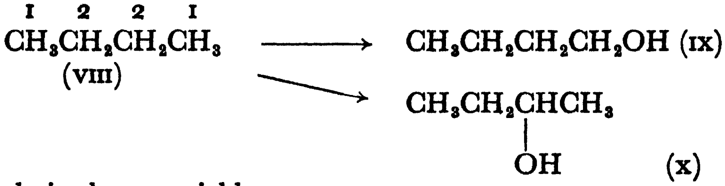
Oxygen may be linked into the carbon-hydrogen system in many ways. The oxygen compounds of interest to the resin technologist are aldehydes, ketones, alcohols, phenols, ethers, and carboxylic acids. It is not the purpose of this book to describe the various processes involved in synthesising these various compounds. Suffice it to say that they may be regarded as stepwise oxidation products of the hydrocarbon series. Thus

Paraffin ⟶ Alcohol ⟶ Aldehyde or ketone ⟶ Carboxylic acid.

Alcohols.

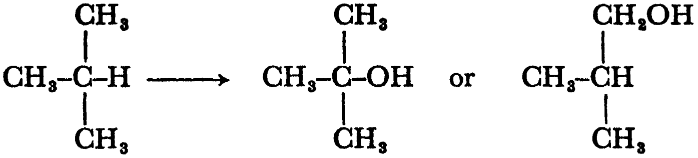
The alcohols have the general formula R–O–H, where R– indicates a group of carbon and hydrogen atoms which in the case of simpler alcohols may be methyl-, ethyl-, etc. Such a group of atoms is called a radicle and is usually represented by the symbol R–.

The formula for ethyl alcohol has already been given (VI). The distinctive group of all alcohols is the hydroxyl –O–H, which is the same group as is in water, H–O–H, and caustic soda, NaOH. Consequently the simpler alcohols are soluble in water, but as the size of the radicle increases the hydrocarbon portion predominates and the water solubility of the alcohol decreases. The alcohols are named after the parent hydrocarbon, with the suffix -ol, *i.e.*, methanol, ethanol, etc., and just as much more than one butane exists so more than one butanol can exist. Actually the two butanes yield together four butanols, normal (formula IX), secondary (X), tertiary (XII) and iso- (XIII), with boiling points of 117°, 100°, 83° and 107°C. respectively. This statement may confuse the student but is easily explained by examining the structural formulæ. n–Butane (formula VIII) has two different types of carbon atoms marked 1 and 2. The terminal carbon atoms (1) are each linked to three hydrogen atoms whereas the internal carbon atoms (2) are linked to only two hydrogen atoms. Consequently two alcohols are possible according to whether the hydroxy group is linked to carbon 1 or 2.



$$\underset{(\text{viii})}{\overset{1}{CH_3}\overset{2}{CH_2}\overset{2}{CH_2}\overset{1}{CH_3}}\ \begin{array}{l}\longrightarrow CH_3CH_2CH_2CH_2OH\ (\text{ix})\\ \searrow CH_3CH_2\underset{\substack{|\\ OH}}{CH}CH_3\quad (\text{x})\end{array}$$

similarly iso-butane yields



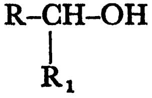
$$\underset{(\text{xi})}{CH_3-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}-H}\ \longrightarrow\ \underset{(\text{xii})}{CH_3-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}-OH}\quad \text{or}\quad \underset{(\text{xiii})}{CH_3-\overset{\substack{CH_2OH\\ |}}{\underset{\substack{|\\ CH_3}}{CH}}}$$

Types of Alcohols.

This series of formulæ allows us to examine the different types of alcohols that exist. Thus there are primary, secondary and tertiary alcohols, depending on the nature of the other groups attached to the parent carbon atom. Thus when R–, R_1–, R_2– represent radicles, methyl-, etc., these different alcohols may be given the following type formulæ :—

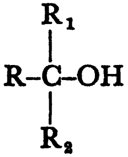
Primary $R-CH_2-OH$

Secondary



$$R-\underset{\substack{|\\ R_1}}{CH}-OH$$

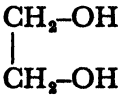
Tertiary



$$R-\overset{\substack{R_1\\ |}}{\underset{\substack{|\\ R_2}}{C}}-OH$$

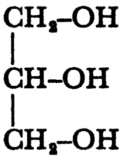
Compare these formulæ with (ix), (x) and (xii) above. These alcohols are very different in their properties. They will be met with very frequently in resin chemistry.

There are other classes of alcohols which are also important —the polyhydric alcohols. These form the basis of a large group of resins. The prefix "poly" means more than one, and "hydric" is another way of saying hydroxyl, so these alcohols are those which contain more than one hydroxyl group in the molecule. Glycerine, glycol, etc. are all members of this group. Their formulæ are given below and they will readily be recognised as alcohols.



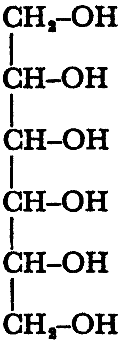
$$\begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array}$$

Glycol



$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}$$

Glycerine



$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH-OH \\ | \\ CH-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}$$

Mannitol

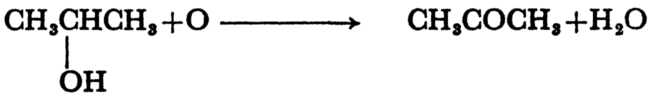
If these compounds are compared with the hydrocarbons already described, it will be seen that glycol is di-hydroxy-ethane and glycerine is tri-hydroxy-propane.

Aldehydes and Ketones.

Aldehydes and ketones are very much alike in their properties. They can both be derived from alcohols by oxidation but aldehydes are produced from primary alcohols and ketones from secondary alcohols. Thus :—

$$CH_3CH_2OH + O \longrightarrow CH_3CHO + H_2O$$

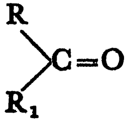
Ethyl alcohol Acetaldehyde



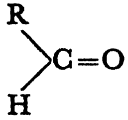
$$\begin{array}{l} CH_3CHCH_3 + O \longrightarrow CH_3COCH_3 + H_2O \\ \quad\;\; | \\ \quad\;\; OH \end{array}$$

Isopropyl alcohol Acetone

These compounds are all extremely reactive and are of great use in the resin industry. It will be seen that the general formula for ketones is



where R– and R_1– are like or unlike radicles. When R– and R_1– are alike we have a symmetrical ketone and when they are dissimilar we have an unsymmetrical ketone, and in the very special case when one of the radicles is hydrogen then we have an aldehyde

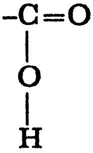


$$\begin{array}{l}R\\ \quad\rangle C{=}O\\ H\end{array} \quad \text{or } R.CHO$$

The simplest aldehyde and the most used commercially is formaldehyde, H.CHO, which is a gas but is usually sold as a solution in water, usually as 30% or 37%. The next member of the series is acetaldehyde, CH_3CHO, which boils at 22°C. The successive members of the series after these two early members are named after the parent hydrocarbons, *i.e.*, propionaldehyde and butyraldehyde. These compounds are neutral, of peculiar, often pungent odour. The lower members of the series are soluble in water, but as with alcohols this solubility decreases as the size of the radicle increases.

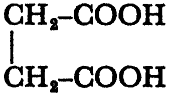
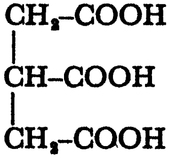
Carboxylic Acids.

The organic carboxylic acids have the general formula R.COOH, the –COOH being the distinctive carboxylic acid grouping. Its structure is



$$\begin{array}{l}-C{=}O\\ \;\;|\\ \;\;O\\ \;\;|\\ \;\;H\end{array}$$

One method of preparing these acids is by oxidising alcohols or aldehydes. Just as polyhydric alcohols exist, so polybasic acids can also exist, the basicity of the acid being determined by the number of carboxyl groups attached to the molecule.

i.e.,	Monobasic	CH_3COOH	Acetic Acid
	Dibasic	 $\begin{array}{l}CH_2\text{–}COOH\\ \mid\\ CH_2\text{–}COOH\end{array}$	Succinic Acid
	Tribasic Acid	 $\begin{array}{l}CH_2\text{–}COOH\\ \mid\\ CH\text{–}COOH\\ \mid\\ CH_2\text{–}COOH\end{array}$	Tricarballylic Acid

In each carboxyl group is a replaceable hydrogen atom which may be displaced by a monovalent metal. These acids are usually fairly strong, they form salts with metals, and dissolve in alkalis, etc. They also form esters by interaction with alcohols. (*See* next section).

There is practically no limit to the length of the carbon chain which may be attached to the carboxyl groups, and it is interesting to note that some of the commonest acids used in resins are those derived from oils, linseed oil, soya bean oil, wood oil, etc., and in all these the length of the carbon chain is usually about 18 carbon atoms. Stearic acid, for example, is $C_{17}H_{35}COOH$ or $CH_3(CH_2)_{16}COOH$.

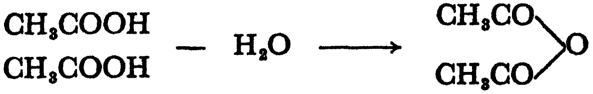
Now that we are discussing compounds of large molecular weight made up of two distinct portions, *i.e.*, a radicle and a carboxyl group, it is interesting to note how these various groups affect the properties of the whole.

Let us consider stearic acid, which contains a long carbon chain, in comparison with formic acid and acetic acid, which are the two lowest members of this series.

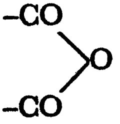
Formic acid	$H.COOH$
Acetic acid	CH_3COOH
Stearic acid	$CH_3\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}(CH_2)_{12}\text{–}CH_2\text{–}COOH$

Now, in formic acid and acetic acid the carboxyl group predominates, and the acid is very strong. Moreover, as the carboxyl group contains a hydroxyl group which has an affinity for water, the acid is water-soluble. But in stearic acid this carboxyl group is only a very small part; the bulk of the molecule is made up by a large hydrocarbon radicle, and the result is a weak acid, insoluble in water, and somewhat like the parent hydrocarbon in appearance.

Before leaving the acids, the acid anhydrides should be mentioned. Anhydrides of monobasic acids may be regarded as compounds made up of two acid molecules from which a molecule of water has been removed.



Note the typical group,



The reaction above indicates how acetic acid might be expected to yield acetic anhydride although actually anhydrides are not generally made by this method. As would be expected, these compounds, in water, are acidic, but surprisingly some anhydrides have to be heated with water before they open up and become acids ; also, although most are soluble in alkalis, some peculiar results are encountered sometimes when trying to neutralise the anhydrides with alkalis. The common anhydrides to be met with in this book are phthalic, maleic and acetic anhydrides.

Esters.

These are important as so many solvents and plasticisers used in the lacquer industry are esters, and because a most important group of resins are ester resins.

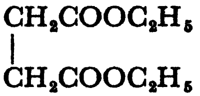
If an alcohol is heated with a carboxylic acid, under certain conditions water is eliminated and ester is formed. Thus

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl alcohol}}{HOC_2H_5} \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

The ethyl radicle replaces the hydrogen in the carboxyl group. Usually a catalyst is necessary to assist this reaction, a common one is strong sulphuric acid, which is only needed in small quantities.

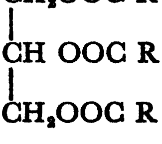
The esters have pleasant smells, the simpler ones having fruity smells, although this again diminishes as the size of the ester increases.

The polybasic acids form esters, *i.e.*, diethyl succinate (formula XIV) can be made in the same way



$$\begin{array}{l} CH_2COOC_2H_5 \\ | \\ CH_2COOC_2H_5 \end{array} \qquad \text{(XIV)}$$

as ethyl acetate. The polyhydric alcohols also form esters. Thus, the vegetable oils are all esters of glycerine with monobasic acids, usually of the 18 carbon series, and if for simplicity we formulate these acids as R COOH, then the oils might be represented as

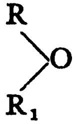


$$\begin{array}{l} CH_2OOC\ R \\ | \\ CH\ OOC\ R \\ | \\ CH_2OOC\ R \end{array}$$

What happens when esters are made from polybasic acids and polyhydric alcohols provides enough matter to fill a whole chapter, and is discussed under Alkyd Resins (Chapter IX).

Ethers.

Ethers can be considered to be oxides of organic radicles, and the general formula is



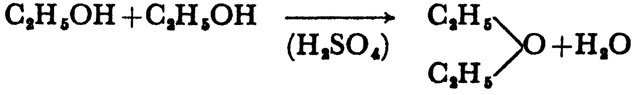
where R and R_1 are again organic radicles, which may be alike (symmetrical ethers) or unlike (unsymmetrical ethers). Examples are dimethyl ether (formula vii) and methyl-ethyl ether (formula xv)

$$CH_3\text{–}O\text{–}CH_3 \qquad \text{(vii)}$$

$$CH_3\text{–}O\text{–}C_2H_5 \qquad \text{(xv)}$$

They are neutral materials, and very stable, and are unaffected by the action of alkalis and acids.

One general method of preparing ethers is to heat an alcohol, or mixture of alcohols, with a strong dehydrating agent, *e.g.*, strong sulphuric acid. The reaction, when ethyl alcohol is used, is :—



This reaction is very important, as many new resins of quite distinct properties are made by etherifying the alcoholic hydroxy groups attached to other resins.

Nitrogen Compounds.

Of the very many organic compounds which exist containing nitrogen, only two groups of compounds will be referred to here, namely the amines and amides.

Amines. These may be considered to be organic derivatives of ammonia NH_3.

In previous paragraphs much has been said about radicles, and except in the case of the methylene radicle, all those mentioned, methyl, ethyl, etc., are monovalent. By the introduction of such radicles in place of hydrogen into the ammonia molecule a class of compounds called amines is formed.

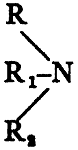
Three types can be made, according to whether one, two or all three of the ammonia hydrogen atoms are replaced.

Thus Primary amines $R\,NH_2$ *e.g.*, CH_3NH_2 methylamine

Secondary amines

e.g., $(CH_3)_2NH$ dimethylamine

Tertiary amines



e.g., $(CH_3)_3N$ trimethylamine

All these compounds are basic, that is, they will form salts with acids.

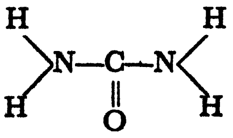
Amides. These should properly be called acid amides ; they are compounds derived from acids in which the hydroxy OH in the carboxyl is replaced by an amino NH_2. Thus :—

$$\underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{ammonia}}{NH_3} \longrightarrow \underset{\text{acetamide}}{CH_3CONH_2} + H_2O$$

Now, the first important thing to be said is that the NH_2 group is called an amino group when present in a primary amine, and is called an amido group when present in an acid amide. Unlike the amines—and as is to be expected by the reaction of an acid with ammonia—these amides are practically neutral, or very weakly basic. The equation given above might lead readers to assume, quite wrongly, that ammonium acetate cannot be made by reacting ammonia and acetic acid. Actually the first product of reaction is ammonium acetate, but by destructive distillation of this salt the amide is formed.

$$CH_3COOH + NH_3 \longrightarrow CH_3COONH_4$$
$$CH_3COONH_4 \longrightarrow CH_3CONH_2 + H_2O$$

An interesting compound which will be met with in resins is urea, with the formula $NH_2CO\,NH_2$ or structurally

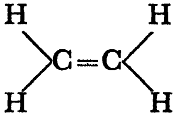


A great deal can be, and has been, written about urea, and its chemistry has been very thoroughly explored, but in resin chemistry its reactions have not been completely explained. This compound may be considered to be a ketone in which the two substituent groups or radicles are amino groups, or it may be considered to be the acid amide of an acid—carbamic acid—NH_2COOH, or better as the di-amide of carbonic acid, HO.COOH, usually written as H_2CO_3.

Unsaturated Compounds.

If for a moment we consider the hydrocarbon series mentioned at the beginning of this chapter, *i.e.*, methane, ethane, propane, butane, etc., it will at once be noticed that these compounds are made up of carbon-carbon chains in which each carbon atom is linked to another carbon atom by one valency, or bond, and the other bonds—two in the case of carbon atoms in the centre of the chain, and three in the case of terminal carbon atoms—are all linked to hydrogen atoms. There are no free valencies to which further hydrogen atoms could link and therefore the hydrocarbon cannot add on more hydrogen, it is *Saturated.*

Now, by various chemical means it is possible to remove some of the hydrogen atoms from such molecules. Take for example ethane (C_2H_6), it is possible to make a compound with the formula C_2H_4. This is called ethylene and the only way to write a structural formula to picture this compound is (formula xvi)



(xvi)

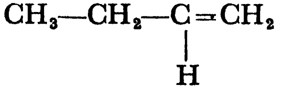
We have to assume that two valencies of one carbon atom join to two bonds of the other carbon, and the remaining two valencies of each carbon atom are used to link up the four hydrogen atoms. The carbon-carbon bond in this case is called a double bond, and these compounds are said to be *unsaturated* because these molecules do not contain the maximum number of hydrogen atoms possible.

Just as it is possible to have a double bond, it is also possible to have a triple bond. Acetylene (formula xvii) is the simplest case, but this chapter is too short to deal with all these compounds

$$H - C \equiv C - H \quad \text{(xvii)}$$

and we will content ourselves with a brief survey of those compounds with double bonds.

These hydrocarbons with a double bond are usually called by the general name of *olefins.* Individual hydrocarbons are named after the parent hydrocarbon, but the suffix " ane " in the parent hydrocarbon is replaced by " ene " or more usually " ylene." Thus, the hydrocarbon with four carbon atoms, eight hydrogen atoms, and one double bond (formula xviii) is called butene, or butylene, after butane (formula iv). For this reason these double bonds are often called ethylenic or olefinic linkages.



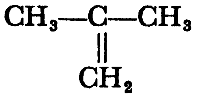
$$CH_3—CH_2—\underset{\displaystyle H}{\underset{|}{C}}=CH_2$$

(xviii)

Isomerisation is still possible and two other butylenes are possible

$$CH_3—CH=CH——CH_3 \qquad \text{(xix)}$$

and



$$CH_3—\underset{\displaystyle CH_2}{\underset{\|}{C}}—CH_3$$

(xx)

So far we have considered only unsaturated hydrocarbons, but other compounds, alcohols, etc., can be unsaturated. Thus comparing saturated and unsaturated compounds we may have butyric acid (formula xxi) and crotonic acid (formula xxii),

$CH_3CH_2CH_2COOH$ (xxi) $CH_3CH=CHCOOH$ (xxii

ethyl alcohol (formula vi) and allyl alcohol (formula xxiii).

CH_3CH_2OH (vi) $CH_2=CHCH_2—OH$ (xxiii)

and so on.

It is possible to have compounds with more than one double bond in the molecule, in which case they may belong to a series of compounds called dienes, trienes or polyenes, " di," " tri," and " poly " of course meaning 2, 3, and " many " respectively. Thus such compounds as butadiene (formula xxiv) are possible

$$CH_2=CH—CH=CH_2 \qquad \text{(xxiv)}$$

Notice how the name is made up, " buta " from butane, the parent hydrocarbon containing four carbon atoms, and " diene," indicating two double bonds in the molecule. You will see that all these complicated chemical names found in organic chemistry books have a sensible meaning.

Where two or more double bonds exist in the molecule, the position of the bonds in relation to one another, and to other groups in the molecule, is important. In the simplest case where two double bonds exist, the two most important arrangements of these double bonds are :—

1. Two double bonds with a saturated carbon atom or series of carbon atoms between, *i.e.*,

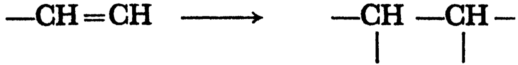
$$—CH_2—CH{=}CH—CH_2—CH{=}CH—CH_2— \text{ etc., and}$$

2. Double bonds alternating with single bonds, *i.e.*,

$$—CH_2—CH{=}CH—CH{=}CH—CH_2—$$

This particular arrangement is said to be a conjugated system, and compounds with this arrangement possess extraordinary properties.

Properties of Unsaturated Compounds. In the first place, unsaturated compounds containing other groups react principally as one would expect. Thus, unsaturated alcohols behave as alcohols and, for example, may be esterified. But the double bond itself is very reactive and is the originator of other types of reaction. The reaction can best be explained by saying that one of the two bonds in the double bond readily opens up, giving two free valency bonds attached to the two carbon atoms, and these valency bonds are able to add on any other monovalent groups that are about.

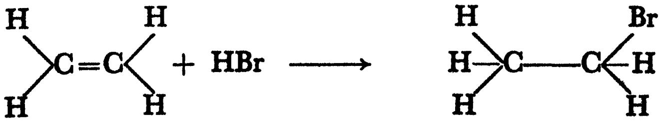


$$—CH{=}CH \longrightarrow \underset{|}{—CH}\ \underset{|}{—CH}—$$

Thus, a molecule of hydrogen, or chlorine, etc., will readily add on forming a saturated compound

$$—CH{=}CH— + H_2 \longrightarrow —CH_2—CH_2—$$

All manner of compounds will react with the double bond in this way, *i.e.*, ethylene (formula XVI) and hydrobromic acid will give ethyl bromide (formula XXV).

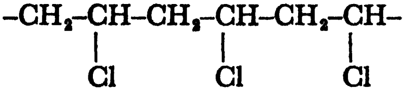


(XVI) (XXV)

But in addition to this the double bond is capable of another type of additive reaction with itself or with double bonds in other olefinic compounds. Thus, consider the compound vinyl chloride (formula xxvi).

$$CH_2 = CHCl \quad \text{(xxvi)}$$

This readily reacts with itself to form a compound called polyvinylchloride, which may be diagrammatically represented by (formula xxvii)



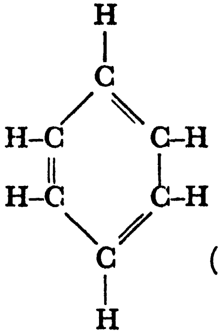
$$-CH_2-\underset{\substack{|\\ Cl}}{CH}-CH_2-\underset{\substack{|\\ Cl}}{CH}-CH_2-\underset{\substack{|\\ Cl}}{CH}- \quad \text{etc.}$$

(xxvii)

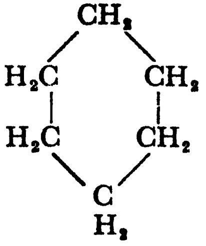
Of course a system with two or more double bonds is more reactive in this way, and if the double bonds are conjugated, then even greater tendencies for reaction are involved.

Aromatic Compounds.

All the compounds previously mentioned have been chain compounds, and all chain compounds are said to be aliphatics, but it is possible for carbon atoms to link together to form "rings," and the commonest type of ring is that made up of six carbon atoms. Benzene (formula xxviii) and cyclohexane (formula xxix) are two examples :—

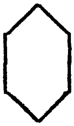


(xxviii)



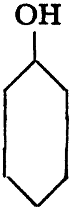
(xxix)

We are interested here only in benzene and its derivatives. All compounds derived from benzene are called *aromatics*, and its formula has to be written so frequently that it is normally simplified to a hexagon (formula xxx).

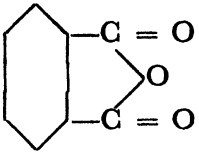


(xxx)

Benzene itself is a solvent, but two compounds containing the benzene nuclei are important, phenol (xxxi) and phthalic anhydride (formula xxxii)

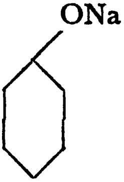


(xxxi)



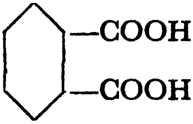
(xxxii)

Phenol with an –OH group would appear to be an alcohol, but this is not so, since the attachment of this –OH group directly to the aromatic ring considerably alters its properties. It has many acidic properties, it burns and will dissolve in caustic soda, forming a sodium salt (formula xxxiii)



(xxxiii)

It is sometimes called carbolic acid. Phthalic anhydride (another aromatic compound) is the anhydride of a dibasic acid, phthalic acid (formula xxxiv).



(xxxiv)

These two compounds are very important constituents of synthetic resins.

Condensation and Polymerisation Reactions.

As will be described later, resin molecules are comparatively large and often complicated structures and they are usually synthesised by one or other of two important reactions, namely Condensation and Polymerisation.

Condensation.

In a condensation reaction two molecules containing reactive groups combine together to form a larger molecule at the same time eliminating simpler products of reaction made up by combination of the reactive groups. The reaction may be written

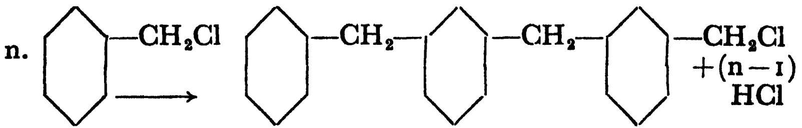
$$A + B \longrightarrow C + D$$

where D will represent water, or ammonia or hydrochloric acid, etc. Simple illustrations are :—

(*a*) *Aldehyde Condensations.* If an aldehyde, *e.g.*, acetaldehyde (formula xxxv), is allowed to stand for several hours in the presence of an alkali, and is then distilled, crotonaldehyde (formula xxxvi) and water are obtained.

$$\underset{(\text{xxxv})}{CH_3CHO + CH_3.CHO} \longrightarrow \underset{(\text{xxxvi})}{CH_3.CH{=}CHCHO} + H_2O$$

(*b*) *Resinification of Benzyl Chloride.* If benzyl chloride (formula xxxvii) which is a thin mobile liquid is heated for a long time in an iron pot, a resin is formed by the condensation of several molecules together. Hydrochloric acid is evolved during the process.



(xxxvii)

(*c*) *Preparation of Nylon.* In the above condensations the molecules condensing together have been molecules of the same substance. Condensations also take place between dissimilar substances and the preparation of Nylon by heating hexamethylene diamine (formula xxxviii) and adipic acid (formula xxxix) is a typical example. Water is formed during the reaction. The initial reaction may be represented as :—

$$\underset{(\text{xxxviii})}{H_2N(CH_2)_6NH_2} + \underset{(\text{xxxix})}{HOOC(CH_2)_4COOH} \longrightarrow$$

$$\underset{(\text{xl})}{H_2N(CH_2)_6NH\text{-}OC(CH_2)_4COOH} + H_2O$$

and the product of this reaction (formula xl) is still capable of further reaction. (*See* Chapter XI).

Polmerisation.

Polymerisation involves the building up of large molecules from smaller molecules without the elimination of by-products of the reaction. It follows therefore that the empirical formulæ of the starting material and the product are the same. The starting material is frequently called the monomer, and the final product the polymer, poly meaning "more than one." The reaction may be simply illustrated as

$$n(A) \longrightarrow (A)n$$

i.e., n molecules of a substance A gives one molecule of a substance (A)n which has the same empirical formula but is n times as large. A simple illustration of this is paraformaldehyde (formula XLI). If a solution of formaldehyde is allowed to stand for several months it will be found to deposit a white sludge which on analysis has the same formula as formaldehyde. But formaldehyde is a gas, soluble in water and this new compound is a white solid insoluble in water. It consists essentially of polymers of formaldehyde which have a molecular weight several times as great as that of formaldehyde.

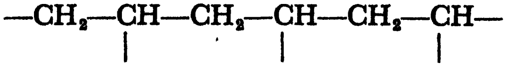
$$\underset{(\text{XLI})}{n\,CH_2O} \longrightarrow (CH_2O)n$$

Note, that on analysis, the same percentage of carbon, hydrogen and oxygen will be found in both compounds.

The most common monomers are substances containing double bonds, these polymerise by linking together by means of the double bond. We have already seen how vinyl chloride (formula XXVI) gives polyvinylchloride (formula XXVII), and vinyl acetate (formula XLII) will by similar means give polyvinylacetate.

$$n.(CH_3COOCH = CH_2) \longrightarrow$$

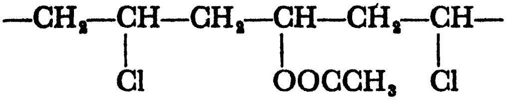
(XLII)



$$-CH_2-\underset{OOCCH_3}{\underset{|}{CH}}-CH_2-\underset{OOCCH_3}{\underset{|}{CH}}-CH_2-\underset{OOCCH_3}{\underset{|}{CH}}-$$

(XLIII)

Actually, by mixing the monomers together polymers can be made up containing both types of groups, these are called interpolymers or co-polymers—*e.g.*, interpolymerisation of vinylchloride (formula XXVI) and vinyl acetate (formula XLII) gives an interpolymer (formula XLIV) with the following structure



$$-\mathrm{CH_2}-\underset{\displaystyle \mathrm{Cl}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\displaystyle \mathrm{OOCCH_3}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\displaystyle \mathrm{Cl}}{\underset{|}{\mathrm{CH}}}-$$

(XLIV)

These polymerisation reactions can be made to take place by using a polymerisation catalyst, *e.g.*, benzoyl peroxide, and either heating, if necessary, heating under pressure, or carrying out the reaction in front of a powerful source of ultra-violet light.

CHAPTER II

THE HISTORY OF SYNTHETIC RESINS

Let us first answer two questions—

What are Synthetic Resins?

Resins generally are non-crystalline compounds, very complex in structure and of very high molecular weight, compared with the large majority of organic compounds in general use. Frequently they are mixtures of such complicated compounds, and they may range from viscous liquids to hard brittle solids. Many natural resins exist, *e.g.*, Canada balsam, colophony (rosin), dammar, congo and manilla copals, kauri gums, etc., and most of these products are derived from the gummy secretions of trees, particularly in tropical and subtropical climes. Synthetic resins are man's attempt to build up products, not necessarily similar in structure, but certainly resinous in character, of high molecular weight, and with fixed properties. In many cases natural products, *e.g.*, colophony or oil, have been used as one of the raw materials for the manufacture of synthetic resins, but the product is still a " synthetic."

Why are synthetic resins made?

For two reasons, to give large quantities of consistent product to the consumer, and to introduce properties which are not present in the natural resins. If we consider any one type of natural resin, *e.g.*, congo copal, this not only varies from area to area, but as it is a fossil resin and is derived from the hardened exudation of trees, the properties may vary, depending on the age of the samples and many other factors. Consequently each bag of resin can vary slightly. Synthetic resins, however, are made in large reaction vessels, sometimes in batches of five tons at a time ; moreover, the processes are controlled by chemists so that each batch is a very close match to the previous one.

Regarding the introduction of new properties, it is now possible to make products of very much better colour, colour retention and quicker drying than hitherto possible. Resistance to heat and weather are other properties which have been improved in the synthetics. Thus, the mass production of such articles as white enamelled gas heaters and refrigerators has been possible only by the introduction of synthetic resins which enable white finishes to be made which may be dried in 15–60 minutes in heated ovens. Natural varnishes in the same conditions would discolour badly.

Synthetic resins are the product of the 20th century. It is true that the first plastic (celluloid) was invented in the 1860's, but the cellulose products are not generally included in the field of synthetic resins although they are closely related. The first synthetic resin developed of any commercial significance was the phenol formaldehyde type, and this was introduced by Dr. Baekeland in the first few years of this century. It was developed largely as a plastic moulding resin, and this type, in very much improved forms, is now popularly known as "Bakelite." In the early days, attempts were made to use it as a film-forming material, with a certain amount of success. It could, for example, be used in spirit varnishes, but its scope in this field was limited, particularly owing to the difficulty of plasticising it.

The next development in synthetic resins was the introduction of the rosin-modified phenolic resin by Albert and Behrend, about 1910. This was an oil-soluble resin, and can best be described as a phenol hardened rosin type because only a relatively small amount of phenolic resin was used in its manufacture; but it became very popular when the initial teething troubles were overcome. These resins have often been called "Albertol" copals and have been used in place of natural copals in oil varnishes.

Oil varnishes consist essentially of a natural resin—a copal usually—dissolved in a natural drying oil, *e.g.*, linseed or wood oil, to which solvents or thinners were added to dilute it to a brushing consistency, and driers are added to speed up the rate of drying. We will ignore the last two components. Natural copal is not soluble in oils, so in order to make it soluble a process known as "gum-running" is used. The gum (resin) is placed in a pot over a burner and heated to about 300–350°C. during which process it decomposes and gives off about 20–25% of volatile matter, gases and so-called copal oil. At this stage it is fluid and will mix with oil.

The synthetic resins did not need this "gum running" and the manufacturers were quick to seize on this as a major deficiency of natural gums. If the loss due to foreign matter in the gums, together with that involved in gum running, is taken into account the synthetic resins are not much more expensive than the natural resins, and they are much more easily soluble in oil and give uniform products.

The introduction of this type of product resulted in quite new and novel ideas being used in the varnish trade, and the next development along this line was the introduction of the so-called alkyl phenolics in 1929 largely as a result of the work of Dr. Honel. These are pure phenolic resins with no rosin modifier, but they had been made oil-soluble by chemically modifying the phenol before reacting it with formaldehyde. Moreover, these resins were not only oil-soluble, they were also oil reactive. The rosin modified phenolic resins are slightly oil reactive. They dissolve in oil and on prolonged heating at a high temperature react to some extent by a process of interchange of acids, that is, some of the resin acids replace the oil acids in the molecule and vice versa. But these new oil reactive resins were far more reactive. A quite different reaction takes place vigorously at a lower temperature, and the phenolic body adds on to the oil molecule forming new and more complex products, which are extremely durable.

The main defect of all the phenolic types has always been the tendency for them to discolour, thus white paints made from them tend to yellow badly. This defect had been progressively reduced as each step had been made in the development of these resins, but around the 1930's a new type of oil-soluble resin was developed, the rosin modified maleic anhydride resin which was somewhat like the rosin modified phenolic resins in appearance, solubility and durability, but was excellent for the production of non-yellowing products. This development was the result of a new reaction discovered a few years previously by Diels and Alder. This can be described as the last major discovery in the oil-soluble types of resin to date.

Meanwhile, in 1913, a new and very important class of resins were being developed by the B.T.H. and G.E.C. companies—the alkyd resins, products of glycerine and phthalic anhydride which were later modified with oils. These resins can in some ways be regarded as already-prepared substitutes for the resin-oil product obtained by cooking natural or synthetic resin into oil, and they are marketed in a form in which they only need thinning with solvent. They make finishes which are excellent for gloss and colour, but are somewhat softer than the hard resin type of finishes. The outstanding property of the alkyd resins is their durability.

Around the 1920's Pollak began to introduce urea formaldehyde resins to overcome some of the well-known deficiencies of the phenolic resins. These urea resins have never been made oil reactive in the same way as the phenol resins. The 100% phenolics had always the defect that they could not be used for pale products due to the after darkening, pastel shades and whites were almost impossible, both from the point of view of plastics and surface coatings, and colour matching was difficult. Also, these products could not readily be used for products which came in contact with foodstuffs as they imparted an unpleasant taste. The urea resins overcame these defects. They are water white and do not change colour, and they can be used for any pastel shade or pure white. Plastic mouldings made from these resins can also be used for foodstuffs without any fear. Those attractive looking picnic articles made in plastic which have become so popular are mostly products of this type of resin.

The 1930's saw the introduction of a whole host of new types of resins. Of particular interest are the vinyl resins developed by the Carbide & Chemical Co., of America, which are the products of addition of various chemicals to acetylene, and the methacrylate resins which have been developed mainly as transparent plastics. Then there are the Nylon type resins, the product of highly organised large scale team research by Du Pont's in America, and polyethylene, a resin derived solely from ethylene gas, which is the product of similar team work by chemists in I.C.I.

To summarise, we can give the following date table for the better known resins.

1907	Phenol formaldehyde resins.	Dr. Baekeland.
1910–17	Rosin modified phenolic resins, oil soluble.	Albert.

1913	Alkyd resins.	B.T.H. & G.E.C.
1923	Urea resins.	Pollak.
1929	Alkyl phenolics.	Honel.
1930	Rosin modified maleic resins.	
1930–40	Methacrylate resins.	
	Vinyl resins.	
	Nylon resins.	Carothers.
	Polythenes resins.	

CHAPTER III

ROSIN AND ITS DERIVATIVES

ROSIN, or colophony, is an important ingredient of some synthetic resins, particularly the rosin modified phenolics, sometimes called "synthetic copals," and the rosin modified maleics. Rosin constitutes between 80–90% of these resins, and before the war about 3,000 tons annually were consumed in making resins for the paint and varnish and allied trades.

Natural rosin, or colophony, is a solid amorphous vitreous mass which exhibits conchoidal fracture. It is insoluble in water and acids, but is soluble in alkalis, in alcohol, ether, and certain other organic solvents. It is derived from the exudation obtained by tapping pine trees. The composition of these tappings is

Water and impurities	10–15%
Essential oil	19–21%
Dry products	66–69%

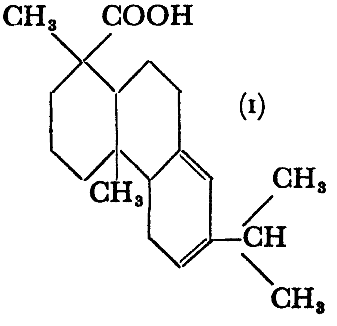
After settling and straining this gummy mass is distilled, usually in the presence of steam, and terpene spirit distils. The residue in the still is emptied out and allowed to solidify, and constitutes rosin; the distillate is marketed as turpentine. This rosin is called gum rosin, because it is obtained from the gummy exudations of the growing trees. In America, after the trees have outlasted their usefulness and have been cut down and cleared, the stumps and roots are blasted from the ground and any residue extracted by means of solvent. By this means another crop of rosin is obtained which, although belonging to the same family as the gum rosin, has certain differences and is therefore called wood rosin to distinguish it.

American, French and Portuguese colophony are the commonest types. The Portuguese variety is distilled more than the other varieties and is therefore more inconsistent in quality, having a tendency to be more crystalline.

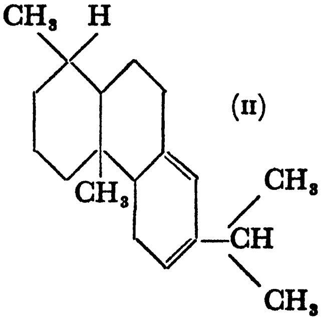
Rosin is graded according to its colour, the palest being the most valuable. The colour scales agree for rosins from any particular place but differ somewhat according to their origin, type, and the nature of the process used. It is possible, although this does not frequently happen, to get rosin of different colours in the same barrel.

According to the American system of rosin colour classification, A.B.C. etc., are very dark and the rosins become paler as the alphabet proceeds until the palest are WW, XWW, and WG, namely Water White, Extra Water White, and Window Glass paleness. The Continental system is the reverse, A grade being very pale, but super pale rosins are differentiated by the number of A's, *i.e.*, 4A and 3A are paler than A. High-class super pale colophonies may be obtained by a solvent purification process, or alternatively by vacuum distillation.

The melting point of rosin (capillary method) is about 55–65°C. and its acid value (*see* page 151) is 150–170. Actually the colophonies are probably oxidation products of the natural turpentines. Colophony contains about 90% abietic acid (or very similar acids) (I), the other 10% being made up of resenes or abietines (II)



(I)



(II)

Abietic acid is a crystalline substance with a melting point of 153°C., but it can exist in many forms. It is optically active; so is rosin. Optical activity is a property which some organic compounds possess, namely of rotating the plane of a flat beam of polarised light which is projected through a solution of the compound. The rotation may be clockwise to the face of the observer, that is to the right, or anticlockwise, or to the left. If the rotation is to the right the compound is said to be dextrorotary, and if it is to the left it is said to be lævorotary, dextro and lævo meaning right and left respectively. Compounds which have this power usually have the prefixes d- and l-, thus d-abietic acid is dextro-rotary. This phenomenon is examined and measured by means of an instrument called the polarimeter, which is described in any practical organic chemistry book, *e.g.*, Sudborough and Jones. The native colophonies are l-rotary. Changes occur during heat treatment of the rosins, and as they are mixtures of components possessing various degrees of optical activity, etc., certain physical properties will depend largely on the origin, history and method of manufacture of the sample, and may mean nothing unless this history is known.

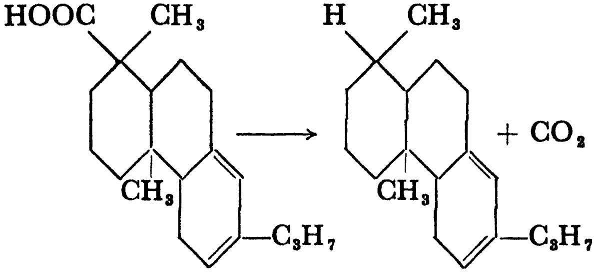
Rosin is an exceedingly cheap raw material. In immediate pre-war years its average price was £10–12 per ton and consequently this was a great incentive towards its use in varnishes. It has, however, certain defects, softness giving rise to slight tackiness in the varnish film, poor water resistance, brittleness, and also a tendency to crystallise in varnishes. Its acid value was also undesirable making it unsuitable to use with basic pigments (*see* page 31). The aim of the synthetic resin industry has been to make use of this cheap raw material while overcoming all these defects.

Storage of Colophony.

Rosin from America usually arrives in sealed light galvanised drums, which are not returnable. It is one solid block and is best kept so. Rosin from the Continent arrives in wooden barrels, usually holding 5–7 cwt., and due to the rough treatment they receive in transit, the barrels, when opened, contain, apart from very large lumps, a considerable proportion of very small nut size pieces and dust. Even though the consignment of rosin may be a super pale variety, this fine material should be separated by means of a large riddle and only the large pieces, bigger than a man's fist, used for super pale products. The dust should be used for darker materials. Rosin oxidises on storage in the presence of air, and rosin dust presents a very large surface for oxidation. If samples of dust and lump rosin are taken from the same consignment, and 50% solutions made in white spirit for comparison, the dust sample will give a darker and dirtier solution. This darkening will be enhanced by storing the solid samples for a few weeks.

Heat Treatment of Rosin.

When rosin is heated at temperatures around 200–250°C. for several hours the first thing that happens is that small quantities of volatile oil in the sample distil over, and the melting point of the rosin increases slightly. On prolonged heating a certain amount of decomposition occurs, decarboxylation, the abietic acids forming abietines.



These abietines are oily substances and consequently tend to lower the melting point of the rosin. The acid value also falls, as would be expected from the above reaction. Alongside this, the abietic acid in the rosin undergoes a change in optical activity. This is best seen in the following experiment.

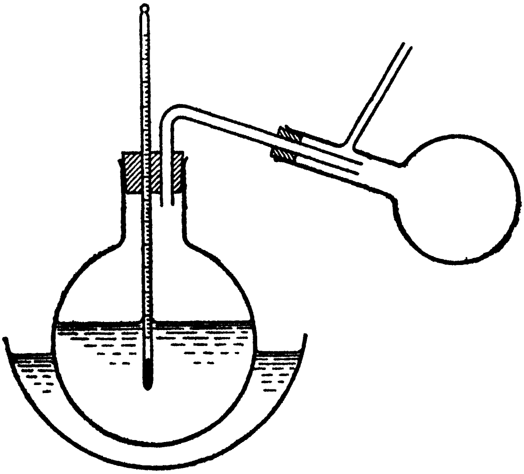


Fig. 1

EXPERIMENT 1.

800 gms. of Portuguese rosin were heated in a 1000 cc. bolthead flask immersed in a solder bath. The flask was fitted with a cork containing a

thermometer and an outlet tube for fumes. (*Fig. 1*). The temperature was kept at 250°C. for 21 hours and samples were taken at intervals and examined for melting point, acid value, optical rotation and crystallising tendency from white spirit and ethyl acetate solutions. The solubility of the various samples was compared by making 50% solutions of the resin in the solvent, warming to 60°C. to get complete solution. The solutions were then allowed to stand 21 days before examination.

TABLE I

Time in hours	M. P. °C	Acid Value	$[\alpha]_{20}^{D}$	Crystallisation W.S.	Et.Ac.	Benzene	Acetone
0	63/72	163	11·0°	Yes	Yes	No	No
7	64/69	148	−12·9°	No	,,	,,	,,
14	56/62	142	2·5°	,,	,,	,,	,,
21	42/53	133·5	25·6°	,,	,,	,,	,,

Optical rotation measured in degrees at 20°C. and was actually carried out on 5% solutions of rosin in methylated spirit.

Note.—Experiments taking several hours have often to be carried out over a period of several days, cooling overnight and then reheating. In the case of all experiments in which the resin is a molten solid, that includes all experiments containing rosin, the batch should not be allowed to cool in a glass flask, but should be emptied into a metal tray, and then when cold broken up and replaced in the flask for reheating.

Resins in flasks are best sampled by means of a glass dipping tube. A suitable sample tube can be made by cutting a length of glass tubing 12 ins. long and 10 mm. diameter. One end is tapered into a hole 3–4 mm. diameter and the other end is merely rounded by heating in a flame. When sampling resins the tube should be clean and dry. Dip the tube carefully into the resins, place a finger over the top end and then carefully remove the sample tube and allow the resin to run into a suitable receptacle. For solid resin a shallow tin dish will be good enough, the resin soon cools and can be broken out, for liquid resins a test tube is usually large enough.

As resins sometimes spit when the sample tube is placed in, care should be taken to see that the top of the tube does not point towards anybody during this operation.

The diagram below illustrates very well the alteration in optical activity of colophony, and the effect on the crystallisation of the rosin of prolonged heating.

It is obvious from this diagram that the optical rotation of the sample is of little use unless something of the previous history is known, since it is possible to obtain two distinct rosins with the same rotation, X and Y, but

X will change from dextro to lævo on heating.

Y will show an increased dextro rotation on heating.

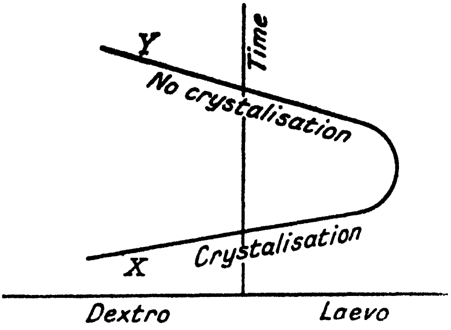


Diagram I

Although heating at high temperature is necessary to overcome the crystallising tendency of rosin in some solvents, it must be remembered that this stage will already have been arrived at in some consignments, due to prolonged heating in the still when removing turpentine.

Reference to Table I will show that quite a fair amount of decarboxylation has occurred during the heating. This may be accelerated and greater yields obtained if catalysts are used. Toluene sulphonic acid has been suggested as a suitable catalyst. If the product so obtained is then vacuum distilled, large quantities of hydrocarbon oils are obtained, boiling at temperatures up to 250°C. and pressures of 5–10 mm. These oils have been suggested as substitutes for linseed oil, but they are poor substitutes, the drying time being sometimes as much as ten times that of linseed oil.

The Effect of Air and Iron on Rosin.

(*a*) *Air.*

The effect of air on rosin at ordinary temperatures has already been referred to under "Storage." At moderate temperatures it is practically unaffected if kept in lump form but it rapidly oxidises when in the form of dust. On heating above its melting point, however, it rapidly darkens, unless kept in an inert atmosphere by using a closed melter and passing a stream of nitrogen, carbon dioxide, or even steam over the surface. This is demonstrated by the following experiment :—

EXPERIMENT 2.

300 gms. of pale French rosin, colour 2A, was heated at 250°C. for

7 hours and a current of air was blown over the surface. It was then cooled and a colour value taken.

Colour before heating	12 units.*
Colour after heating with air	170 units.

(*b*) *Iron.*

At ordinary temperatures metals have no effect on rosin but at high temperatures traces of metals have an appreciable effect. Iron causes considerable darkening of the rosin, consequently it is essential that no iron of any sort should enter reaction vessels. Particular care should be taken to exclude iron nails from the barrels in which rosin is contained. The effect is shown in the following experiment:—

EXPERIMENT 3.

300 gms. of pale French rosin were heated at 250°C. in an atmosphere of CO_2. The rosin was contained in a 500 cc. bolthead flask fitted with a cork in which were a tube for the entry of CO_2, an outlet tube for fumes and a thermometer. The flask was heated in a lead bath. A piece of iron weighing 0·3 gm. (0·1%) was introduced into the molten rosin and heating continued all day. A blank experiment without the iron was also carried out.

Colour of original rosin	12 units.
Colour of rosin heated 7 hours without iron	18 units.
Colour of rosin heated 7 hours with iron	220 units.

It should be pointed out that in spite of this, molten resin made from rosin is emptied from kettles into iron cooling trays with no detrimental effect. This is for several reasons. The surface of the iron trays in continual use becomes passive, the resin itself rapidly forms a cold crust on the outside which prevents the bulk of the resin getting in contact with the sides of the tray, and, of course, in most synthetic resins the acidity of the rosin has been neutralised.

Ester Gums and Lime-Hardened Rosins.

All natural rosins have very high acid values, about 150–170, and therefore these rosins cannot be used in varnishes in which basic pigments are incorporated, or which have to withstand washing with an alkali. Regarding the use of basic pigments,

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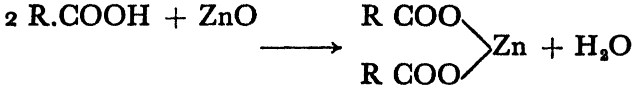
[*] Various methods are used to determine colour. In this particular instance a piece of resin 1 cm. thick was compared with tinted glass discs in a Hellige-Stock-Fonrobert Colorimeter. The tinted discs are so arranged to compare in colour with solutions of different strengths of iodine in potassium iodide solution, also in 1 cm. depth. Thus the rosin with colour 170 units had the same colour as a solution of potassium iodide containing 170 mgms. of iodine/100 cc.

the fault which occurs is called thickening, and is due to a salt of the rosin being formed by the pigment. To explain this simply, if we assume the rosin acid to have the formula R.COOH, then the reaction which occurs, if, for example, zinc oxide is used as a white pigment, can be represented as :—



$$2\ \mathrm{R.COOH} + \mathrm{ZnO} \longrightarrow \left.\begin{matrix}\mathrm{R\ COO} \\ \mathrm{R\ COO}\end{matrix}\right> \mathrm{Zn} + \mathrm{H_2O}$$

This salt is more complex in structure than the rosin and thickening of the paint occurs, which is most undesirable.

The resistance to alkali is also important. Consider the simple case of a housewife washing down paintwork, usually with soda in the water. This is a frequent occurrence and will soon have an effect on paint containing rosin.

A slight acidity is not undesirable in a varnish, because it helps to fix the pigment in a paint.

The high acidity of rosin can be reduced in two ways.

(*a*) By esterification of the rosin with glycerine, and

(*b*) By treatment of rosin with lime to form lime hardened rosin, or with zinc oxide to give zinc resinates.

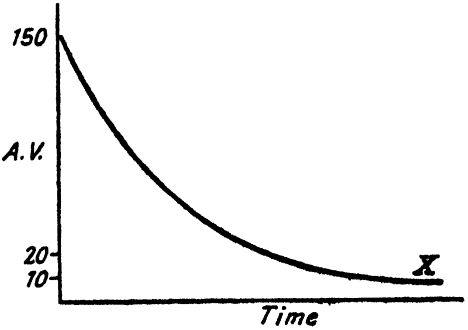


Diagram II

Esterification of Rosin.

Normally glycerine is used to esterify rosin and the products are called " ester gum " and are essentially glyceryl triabietates. Some forms of natural colophony yield ester gums which are prone to crystallisation from solvents, especially from ethyl acetate solutions. By heating the rosin at 250°C. until it has been made lævo rotary, and then dextro rotary again (*see* page

30), or alternatively by using certain forms of polyglycerol in place of ordinary glycerine, ester gums which can be guaranteed non-crystallisable can be made. It should be noted here that whereas the crystallising tendency of ester gums can be altered by heating the rosin, a crystalline ester gum cannot easily be converted into a non-crystallisable gum by the same treatment.

Ester gums are usually made with acid values of 5–10. It is not worth while trying to reduce the acid value below this. Diagram II shows how the acid value falls with time.

It will be seen that the acid value falls quite rapidly at first, but a point (x) is reached where the drop in acid value is very slow, and it is not a commercial proposition to attempt to reduce the acid value further.

In making ester gums the rosin is weighed into the reaction vessel and about 12% by weight of glycerol is added. This is approximately 20% in excess of the theoretical amount required to reduce the acidity to 5. The mixture is heated to 250–260°C. which is the optimum temperature. Below this temperature esterification is too slow, and above it the glycerine begins to vaporise too rapidly. Glycerine boils at between 290°C. and 300°C. Esterification catalysts are sometimes added but they are not absolutely necessary. Usually these esterification plants are fitted with a simple reflux condenser kept at a temperature of about 100°C. which is sufficient to allow water of reaction to escape, but will cool the glycerine as it vaporises and cause it to return to the reaction vessel. The course of the reaction is followed by determining the acid value. If the acid value is constant but is too high then insufficient glycerine has been added and more must be added. If, however, the acid value is sufficiently low, but a solution of the resin in white spirit, 1 : 1 is cloudy, then too much glycerine has been added and this can be cured by two methods, either by adding more rosin to absorb this excess, or by evaporating it out of the gum, usually by blowing in superheated steam.

When corrections have to be made

1 part of glycerine/1000 parts of resin lowers the acid value 1 unit.

1 part of rosin/100 parts of resin raises the acid value 1·5 units.

Before correcting the acidity of a batch of ester gum it is essential to make certain that it is constant, preferably over a period of 2 hours.

It is more practical to use extra glycerine at first, and to bring up the acid value if required, than to use insufficient, since in the latter case a little more glycerine will have to be added at a late stage in the reaction when the rate of esterification has slowed down considerably and the time required to bring the acid value down to within the correct limits will be much too long. Ester gums are cheap materials and speed of production is important.

Experimental.

In order to simplify these experiments no serious attempt was made to condense the glycerine vapour and return it to the reaction vessel. The apparatus which seemed satisfactory consisted of 1-litre flasks, fitted with corks bored to take carbon dioxide inlet tube, thermometer, and a short air condenser about 30 cms. long and 1 cm. diameter. The flasks were heated in lead baths.

EXPERIMENT 4. *Crystalline Ester Gums.*

400 gms. of French and American rosins were melted and heated to 250°C. 48 gms. of glycerine were added while the temperature was rising and the mixture well stirred, then kept at 250–260°C. for 8 hours.

	Acid Values.	
	French	American
0 hrs.	170	151
4 „	22·4	25
8 „	17·3	14

50% solutions of these products were made in various solvents and they were allowed to stand for several days.

Results—

	Acetone.	*Ethyl Acetate.*	*White Spirit.*	*Benzene.*
French gum		crystals	cloudiness	
American			cloudiness	

EXPERIMENT 5. *Non-Crystalline Ester Gums.*

400 gms. of pyrogenated French and American rosins were heated with 44 gms. of glycerine at 250°C. for 8 hours. The esterification was carried out as described above

	Acid Values.	
	French	American
0 hrs.	123·5	110
8 „	6	11

These products were quite soluble in acetone, ethyl acetate, white spirit and benzene and showed no signs of crystallisation.

Properties of Ester Gums.

Ester gums are somewhat harder than the corresponding rosins ; they do not tend to be so tacky when pressed between the fingers. The melting point is usually about 10°C. higher than the parent rosin, although new types of esters are now appearing on the market, using other alcohols, *e.g.*, pentaerythritol (which contains 4 alcohol groups), in place of glycerine, which melt as much as 30–40°C. higher than the rosin used. In other cases, alcohols of lower reactivity, *e.g.*, glycols and monohydric alcohols are used. These produce softer resins which are chiefly used as plasticisers.

The colour of the ester gum, if it has been properly made, is usually about the same as the original rosin.

Ester gums are more resistant to water and alkali than rosin. They are soluble in hydrocarbons, esters, acetone, etc., but unlike rosin, are insoluble in alcohols.

Lime Hardened Rosins.

Another method of reducing the acid value of rosin is to partially neutralise it with lime. These products are essentially calcium resinates. There are two methods of making these materials, one (EXPERIMENT 6) is to melt rosin at about 150°C., and to add the lime, as calcium hydroxide, in a very finely divided state, very slowly, to allow it to mix in without forming insoluble particles. It is essential that the lime for this purpose should be free from carbonates, as the rosin acids are not sufficiently strong to displace the carbon dioxide, and insoluble calcium carbonate would remain in the resin as insoluble white specks. The temperature is then raised to about 180–200°C. and kept just sufficiently long for a constant acid value to be obtained, then it is run out. An alternative method (EXPERIMENT 7), is to carry out the reaction in solution, using white spirit as the solvent. In this case a spirit of high boiling range, over 160°C., is used, but the reaction is carried out at about 100–120°C.

The usual quantity of lime used for hardening rosin is 6% of the quantity of rosin. This is sufficient to reduce the acid value of rosin from about 150 to 75 units and it will raise the melting point 40–50°C. The product is pale, but is not too soluble in solvents, and solutions should not be made by heating, preferably cold churning should be adopted.

EXPERIMENT 6.

Melt 500 gms. of pale rosin in a 1000 cc. bolthead flask, immersed in an oil bath. Raise the temperature to 150–160C° and stir well. Then add slowly, over about 30 minutes, 30 gms. of calcium hydroxide. When the addition is finished raise the temperature slowly to 180° and keep until the acid value is reasonably constant. Then pour out into a shallow iron tray.

EXPERIMENT 7.

Dissolve 250 gms. of rosin in 260 gms. of white spirit of boiling range over 160°C. This solution should be made in a 1000° cc. bolthead flask. Immerse in an oil bath and raise the temperature to 110°C. Then, with good stirring, add 15 gms. of calcium hydroxide and stir well for several hours until the acid value is reasonably constant.

CHAPTER IV

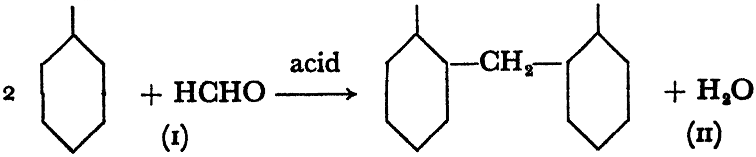
PHENOL FORMALDEHYDE RESINS

THE first of these resins made commercially were the so-called Bakelites which were introduced around the beginning of this century. They exist as two distinct classes, the Novolacs, which are products of condensation of phenol and formaldehyde, using an acid catalyst, and the Resoles, which are products of condensation of the same materials, but using an alkaline catalyst. Generally less formaldehyde is used in making Novolacs than Resoles. Many theories have been put forward to explain the manner in which this resin-forming reaction takes place, but as they are continually altering, and in many cases too advanced for this book, we will only deal with the simplest and most popular theory. Although this may not be strictly accurate it will at any rate help to explain many of the properties of these resins.

Resins in general may be divided into two distinct types, "Thermoplastic" and "Thermosetting." The names should be self-explanatory. Thermoplastic resins are those which fuse or soften on heating but solidify again on cooling, whereas thermosetting resins become harder, and more infusible and insoluble on heating. Novolacs are sometimes considered to be thermoplastic phenolic resins, although this is not strictly true, while Resoles are definitely thermosetting products.

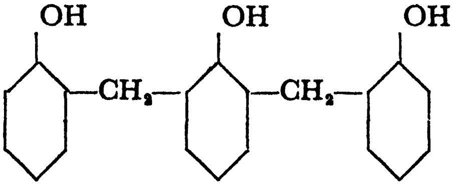
Acid Condensation.

The essential reaction may be illustrated as follows :—

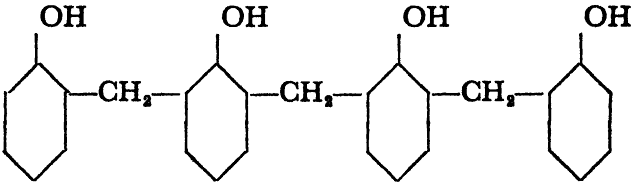


Remember that in the simplified formula for phenol (*see* page 16), each corner of the hexagon represents a C–H group, and in the above equation one hydrogen atom from each phenol has combined with the oxygen in the formaldehyde to form water, and the two phenol molecules are then joined by a *methylene bridge* (*see* page 3). Try working out the same reaction using the proper formula for phenol.

Now, according to the relative proportions of reactants and the time and temperature of heating it is possible for longer chains to be formed, namely :—



(III)



(IV)

and the average Novolac resin is a mixture of compounds of this type. Notice that in all these compounds the f/p* ratio is less than one, in the simplest case (II) it is 0·5, and in successive cases it is 0·66, 0·75, 0·80, etc. These resins are all soluble in alcohols and insoluble in hydrocarbons, and as the size of the molecules increase, due either to using excess formaldehyde, excessive heating or too much catalyst, the viscosity and melting point of the resin rises, and it becomes progressively less soluble in solvent, until eventually it is insoluble and infusible.

This can be illustrated by a series of experiments described later (EXPERIMENT 8, a, b and c), in which 1 molecule of phenol was condensed with ½ mol., ¾ mol., and 1 mol. of formaldehyde, using the same quantity of hydrochloric acid catalyst and the same reaction conditions in each case. The results were :—

f/p ratio	*Melting point.*	*Other properties.*
0·5	52/57°C	sticky and alcohol-soluble.
0·75	76/86°C	non-sticky and alcohol-soluble.
1·0	100/110°C	hard, and soluble with difficulty in alcohol.

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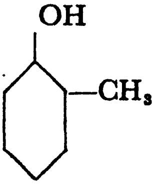
* $f/p = \frac{\text{number of gram molecules of formaldehyde}}{\text{number of gram molecules of phenol used.}}$

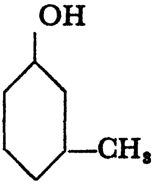
These resins are sometimes used in spirit varnishes, but their resistance to light and alkali, etc., is not too good.

Acid Condensed Cresol Resins.

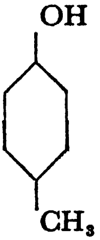
Cresols are derivatives of phenol in which one of the hydrogen atoms in the ring has been replaced by a methyl group, and consequently three structural isomers exist, namely ortho-, meta- and para-cresols.



ortho



meta



para

Notice that in ortho-cresol the hydroxy and methyl groups are adjacent, in meta-cresol they are separated by one carbon atom, and in para-cresol they are separated by two carbon atoms. Comparative experiments (*see* Experiments 9a, b and c) carried out with o-, m- and p-cresols using a fixed f/c* ratio, and acid catalyst show that meta-cresol is more reactive (*see* also p. 50). The condensation in this case took 3–4 hours to get a product substantially free from the smell of formaldehyde while the other isomers required 8–9 hours condensation, moreover the meta-cresol product was harder and of higher melting point. The results may be summarised as :—

	Time of Condensation.	*M.Pt.*	*Appearance.*
o-Cresol resin	8–9 hours	36/41°C	very sticky.
p-Cresol resin	8–9 „	58/64°C	hard and brittle.
m-Cresol resin	3–4 „	73/78°C	hard and brittle.

All these resins were completely soluble in methylated spirits but insoluble in white spirit.

Acid Condensations with Crude Cresols.

In industry, only crude cresols are used, the pure cresols

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* f/c=formaldehyde/cresol molecular ratio.

are too expensive. It is worth while seeing how this arises.

In this country the main source of phenols and cresols is the coal-tar industry. Coal tar, as it is first obtained from the retorts, is a complex mixture of compounds, and the first step in its purification is to wash it successively with acid and alkali, and so divide it up into basic materials, soluble in acid, acidic materials soluble in alkali, and neutral compounds. From the alkaline washes, by reacidification, with sulphuric acid, the organic acidic material is thrown out of solution, it is separated and distilled. This fraction consists essentially of phenols and cresols. The boiling points of these compounds are

Phenol	*B.P.* 181°C.
o-Cresol	191°C.
m-Cresol	203°C.
p-Cresol	202°C.

Unless costly methods of distillation are used it is only possible to obtain very rough separations. During such a distillation, pure phenol may be quite readily obtained in the first distillate, then a fraction of phenol containing also ortho-cresol, and, finally, a crude cresol fraction containing mixtures of all three cresols, but with a low or high proportion of meta- and para-cresols depending at just what stage in the distillation the fraction is taken. The meta-cresol content is always regarded as being the most important factor, consequently if a large amount of ortho-cresol is left in the high boiling fraction then the meta-cresol will be low, possibly 38–40%, but if the cut is taken at a higher temperature, when some of this ortho-cresol has already distilled into the phenol/o-cresol mixture, then the meta-cresol content of the crude cresols may be as high as 60%. Nowadays three forms of commercial cresols are available with 38–42%, 50–52% and 60% meta-cresol contents. As the meta-cresol content is important methods are given for its determination on page 156.

Composition of Commercial Cresols Nos. 554, 555, 559.

	554	555	559
% of m-Cresol	60·5	54·4	38·5
% of Pyridine	0·13	0·07	0·11
% of Naphthalene	nil	nil	0·26

Distillation Range.

	554 % *Distillate*		555 % *Distillate*		559 % *Distillate*
170–195°C	0·8	160–191°C	2·4	99–100°C	4·8
195–197	7·2	191–194	8·8	190–192	6·4
197–199	8·0	194–196	17·6	192–193	7·2
199–200	72·0	196–198	64·8	193–194	15·2
200–201	11·2	198–199	5·6	194–195	22·4
				195–196	20·0
				196–197	8·0
				197–198	8·0
				198–199	4·0
				199–200	2·4
				200–201	0·8

No. 554 is a good commercial cresol 60%/40% m-/p-.

Condensations carried out with various grades of crude cresols again using the same formula as for previous experiments (*see* EXPERIMENT 9) give resins of somewhat higher melting point than those obtained under similar conditions with pure meta-cresol. Meta-cresol is more reactive than o- and p-cresols, or conversely the reactivity of the two latter cresols is comparatively small, consequently the ratio formaldehyde/meta-cresol is higher in the case where crude cresol is used, and although the softer o- or p-cresol resins would tend to reduce the melting point, they have to be present in excessively large amounts before exerting this effect when the extra amount of formaldehyde is employed. The results of experiments 10 a, b, and c, below, in which one molecule of crude cresol is condensed with a half molecule of formaldehyde are :—

% *meta-Cresol content of Cresol.*	*Melting point of Resin.*
60	78/87°C.
54	74/80°C.
38	69/78°C.

Further additions of formaldehyde to these resins tend to increase the melting point. Thus, when one molecule of crude cresol is condensed with ½ molecule of formaldehyde (as above) and then with a further ¼ molecule making ¾ molecule in all, these results were obtained :—

	Melting point of Resin.
60% meta-cresol	94/105°C.
54% „ „	92/102°C.
38% „ „	82/93°C.

So far we have dealt nebulously with the ways phenols and formaldehyde can react together without actually describing the methods of manufacture. Now is a suitable time.

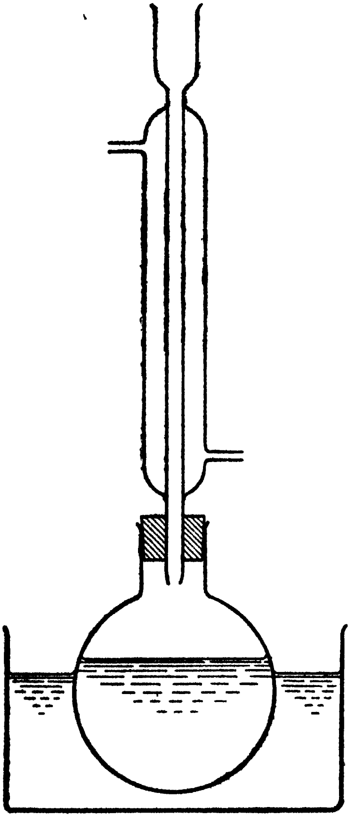


Fig 2

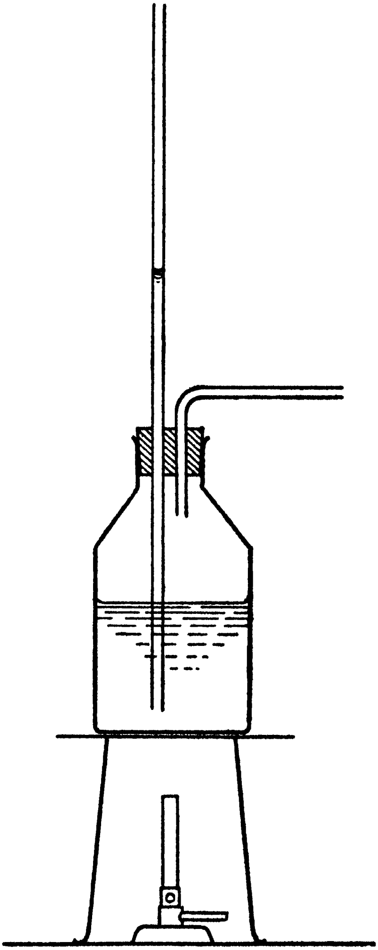


Fig. 4a

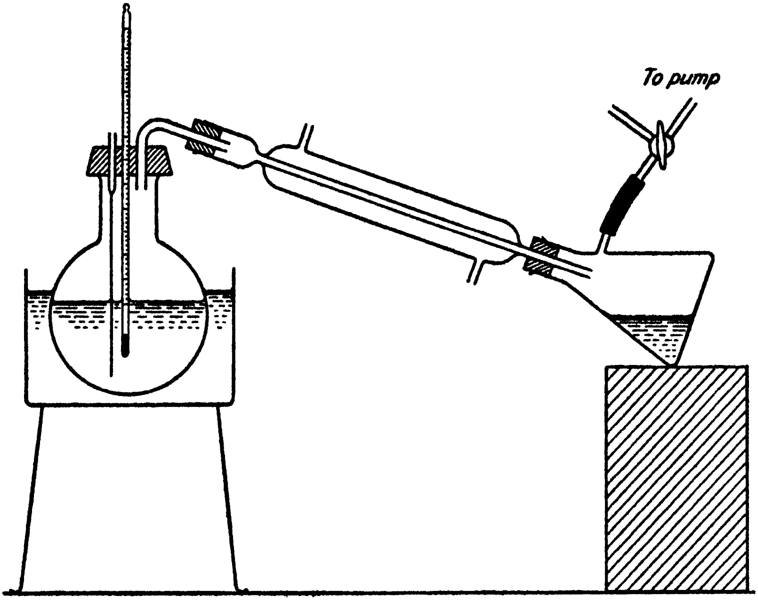

To pump

Fig. 3

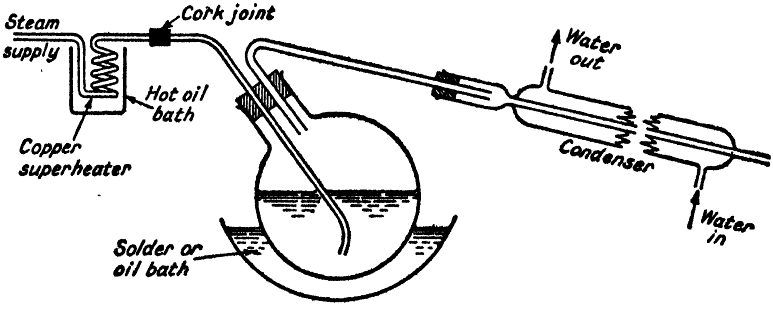

Steam supply
Cork joint
Water out
Hot oil bath
Copper superheater
Condenser
Water in
Solder or oil bath

Fig. 4

Methods of Manufacture of Acid Condensed Resins.

The type of apparatus required in the laboratory is shown in *Figs. 2, 3, and 4,* but a comprehensive plant unit is shown in *Fig. 5.*

The reaction vessel *A* is fitted with an outlet cock *O*, a stirrer *S* driven by a motor *M*, a thermometer *T*, and various other fittings, such as charging hole, sight glasses and vacuum gauge, relief valve, etc., all fitted to the lid of the vessel. The lower portion is jacketed (*B*) and this jacket allows steam-heating or water-cooling. Thus, by closing the water in and out valves, the latter leading to a steam trap, the pot can be heated by steam, and by alternatively closing the steam valves and opening the water valves, it may be cooled. The vessel is also fitted with a condenser *C* for refluxing and distilling. On refluxing the vapours pass up the tube *E*, condense in the condenser and return through the bent tube *P*. When distillation is required

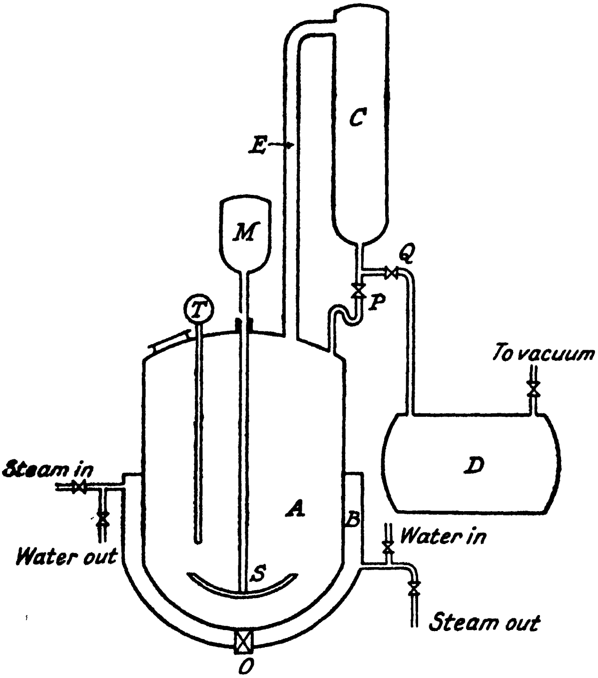


Fig. 5

the valve *P* can be closed, and *Q* opened and the distillate from condenser runs into the receiver *D*. Vacuum may be applied if necessary.

When phenol (or cresols, etc.) and aqueous formaldehyde, which is normally a 37% solution by weight of formaldehyde in water (usually containing a trace of an alcohol as a stabiliser) are heated together in a reaction vessel in molecular proportions of $1 : <1$, with an acid catalyst, *e.g.*, sulphuric acid, or formic, oxalic, etc., the mixture first forms a clear homogenous solution, but after boiling for a time it begins to go cloudy, and resin falls out of solution in droplets. In a short time, if there is no efficient stirring, two layers are formed, the lower one being resin, and the upper one aqueous, consisting not only of water arising from the aqueous formalin, and also of reaction, but also containing unreacted phenol and formaldehyde, and a small amount of water soluble resin. Consequently, to get good yields, the heating is normally continued for some time after the " drop point." The time at reaction temperature before the resin drops out of solution is called the " drop time," or " time of clouding," etc., and it is a critical time in the resin reaction; its length is dependent on many factors, *i.e.*, the ratio of raw materials, quantity of catalyst, and the reaction temperature. It should always be noted, as it can be used to measure the relative reactivities of various raw materials, or to compare the strengths of catalysts, or where several batches of the same resin are being made, it will indicate whether the charges are identical or not.

As the presence of free water and uncharged reactants in a resin causes serious defects, whether it is used for plastic moulding or for synthetic lacquers, it must be removed. Two methods are sometimes used, one is to distil the volatile products from the resin by distillation under reduced pressure and the other is to distil these volatile materials at a higher temperature, and blowing hot steam through at the same time. Modifications may be made to these methods. Thus, some workers remove the acqueous layer which has settled out, either by decantation, or by sucking it out, thereby hoping to shorten the time of distillation, but where this method is practised poorer yields are obtained as the aqueous layer contains soluble resin. Whichever method is used, however, the resin is normally distilled until it is a hard solid when cold. It can be made to low or high melting points according to the degree of heating, and the proportion of formaldehyde to phenol in the original formula.

It has been stated above that in these resins an f/p ratio 1 : 1 is used. If a formula is used in which the initial f/p ratio is greater than one it is merely a waste of formaldehyde, as the aqueous layer, after the initial refluxing, will be found to have a high formaldehyde content, accounting for this excess, although in some cases, this extra formaldehyde causes the formation of heat-hardening resins (page 57).

Experimental.

Before repeating any of these experiments a word of warning is necessary about the handling of phenol and formaldehyde. Phenol, or carbolic acid to give it its common name, is a solid, m.pt. 40°C., and is very corrosive. When cold it is very hard, and attempts to break the lump phenol may result in pieces flying around. Care must be taken to prevent it coming in contact with the skin, particularly the face. It is a wise precaution to wear goggles or eye-shields when handling it. An easier way of weighing up the phenol for experiments is to melt it, either by standing the can in an oven or in a bath of hot water at about 50°C. It can then be poured out. In some laboratories the stock is kept as phenol hydrate, *i.e.*, $2C_6H_5OH.H_2O$. This is made by diluting the molten phenol with sufficient water to make it into a solution, 92% phenol, 8% water. This phenol hydrate is liquid at temperatures of about 20°C. Allowance must of course be made for the water when using phenol hydrate in formulæ containing phenol.

Formaldehyde is less dangerous. It has an unpleasant smell to which one soon becomes accustomed, but it causes the skin to harden on contact. After using either phenol or formaldehyde the hands should be washed; also any place which may have been splashed.

Experiment 8. *Phenol formaldehyde Condensation using Acid Catalyst.*

Three experiments were carried out—a, b, and c.

	a	b	c
Phenol	94 gms.	94 gms.	94 gms.
37% Formaldehyde	40 gms.	60 gms.	80 gms.
Conc. HCl	1 cc.	1 cc.	1 cc.
f/p ratio	·5	·75	1·0

The mixtures were heated in 500cc. round-bottomed flasks fitted with reflux condensers (*Fig. 2*). The flasks were immersed in water baths at 95°C. and refluxing was continued until there was no further smell of formaldehyde, then they were removed from the water, carefully wiped dry, and heated in a solder bath (*see Fig. 4*). The neck of each flask was closed with a cork in which was fitted a thermometer, an outlet to a condenser and an inlet tube dipping into the resin, which was later to be fitted to a superheated steam supply. At first the resin was distilled without steam, until the aqueous products of reaction were removed and the temperature inside the flask began to rise to 150°C., then superheated steam was blown through at 180°C., and the resin itself maintained at 150°C. The steam travels through the resin, then condenses in the condenser. It carries with it steam volatile constituents of the resin, chiefly unreacted phenol, and the steam distillation is continued until the distillate no longer smells of phenol. The apparatus for the supply of steam, if it is not available in the laboratory, is fairly simple and is illustrated in *Fig. 4a.* It consists of a 1 gallon can into which is fixed a cork with two holes. In one hole is inserted a length of glass tubing, about 4 ft. long, and ¼-in. base which dips into the can to about ½-in. from the bottom. It is essentially a safety valve allowing a steam pressure of about 36-in. but no more. Into the second hole is inserted a length of copper tubing. This is joined to a superheater which is essentially a copper coil heated in an oil bath, kept at about 200°C. By heating water in the can, wet steam is obtained which on passing through the superheater becomes dry steam, and this can be blown through the resin. A few tips are worth noting here.

(1) The join from the copper tube to the glass tube going into the flask is best made with a bark, or asbestos cork, but not with rubber tubing which soon becomes gummy.

(2) The flask for the steam distillation is best arranged, as in *Fig. 4*, tilting backwards so that resin does not splash up into the outlet tube and thence into the condenser.

(3) Be very careful that dry steam, and not wet steam, *i.e.*, steam containing droplets of water is passed into the resin. A drop of water entering hot resin readily vaporises and causes nasty foaming or splashing. This can be avoided if the join from the superheater to the steam inlet tube in the flask is left unmade until hot steam is blowing through, then the flame should be removed from the boiler for a few seconds, the joint rapidly made, and the steam started again. The cork used for the join need not be a tight fit, it can be a bit loose, sufficiently so to allow a rapid join to be made.

The results of experiments a, b, and c have already been tabulated, page 38. They show how the resins increase in melting point as the f/p ratio rises from 0·5 to 1·0.

EXPERIMENT 9. *Cresol Condensations. Difference between o-, m-, and p-.*

Three parallel experiments were carried out as described above, using the following formula.

o-, m-, or p-Cresol	108 gms.
37% Formaldehyde	40 gms.
Conc. HCl	1 cc.

The mixtures were condensed at 90°C. until no smell of formaldehyde remained, then steam distilled until the distillate was free of cresols. The results have been discussed on page 39. The resin from para-cresol was by far the palest in colour.

EXPERIMENT 10. *Crude Cresol Condensations.*

These experiments were made using the same quantities as those in experiment 9, but using commercial cresols in place of the pure cresols. The results have been shown in the table on page 41.

Vacuum Distillation in Place of Steam Distillation.

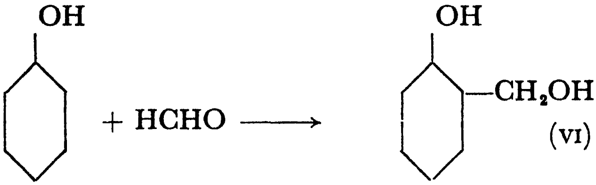
In many cases, after the initial condensation, the volatile products are removed by vacuum distillation. The method is clean, and simple, but it may not give products as completely free from uncombined phenol as the method of steam distillation. The apparatus is shown in *Fig. 3.* For vacuum distillations rubber bungs are essential. If we work backwards from our source of vacuum, which may be a mechanical vacuum pump, or a water pump, thickwalled rubber tubing is used to connect the pump first to a three-way stopcock, then to a receiver, which can be a vacuum filter flask. Into the vacuum flask is fixed a good condenser, preferably a double surface condenser, although only a Liebig condenser is shown in *Fig. 3.* The condenser is joined to the resin reaction flask by a wide bent tube which is fitted to a large rubber bung, into which are fitted a thermometer, and a glass bubbler, made by drawing a piece of glass tubing out into a fine capillary. This allows a fine stream of bubbles to pass through the resin during distillation and avoids bumping of the flask which might cause an accident.

It will be noted that the rubber bung connecting the flask to the condenser is upside down. There is a reason for this. If a rubber bung is used for vacuum distillation and is pushed into the neck of the flask in the normal manner, then when vacuum is applied it is sucked well into the neck. This makes it difficult to remove when the experiment is finished. But there is another reason. Sometimes the resins being distilled give off materials which are solid at normal temperatures and if these solidify in the condenser, or even in the rubber tubing without being noticed, a pressure, and not a vacuum may begin to build up in the flask, and a nasty accident might occur. Now all bolthead flasks nowadays are made with level tops to the necks, and if an excessively large bung is used, inverted, it may be held against the top of the neck of the flask for a minute or two when the vacuum is first applied, and the vacuum is sufficient to hold it. The bung is easily removed by breaking the vacuum when required, but, if a blockage occurs, it acts as a safety valve and falls off as soon as the vacuum is reduced.

When only the products of a phenol formaldehyde condensation are being distilled under reduced pressure and a water pump is being used, if the distillate is not required, then the condenser may be dispensed with and an apparatus like that shown in *Fig. 1* can be used.

Alkaline Condensation.

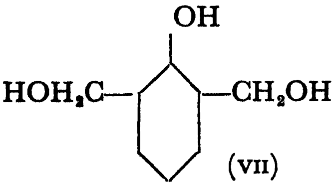
With alkaline condensations of phenol and formaldehyde compounds quite different in properties from the Novolacs are formed, these are the so-called phenol alcohols. The reaction is in its simplest form :—



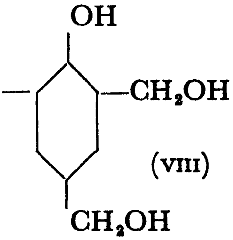
(VI)

Note that no water has been eliminated yet. Work out this reaction using the proper structural formula for phenol.

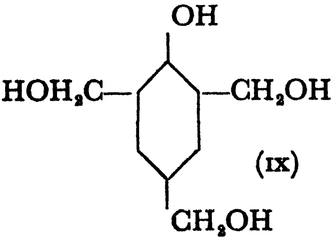
In actual practice as many as three formaldehyde molecules will react with one molecule of phenol, and phenol dialcohols (formulæ VII and VIII) and a phenol trialcohol (formula IX) as well as the phenol monoalcohol above (formula VI) may be formed.



(VII)

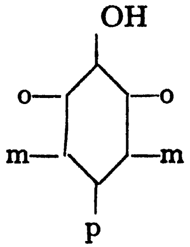


(VIII)



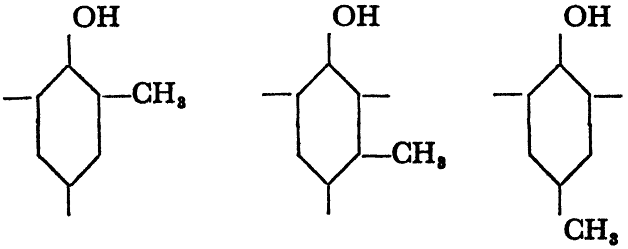
(IX)

At this point it is as well to discuss the reactivities of various phenols, etc. If we examine the simple formula for phenol it will be seen that



the six carbon atoms in the ring are different. One carbon atom has the phenolic hydroxy group attached to it. Two carbon atoms marked o- are adjacent to this group and are equally influenced by its reactivity, two other carbon atoms marked m- are further away, but again equal to one another, and the last carbon marked p- is entirely on its own. These various positions in the phenol ring are named ortho-, meta-, and para- respectively, and have been referred to in the case of the various cresols already mentioned under acid catalysed resins.

Now, if we examine the phenol alcohols above (page 49) it will at once be noticed that the formaldehyde does not attach itself to a phenol molecule at the meta- position, only the ortho-, or para-. This is a very positive statement made with very little proof, but let us now examine the cresols.



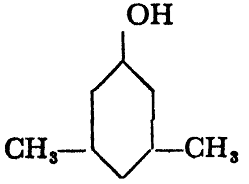
ortho-cresol meta-cresol para-cresol

If we apply our rule that in an alkaline condensation with formaldehyde, no addition can occur at the meta- group, we will see that :—

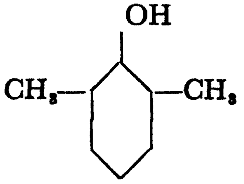
Ortho-cresol	has 2 reactive positions only.			
Meta-cresol	has 3	„	„	as with phenol.
Para-cresol	has 2	„	„	only.

That is, meta-cresol is far more reactive than ortho- or para-cresols. This has already been shown to be true in the case of the acid condensed resins, page 39, but it can also be shown in the case of the alkaline resins, Experiment 15.

Again, the substituted phenol, 3·5·xylenol (formula x) where both meta- positions are blocked by methyl groups is as reactive as phenol, as would be expected, but the symmetrical 2·6·xylenol



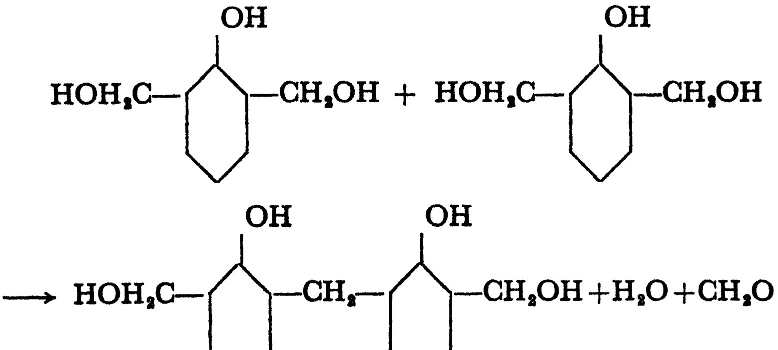
(x)



(xi)

(formula xi) with both ortho- groups substituted, reacts very slowly with formaldehyde and does not resinify.

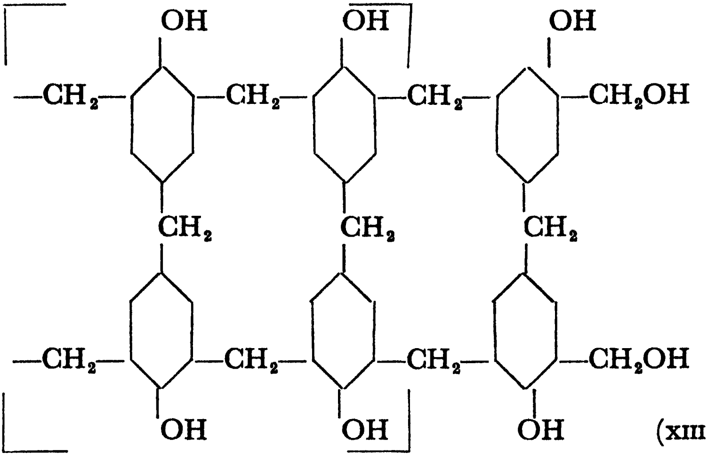
Consider another fundamental property of these resins. Note that in the case of phenol and meta-cresol, two or three molecules of formaldehyde will react with one of phenol, and in the case of the ortho- and para-cresols only one or two molecules of formalin are required for one of cresol, *i.e.*, the f/p ratio in this case is far greater than 1 and is normally about 1·5. The reason for this is very clear when we consider how the resin combines with itself to form the final thermoset product. This is done by the molecules of phenol alcohols linking together and forming huge molecules, losing water, and sometimes formaldehyde in the process, *i.e.*,



(xii)

Notice that again the molecules are linked together by a *methylene bridge*.

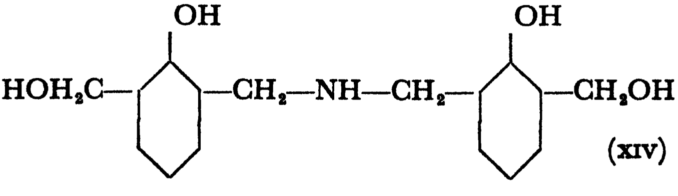
Now, if we remember that a phenol trialcohol can be formed, then the most complicated structure we can picture, by having many such trialcohols linked together is depicted below (formula XIII), and the smallest unit that can be reproduced is that shown in large brackets, which is made up of 4 phenol nuclei and 6 methylene groups, *i.e.*, an f/p ratio of 1·5. Obviously it is a waste of formaldehyde to start the reaction with an f/p ratio greater than 1·5 unless some special properties are required of the resin before it reaches the infusible state.



(XIII)

Types of Alkaline Condensed Resins.

There are two distinct types of alkali catalysed resins, those in which ammonia is used as a catalyst and those in which other alkalis, caustic soda, barium hydroxide or magnesium oxide, etc., are used. The ammonia condensed resins have a somewhat different structure from the compounds made with stronger alkalis which have been formulated above. The ammonia actually combines into the resin yielding a product with a structure which may be represented diagrammatically as



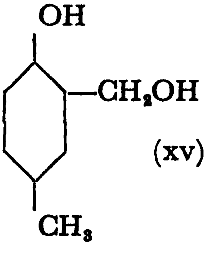
(XIV)

It is assumed that the nitrogen is bound into the molecule in some such form as this for the following reasons :—

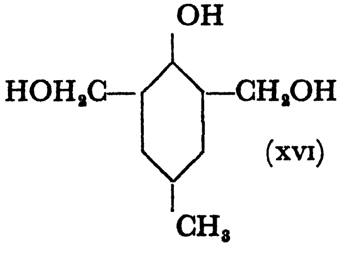
On boiling these resins with strong caustic soda solution, the normal method employed to release ammonia from compounds in which it is loosely bound, practically no ammonia is evolved; but these products all have a relatively high nitrogen content which can be determined by the rather drastic methods normally employed in quantitative organic analysis, *i.e.*, the Kjehdahl method.

The main differences between these nitrogen containing resins and those made from the stronger alkalis are best seen in their applications. Thus in the plastics industry the ammonia condensed resins are preferred for articles which are to be used for electrical purposes, as the small amount of sodium salts left in the alkaline condensed resins acts as an electrolyte and results in poor electrical insulation properties.

Regarding these alkaline condensed resins, it has been possible to prepare and isolate as crystalline compounds some of the first products of reaction of formaldehyde and phenols. Thus when para-cresol is reacted with various quantities of formaldehyde under carefully controlled conditions, two crystalline compounds which may be called para-cresol mono alcohol (formula xv) and p-cresol dialcohol (formula xvi) can be isolated. The structures of these compounds



(xv)



(xvi)

have been determined and the method in which they condense with themselves to form resinous bodies has been studied with the result that we now have some slight idea of the general way in which phenol formaldehyde products are built up. These final hardened products, by the way, are sometimes called Resites.

Methods of Manufacture of Alkaline Condensed Resins.

Essentially the methods of manufacture are the same as those used in acid condensed resins. Similar reaction apparatus is used (*see Fig. 5*) and the process involves an initial condensation reaction during which time the mixture is refluxed, followed by a dehydration process at reduced pressure. The steam distillation process of dehydrating is rarely if ever used for this type of resin, and owing to the extreme sensitivity of these products, the dehydration is normally carried out at as low a temperature as possible, usually around 60°C.

Now, these alkaline condensed resins are the true thermohardening products and they must be treated with respect. All the time they are being heated, and even when they are being stored at room temperature, they are thickening up and hardening, and they must be carefully controlled throughout the process to avoid fully hardened resins resulting. This state of affairs can be observed right from the beginning of the process. Thus, on heating phenol and formaldehyde together with a trace of caustic soda, the mixture first forms a homogeneous mixture, and the temperature gradually rises until a time arrives, at a temperature around 60–80°C., depending on whether large or small amounts of catalyst have been used, when the reaction between the phenol and formaldehyde begins. This is an " exothermic reaction," *i.e.*, a great deal of heat is formed which is actually sufficient to heat the batch of material to boiling point and keep it boiling for some time. It is obvious that when this point is reached where the initial " kick-off " begins the source of heating must be removed, and if necessary some means of gently chilling the product is desirable since otherwise a very vigorous reaction resulting in the product foaming out of the apparatus may result. In the apparatus shown in *Fig. 5* and described on page 43, the product can be heated by circulating steam or hot water in the jacket and cooled by turning off the steam and running cold water through it.

After this initial reaction, the resin is kept refluxing for a given time which depends on the properties required, then cooled and vacuum distilled.

The point when the dehydration is finished is usually determined by working to a fixed viscosity of the resin, but sometimes a fixed yield of resin is worked to. In the laboratory this is easily accomplished by weighing the flask and resin, assuming that the weight of the empty flask is known. In a resin pot, the volume of the resin is measured by means of a dipstick.

During the refluxing the resin " drops " (*i.e.*, precipitates) and this point is often taken as the end of that stage of the reaction. Too long heating however during this condensation, or too high a temperature during dehydration, may result in the resin beginning to thermoharden, which again is an exothermic reaction, which progresses at an ever increasing rate. It is as well to remember, too, that these resins in their thermoset state are very good heat insulators, and therefore attempts to cool resins by circulating cold water round the outside of the reaction vessel have little effect on the inner hot core. Unfortunately, in these days of high speed production in industry users of phenolic resins for either plastic moulding, or surface coating applications insist on the products they are using taking as short a time as possible to " cure " or thermoset, consequently the resin manufacturer has to keep his products in the reaction vessel for a dangerously long period to take them as near this final stage as possible.

It is possible to compare the relative reactivities of various resins of this type by measuring what are called transformation times or temperatures. These are described on page 157.

Experimental.

In these experiments the quantity of catalyst used and the control of the reaction temperature is most important.

EXPERIMENT 11. *Alkaline Condensation of Phenol and Formaldehyde.*

Phenol	94 gms. (1 gm. mol.)
37% Formaldehyde	80 gms. (1 gm. mol.)
N NaOH	12 cc.

were condensed together for 6 hours at 80°C. and 2 hours at 90–95°C. using a 500 cc. round bottom flask and reflux condenser, as shown in *Fig. 2*. The resin dropped and separated into two layers, the upper aqueous layer was removed by decanting and the resin was distilled in vacuum until it was clear, and a drop taken out was cold clear. Note the various stages of the resin during distillation. At first it is hot cloudy, then it becomes hot clear, and finally cold clear. The product is a brown viscous gum soluble in methylated spirits.

If a similar experiment is carried out using double the quantity of formalin, the product after refluxing for the full 8 hours is a pale thick hard resin which cannot be removed from the flask. In order to make a soluble resin with this quantity of formalin a much shorter reaction time is necessary, about 2 hours.

EXPERIMENT 12. *Preparation of Phenol Dialcohols.*

Phenol	94 gms. (1 gm. mol.)
$Ba(OH)_2$	5 gms.
Formalin	160 gms. (2 gm. mols.)

A mixture was made of the phenol and barium hydroxide by warming in a 500 cc. flask fitted with condenser. It was then cooled and the formaldehyde added slowly through the condenser, mixing well by shaking. The mixture was heated at 60°C. for 3 hours; then carbon dioxide was bubbled in to precipitate the barium salts as carbonates. The liquid was filtered free from barium carbonate and was vacuum distilled until the residue weighed 154 gms. This product was assumed to be a mixture of phenol dialcohols, although it was probably contaminated with mono- and trialcohols.

EXPERIMENT 13. *Preparation of p-Cresol Monoalcohol.*

Caustic Soda	80 gms. (2 gm. mols.)
Water	2000 gms.
p-Cresol	216 gms. (2 gm. mols.)
37% Formaldehyde	160 gms. (2 gm. mols.)

The caustic soda was dissolved in the water and the p-cresol added. The solution was well cooled and the formaldehyde slowly added with shaking. The mixture was allowed to stand for 8–10 days at room temperature in a closed flask. At the end of this period CO_2 was passed into the mixture to decompose the Na salt. The solid material was extracted three times with ether, and the aqueous portion twice. The ether extracts were combined and vacuum distilled at 20°C.

The residue which consisted of monoalcohol and cresol was shaken with chloroform and filtered, the solid being well washed with chloroform to free it from cresol. It was then recrystallised from chloroform, and was obtained as white crystals, m.pt. 105C°. Yield 15%.

Effect of Heat. On heating it decomposes giving off formaldehyde. It then distils slightly, with a cresolic smell, and finally chars, giving an infusible resite.

EXPERIMENT 14. *Preparation of p-Cresol Dialcohol.*

A solution of 16 gms. of NaOH was made in 30 cc. of water, in a 1500 cc. flask, and 216 gms. (2 gm. mols.) of p-cresol were added in small portions, with much shaking and gentle warming, thus making a solution. 324 gms. (4·05 gm. mols.) of 37% formaldehyde were slowly added with much shaking, the temperature being kept below 40°C. The mixture was then heated at 40°C. for 2–3 days, until crystals began to separate. It was then allowed to stand overnight, and the thick crop of crystals was filtered off, freed from mother liquor, washed with cold water and dried in a vacuum desiccator.

The mother liquor was neutralised with CO_2 and some crude dialcohol was filtered free of cresol. After well washing it was added to the main yield.

A portion was recrystallised from alcohol, giving white prisms, m.pt. 128·5C°.

Yield of Dialcohol—69–70%.

EXPERIMENT 15. *Alkaline Condensation of Commercial Cresols.*

Three experiments were carried out using commercial cresols Nos. 554, 555 and 559, containing 60, 54 and 38% m-cresol respectively. The formula used was :—

Commercial cresol	108 gms. (1 gm. mol.)
37% Formalin	80 gms. (1 gm. mol.)
N Caustic Soda	12 cc.

Heat at 65–70°C. for 5 hours, using the apparatus described in experiment 8. The resin is then distilled in vacuum at 55°C. until it becomes clear.

A further 40 gms. of formaldehyde is then added and the reactions continued until there is no further smell of formaldehyde. The product is again distilled in vacuum at 60C°, until a solution in alcohol is clear. The products are now compared.

Results.

Cresol No. 559	Gave a dark brown fluid gum.
Cresol No. 555	Gave a brown sticky gum.
Cresol No. 554	Gave a pale, cloudy and elastic resin which could not be vacuum distilled.

All samples were spirit-soluble, although the latter was not extremely soluble.

Phenol Formaldehyde Resins as Plastics Raw Materials.

Generally speaking the greater part of this book deals with synthetic resins utilised for paints and varnishes, but no account of the chemistry of phenol formaldehyde resins would be complete without some reference to their use in the plastics industry, as laminating resins, and as constituents of moulding powders, used for the manufacture of so-called bakelite mouldings, which are now so common. By far the greater bulk of modern plastic mouldings are made from such materials.

It has already been shown that phenol formaldehyde resins made with an excess of formaldehyde are thermosetting, they are converted to infusible insoluble resites by long standing at low temperatures, and more rapidly by heating at temperatures up to about 200°C. The resites take the shape of the vessel in which they are heated but are porous, due to the free evolution of water and formaldehyde while being heated, and they are also extremely weak and brittle. By very careful preparation resins can be made which may be cast into shapes and cured by moderate heating, these are usually not brittle but are of low strength. Stronger moulded articles can be made more easily by using resins which have had large quantities of fillers incorporated which increase the tensile and impact strengths considerably, and if the curing process is carried out under high pressures the porosity is eliminated.

Moulding Powders.

Moulding powders consist essentially of equal parts of resin and filler, together with colouring materials, plasticisers, catalysts and lubricant. The common fillers are wood flour, cotton clippings, chopped fabric, or minerals such as mica or asbestos. Their function is to increase the strength of the resin and to cheapen the product.

The strength of mouldings made from the same phenolic resin using different fillers can be shown below :—

Filler.	*Tensile Strength**	*Impact Strength**
Wood Flour	7000–8000 lbs./sq. in.	0·16–0·20 ft. lb.
Mica	4000–5500 lbs./sq. in.	0·12–0·18 ft. lb.
Ground Cotton	6000–7000 lbs./sq. in.	0·30–0·35 ft. lb.
Long Cotton Fibres	5000–6000 lbs./sq. in.	0·50–0·80 ft. lb.
Fabric Cuttings, ½-in. squares	4500–5500 lbs./sq. in.	1·00–1·60 ft. lb.

If wood flour is used as a filler, the moulded articles have fairly high tensile strength, *i.e.*, strength in tension, but low impact strength, *i.e.*, resistance to impact. By the use of cotton fibres for fillers, the long fibres, intermeshing in the moulding increase the resistance to impact, but the existence of fine fibres coated by resin means that under tension a slipping action is possible between these fibres and this causes a lowering of the tensile strength. In the same way, when fabric cuttings are used the overlapping which occurs gives even greater impact strength to the moulding, but as there exist larger surfaces of weaker resin between the pieces of fabric the tensile strength is reduced even more. Mica of course is used when improved electrical properties are required.

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* *See* B.S.S. 771.

Flow of Moulding Powders.

An important property of moulding powders which will be referred to during their manufacture is the flow of the powder. Plastic mouldings are made by placing the moulding powder into a heated mould and applying pressure. During this operation the powder first softens and flows to take up the shape of the mould, then it undergoes chemical changes and sets to a rigid infusible moulding. Obviously some difference in the flow properties of a powder are to be expected if on the one hand it has been made for a moulding involving a great deal of flow, *i.e.*, a picnic beaker, or a wireless cabinet, and alternatively if it has been prepared for a solid article in which no flow has occurred, *e.g.*, a doorknob, or a button. Easy flowing powders are said to be " Free Flow," and there are also " Medium Flow " and " Stiff Flow " powders. Anything stiffer than a " Stiff Flow " powder is unmouldable.

There are two methods of making moulding powders, known as the One Stage Process, and the Two Stage Process respectively.

The One Stage Process.

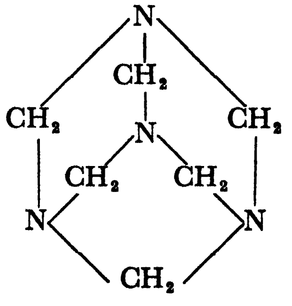
This is the older process but is still used for certain special types of moulding powder. The resin used is an alkaline condensed resole, with an f/p ratio of 1·1–1·5. Such compounds thermoset quite rapidly. These resoles are usually viscous syrups and the moulding powder is made by mixing the resin with the filler, together with colouring materials and lubricant which assists during the later moulding operation. Occasionally a solvent for the resin is used to assist the mixing. The mixing can be carried out in tumblers, or in rotary blade mixing apparatus, for example in a Baker Perkin mixer. The next stage is to dry the product, either in tray ovens, or by passing through a rotary drier, and by this means the solvent is removed and the resin is heated to such a stage that it is still fusible, but needs only a short time of further heating to completely cure it. It is then ready for the moulder. This last process is tricky. The moulder, using very expensive moulding apparatus, requires moulding powder which cures very rapidly in his presses, so that he can have a very rapid rate of production. Consequently, in order to curtail the time of heating in the press the moulding powder must be heated in bulk to such a stage that only a few more minutes heating will be required to convert it to the infusible product. Obviously great skill is required to judge this.

The Two Stage Process.

This process was evolved to eliminate many defects that existed in the one stage process. The main drawback to the one stage process arises from the use of resole resins, which age considerably even on storing at quite cool temperatures. As these resins altered considerably on standing it was impossible to keep a reasonable working store of resin, and the inconsistencies from day to day made it necessary to treat each successive batch of moulding powder differently in order to obtain reasonably uniform batches of moulding powder. But the difficulties did not stop there, as the resin in the moulding powder continued to age with the result that powders which were easy to mould, *i.e.*, free flow powders, became stiffer on storage and more difficult to mould, and sometimes even unmouldable.

The introduction of the Two Stage Process has eliminated all these troubles.

In this process the resin used is a Novolac, *i.e.*, an acid condensed resin with an f/p ratio of 0·9. Such resins are solids, and can be stored even in powder form for years without altering very considerably in properties. The first defect in the old process is thus overcome. The resin is finely pulverised and mixed in the dry state with the usual fillers, colouring materials and lubricant, but in addition a substance called hexamine (formula XVII) and also lime, or magnesia is added.



(XVII)

Hexamine is actually a shortened name for hexamethylenetetramine, and is made by condensation of ammonia (4 molecules) with formaldehyde (6 molecules).

The extremely stable Novolac resin is deficient in two materials necessary for it to become a rapid thermosetting resin, formaldehyde and alkali ; and both these are supplied by the hexamine and lime. When the novolac, hexamine and lime are heated together, as happens to a minor extent while mixing the moulding powder, and to a greater extent in the moulding process, the lime neutralises any acid in the novolac, and catalyses the decomposition of hexamine into formaldehyde and ammonia, consequently all the constituents for resole formation and subsequent thermohardening are present. The reason for calling the process a two stage process is now apparent, the first stage is the preparation of a resin of low formaldehyde content, and the second stage involves the addition of formaldehyde liberating compounds.

The composition of a typical moulding powder is :—

Novolac Resin	42%
Wood flour	42%
Hexamine	6%
Lime	2%
Colouring matter	6%
Lubricant	2%

The dry mixture, resin, hexamine, lime, filler, etc., are dry mixed in tumblers, then finally mixed and heated to the correct degree of flow either in a Bridge Banbury mixer (which is a high speed internal mixing machine), or frequently by grinding on a system of hot rolls. This milling operation also compresses or densifies the material so that the final moulding powder is not too bulky. After the required time of heating on the rolls, the product is removed as a sheet, cooled, crushed and disintegrated. The result is a moulding powder. This can be converted into mouldings by heating in closed moulds at temperatures of 145–170°C. and pressures of 1–2 tons/sq. in. Similarly moulding powders can be made from urea-formaldehyde resins (*see* Chapter VIII). These are usually made by the one stage process mentioned above.

Laminating Materials.

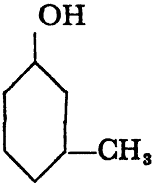
Where flat sheets, or moulded articles of extremely simple shape, but of great strength are required, the fillers used for phenolic resins are in sheet form. Laminated paper, fabric, wood and asbestos boards are made in large quantities. The process is to pass paper or fabric base, etc., from a roll through an impregnating bath containing a phenol formaldehyde resole dissolved in a solvent. As the paper or fabric emerges from the bath it is passed through a set of squeegee rolls to remove surplus resin and control the resin content, then through a heated chamber to remove solvent, and partially cure the resin, and finally the base is cut into sheets, stacked, and packs of these sheets are pressed between the flat heated platens of a press, where curing is completed, and so converted into a board. The process is essentially the same as in moulding powder manufacture except that the ability of the product to flow into shapes has been curtailed.

CHAPTER V

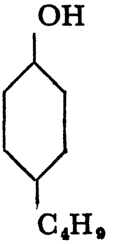
SIMPLE MODIFICATIONS OF PHENOL RESINS

THERE are many reactions by which phenols and phenolic resins may be modified to give quite distinct and novel products. The most common type of modified resin is that in which colophony (rosin) has been used as the modifying agent and this class of resins is dealt with in Chapter VI. Next in importance are the alkyl phenolics and these also deserve a chapter to themselves, but it is worth mentioning here that they are formed from synthetic phenols which are somewhat like the cresols in structure. A cresol molecule is a phenol molecule with a methyl group attached to the ring, and these alkyl phenols are phenols in which relatively large radicles have been attached to the ring in a similar manner.

(I) phenol



(II) m-cresol

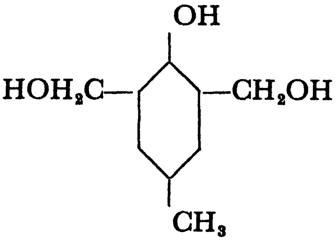


(III) p-butylphenol

Compare the formulæ for phenol (I), m-cresol (II) and butyl phenol (III) above.

Several of these substituted phenols have been made, the ones in common use are tert-butyl phenol, amylphenol, and octylphenol, and just as phenol and cresols form resins with formaldehyde so do these products, but the substituent groups have a very definite modifying influence. All this will be dealt with in Chapter VII.

Now let us examine the phenol resin molecule for other methods of modification. Generally speaking the resoles or phenol alcohols are the resins most frequently modified, and the formula for a very common and easily prepared dialcohol, p-cresol dialcohol (formula IV) is given as an example.

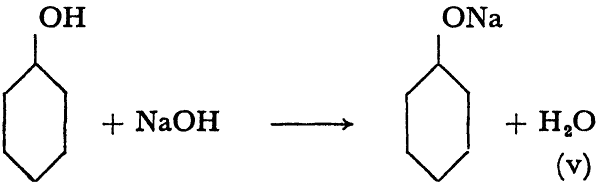


(IV)

How can this be chemically modified ? It can be modified at the phenolic OH group, also on either or both of the methylol CH_2OH groups and even at the free meta positions on the phenol nucleus, although this latter case would be extremely difficult particularly as resoles are very reactive and will thermoharden on the slightest provocation. The phenolic OH and methylol groups can however be modified quite readily.

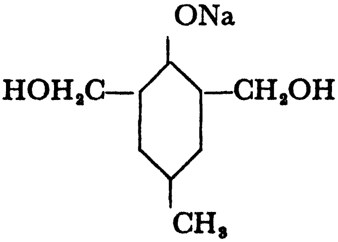
Modification of Phenolic OH Group.

Consider first the phenolic hydroxy group. Phenols are pseudo-acids, that is, they have some acidic properties and one is that they dissolve in caustic soda forming sodium phenates ; actually the sodium atom replaces the hydrogen atom in the hydroxy group. The reaction is :—



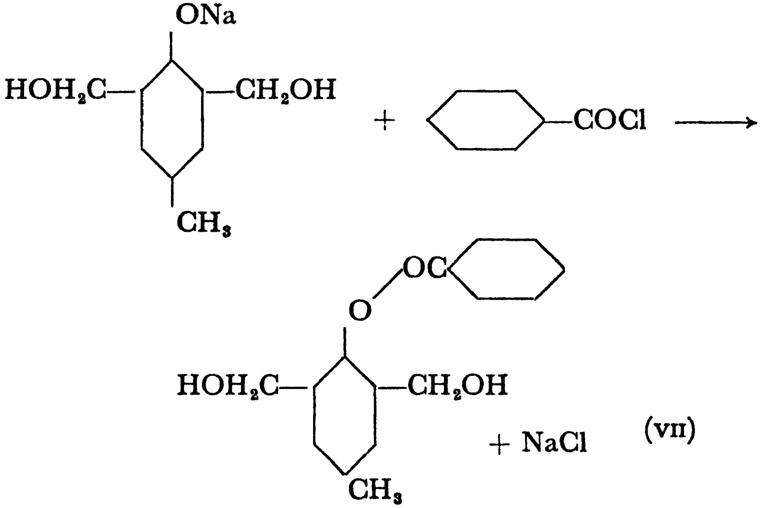
(V)

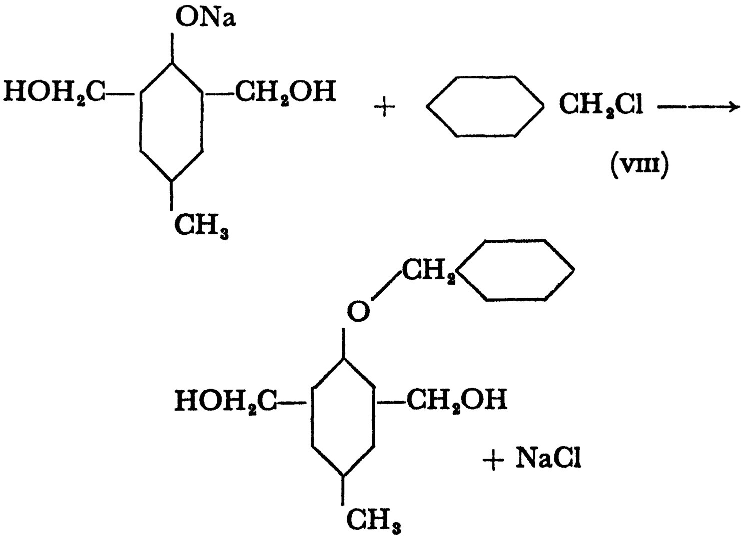
Phenolic resins behave in a similar way, thus paracresoldialcohol readily forms the corresponding sodium salt (formula VI).



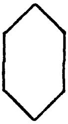
(VI)

Now, this compound can be made to react with such compounds as benzoylchloride (formula VII) and benzylchloride (formula VIII) to form esters or ethers together with sodium chloride. The reaction is very easy to carry out, it goes very well by vigorous agitating of the reactants, either in the cold, or warming gently, and can be represented as


(VII)


(VIII)

How have these modifications altered the properties of the resin? First, the hydroxy group which was soluble in alkali has been replaced in the second case by an ether group which is chemically inactive so that the alkali resistance of these resins has been increased. Secondly, the elimination of the phenolic group has reduced the reactivity of the resin since it is the phenolic group which caused the initial reactivity to form resins. Benzene (formula XI) for example, which has the same formula as phenol without the hydroxy group, does not resinify, or form


(XI)

resins with other compounds. This reduction in reactivity means that the resin will take much longer to cure, stove or bake to a hard resite, and it will be further illustrated in the next chapter.

Experimental.

These experiments must be carried out in a fume cupboard with a good draught.

EXPERIMENT 16. *Preparation of Benzoyl derivative of p-cresol dialcohol.*

p-cresol dialcohol	168 gms. (1 gm. mol.)
caustic soda	40 gms. (1 gm. mol.)
water	360 gms.
*benzoyl chloride	140·5 gms. (1 gm. mol.)

The caustic soda was made into a 10% solution by dissolving in water in a 1-litre round bottom flask. The p-cresol dialcohol was then dissolved in the caustic soda, warming was necessary, then the solution was cooled and the benzoyl chloride added with vigorous shaking. When all the benzoyl chloride was in, the flask was stoppered with a rubber bung, and well shaken, with strong cooling. It was allowed to stand for 4–5 hours, shaking well at half-hourly intervals, and by this time no further smell of the benzoyl chloride remained. The liquid was then allowed to settle and the aqueous solution decanted. The product was repeatedly washed by shaking with warm water, and as there were visible traces of unchanged p-cresol dialcohol it was washed once with warm alcohol. It was then dried by heating in a flask immersed in boiling water and connected to a vacuum pump.

Yield—228 gms. *i.e.*, 84%.

EXPERIMENT 17. *The preparation of the Benzyl Ether.*

p-cresol dialcohol	168 gms. (1 gm. mol.)
10% caustic soda solution	400 gms.
*benzyl chloride	127 gms. (1 gm. mol.)

---

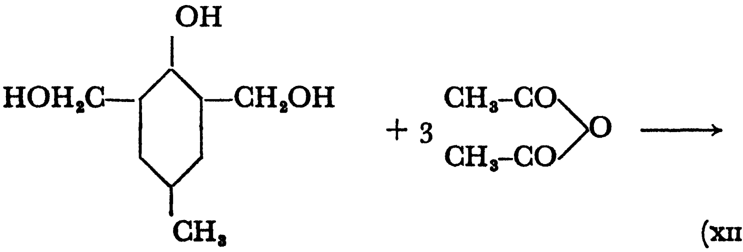
* *Note.*—These products are lachrymatory, that is, they cause the eyes to smart. The effect is very much worse when they are heated. Therefore these experiments must be carried out in a fume cupboard with good ventilation.

This experiment is carried out as experiment 16 above but, in order to complete the reaction, the flask is fitted with a reflux condenser and heated at 60°C. for a few hours, well shaking it at intervals. The product was worked up as above. The product was a brown viscous liquid.

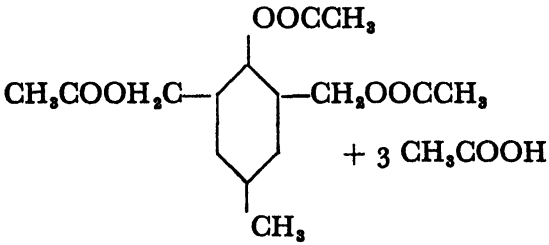
Yield—205 gms., approximately 80%.

Modification of the Methylol Groups.

Just as the phenolic hydroxy group can be esterified or etherified, so can the methylol groups, but somewhat different methods have to be used as they do not form sodium salts. Esterification can be easily accomplished by heating the dialcohol with an acid anhydride, *i.e.*, acetic anhydride (formula XII), but this also esterifies the phenolic hydroxyl group.



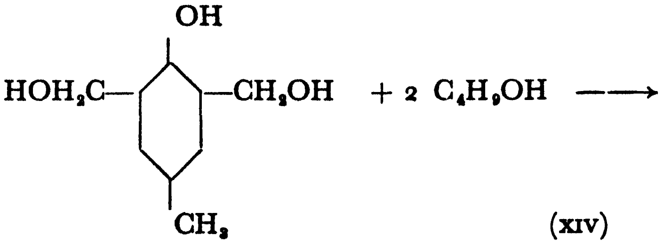
(XII)



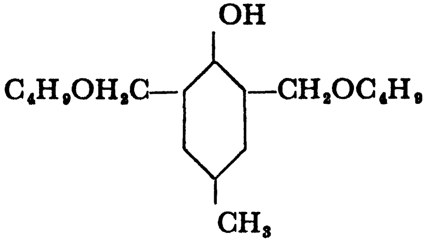
(XIII)

This compound is of no particular interest except that it has all three hydroxy groups blocked, and is very unreactive, thereby proving that the reactivity of these phenolic resins is due to the presence of the hydroxy groups.

Etherification of the methylol groupings is, however, very important and it is the basis of a very important class of resin which is soluble in aromatic solvents, and gives films which on stoving on metal are very hard yet flexible, chemically resistant, and heat resistant. This etherification is carried out by refluxing the dialcohol with a monohydric alcohol and butanol (formula XIV) is usually used. The reaction can be represented by



(xiv)



(xv)

Water is formed and has to be removed by distillation.

It must be realised that all these reactions have been shown in their simplest form. In actual practice more complex resinous compounds are used but provided the resin has one or more methylol groups attached to the molecule these reactions will occur.

Experimental.

EXPERIMENT 18. *Preparation of the Triacetic Ester.*

p-Cresol dialcohol	168 gms. (1 gm. mol.)
Acetic anhydride	500 gms. (4·9 gm. mols.)

The mixture was boiled for 5–6 hours, then distilled *in vacuo*, keeping the temperature below 100°C. By this means the unchanged acetic anhydride, and acetic acid was removed. The product was a mobile liquid.

Yield—237 gms. 83%.

EXPERIMENT 19. *Etherification of p-Cresol Dialcohol using Butanol.*

p-Cresol dialcohol	168 gms. (1 gm. mol.)
Butanol	296 gms (4 gm. mols.)

The solution was made acid with 1 cc. of 10% phosphoric acid, then refluxed for 3 hours. The mixture was then vacuum distilled slowly until about 140 gms. of distillate were removed. This distillate was wet butanol, *i.e.*, it was mainly butanol but contained water of reaction. The final product was a clear resin which could be diluted 1 : 1 with xylol, and which gave a clear film when painted on to a piece of tinned sheet and stoved at 180°C. for 15 minutes.

CHAPTER VI

ROSIN MODIFIED PHENOLIC RESINS

These products are usually associated with the name " Albertol," derived from Dr. Kurt Albert, one of the two original inventors of this type of resin. They were first made around 1910–1912 and were the results of attempts to make the phenolic resins oil-soluble. These unmodified phenolic resins, which have already been described in Chapter IV, are occasionally used as surface coating materials, but they could in no way replace the resin-oil varnishes which were then the basis of all paints. But it was thought that some use could be found for them if they could be made oil-soluble, and dissolved in drying oils in the same way as natural gums were used. Albert and Behrend found that if rosin was incorporated into the resin a measure of oil-solubility was achieved. The earlier resins were essentially Novolacs, *i.e.*, acid condensed phenol formaldehyde resins into which relatively small amounts of rosin were introduced, the rosin acting as acid catalyst, but better results were obtained when resoles were used, and in these resins the rosin was present in excess. One can say that nowadays the bulk of these rosin modified resins are the reaction products of ester gums with resoles. The resoles may be added direct to the ester gum and heated until combination occurs, or they may be first condensed with rosin and the product esterified with glycerine. In some particular cases these two methods give different products but generally speaking one can say that the same product is obtained in both cases, and the latter process is cheaper. The products are all non-crystalline. They are hard, high melting, and relatively light fast compared with the 100% phenolic resins.

In order to study the formation of these rosin modified phenolics, a simple phenol dialcohol is required. Phenol dialcohol itself has not been isolated as a pure compound, but a product of indeterminant composition which is believed to consist mainly of dialcohol has been made. It is more reactive than the cresol dialcohols. The dialcohols of o- and m-cresol are both difficult to prepare as pure compounds but *p-cresol dialcohol* is very readily obtainable by a simple method, page 56, and for that reason it has been selected to illustrate the processes to be described, but it must be understood that in general practice *p-cresol dialcohol* is not used, partly because it is not commercially available and partly because it yields inferior products.

Commercially these rosin modified phenolic resins are made in large nickel, aluminium or stainless steel reaction vessels, which must be well stirred, and capable of being heated to temperatures of about 300°C. As an esterification process is involved they are fitted with suitable reflux condensers which are sufficient to retain the glycerine and allow water of reaction to escape, but to simplify the few laboratory experiments to be described here no attempt will be made to save glycerine by refluxing it. The apparatus required is illustrated in *Figs. 1* and *6*.

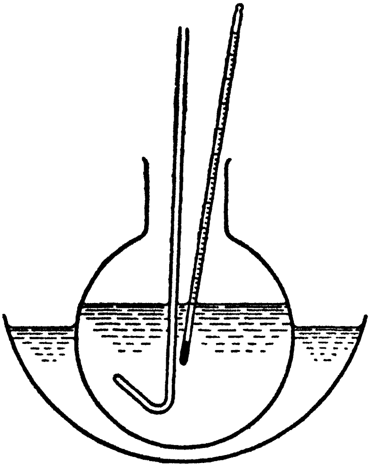


Fig. 6

Experimental.

A. *Condensation of p-Cresol dialcohol with Colophony.*

Three experiments were carried out using varying quantities of p-cresol dialcohol.

	Experiment 20	Experiment 21	Experiment 22
Colophony	300 gms.	300 gms.	300 gms.
p-Cresol dialcohol	30 gms.	60 gms.	90 gms.
% p-Cresol dialcohol	10%	20%	30%

In each experiment the colophony (rosin) was melted in a 1-litre round bottom bolt neck flask and heated in oil baths at 120–130°C., with carbon dioxide blowing over the surface of the colophony. The rosin was well stirred while the p-cresol dialcohol was added slowly, as considerable frothing occurred. The addition of the 10% p-cresol dialcohol was fairly easy and could be accomplished in about 30 minutes but about 1½–2 hours were necessary for the large amounts of dialcohol. When the additions were completed the temperature was raised slowly, as frothing allowed, until it was about 220–240°C., and it was held at this temperature until samples of the resin gave clear solutions when dissolved in the proportions 1 : 1 in white spirit, and the melting points of the resins were constant. In the first two experiments only 2–3 hours were needed but in the case of the product containing 30% dialcohol very much longer was necessary, and the resin never became completely soluble, in fact 30% may be taken to be the limit of the amount of resole which could be incorporated.

Results. TABLE II

Experiment No.	*Quantity of p.c.d.*	*M. Pt. °C.*	*A.V.*	*Solubility in white spirit*
Original Rosin	0	57/63	157	Soluble
20	10	88/99	143	,,
21	20	116/124	128	,,
22	30	124/138	103	Not compl. soluble

B. *Esterification of Products of Condensation of Colophony and p-Cresol dialcohol.*

The products of experiments 20, 21 and 22 were treated with sufficient glycerine to reduce the acid value to 20. In actual practice the theoretical amount of glycerine plus 20% excess was used. The apparatus for making ester gums, *Fig. 1*, was used, but owing to the small amount of resin only 500 cc. flasks were required. Assuming that 200 gms. of resin is to be esterified the amount of glycerine needed can be calculated as follows :—

The acid value of the resin is the number of milligrams of potash (KOH) required to neutralise 1 gm. of resin. *See* page 151.

Then we have 200 gms. of resin of A.V. 143 to be reduced to A.V. 20, *i.e.*, a drop of A.V. of 123.

This is equivalent to 200 × 123 mgms. of KOH.

Now the equivalent weights of potash and glycerine are 56 and 30·7 respectively, *i.e.*,

$$56000 \text{ mgms. potash} \equiv 30700 \text{ mgms. glycerine.}$$

$$\text{Amount of glycerine} = \frac{200 \times 123 \times 30\cdot7}{56} \text{ mgms.}$$

$$= \frac{200 \times 123 \times 307}{56 \times 1000} \text{ gms.}$$

Allowing for 20% excess it will be

$$\frac{200 \times 123 \times 30\cdot7 \times 1\cdot2}{56 \times 1000}$$

i.e., Amount of glycerine—16·2 gms.

Therefore 200 gms. of the product of Expt. 20 need 16·2 gms. of glycerine.
Similarly „ „ „ „ „ 21 „ 14·2 „ „
and „ „ „ „ „ 22 „ 11·0 „ „

The reaction mixtures were heated at 250–260°C. under carbon dioxide until the white spirit solutions were clear and the acid value less than 20. About 8 hours were necessary.

Samples were examined and compared in respect of melting point, acid value, and solubility in white spirit and alcohol. All the products were insoluble in alcohol, but were soluble in white spirit except the product with the highest amount of p-cresol dialcohol. The solutions in white spirit were kept for 3 weeks and showed no tendency to crystallise out. The first two samples dissolved readily in linseed oil on heating to 200°C.

Results. Table III

Experiment No.	*Quantity of dialcohol*	*M.Pt. °C.*	*A.V.*
20	approx. 9%	94/104	19·0
21	approx. 18%	114/126	13·2
22	approx. 27%	127/140	18·5

Note that the percentage of dialcohol in the products has decreased. This is because esterification tends to increase the molecular weight of the resin, and therefore the percentage of the phenolic component is proportionally smaller. Note also how the esterification has caused an increase in melting points.

Condensation of p-Cresol Dialcohol with Crystalline Ester Gum.

Three Experiments, Nos. 24, 23, and 25 were carried out in which 10%, 20% and 30% of p-cresol dialcohol was added to three samples of crystalline ester gum. The additions were made at about 120–140°C. and there was considerable frothing. When the addition was complete the temperature was raised to 200–220°C. The heating was continued until the white spirit solutions were clear. The products were insoluble in alcohol and soluble in white spirit, except again the product with the largest addition of synthetic resin. This was dark, full of bubbles, and insoluble.

Table IV

Experiment No.	*% Quantity of p-cresol dialcohol added*	*M.Pt. °C.*	*A.V.*
	Original Ester Gum	64/70	12·3
23	10%	95/106	10·0
24	20%	120/129	5·5
25	30%	—	—

The above experiments show that the addition of a cresol dialcohol causes a considerable rise in the melting point of colophony or ester gums, the solubility of the resin diminishes as the amount of phenolic component increases and also there is a limit to the amount of pure synthetic which may be added, this limit is between 20 and 30%.

Actually when making resins two desirable properties in the final resin are hardness, or high melting point—which are related—and solubility, generally as the former increases the latter decreases, so actually a compromise has to be made.

A few points are worth noting here. The addition of phenol alcohols to rosin is best carried out at temperatures around 130°C. If the temperature is raised much above this very serious foaming occurs which is difficult to control, and if the addition is carried out at lower temperatures the reaction between rosin and phenol alcohol occurs only slowly, and the resole itself floats about in the hot rosin, slowly hardens and forms particles of insoluble resite which do not react. Consequently, the final product contains lumps of hardened resite, and is also of lower melting point than it should be as the quantity of phenolic component combined in the rosin is lower.

In order to determine the effect that modification of the p-cresol dialcohol molecule has on the reaction with rosin, three derivatives of p-cresol dialcohol, namely the benzoyl and benzyl ethers, and the triacetate, were reacted with rosin by the same methods as those described above. The preparation of these compounds has been described in Chapter V. Actually when comparing these derivatives it is not sufficient to add 10 or 20% to rosin. Some allowance should be made for the difference in molecular weight, so in all cases one-tenth of the gram molecular weight was added to 100 gms. of rosin. The molecular weights of these compounds are

	Mol. Wt.
p-Cresol dialcohol	168
Benzoyl ester of p-cresol dialcohol	272
Benzyl ether " " "	244
Triacetate " " "	294

so in the following experiments 17, 27, 25 and 30 gms. were used respectively per 100 gms. of rosin.

EXPERIMENTS 26–29. *Condensation of Derivatives of p-Cresol dialcohol with Colophony.*

Four samples, each of 100 gms. of colophony, were melted at 120°C. and the correct amount of each of the p-cresol dialcohol derivatives was slowly added to the appropriate sample. The temperature was raised gradually to 220°C. and kept at that temperature until a drop of resin on a glass plate was clear when cold (commonly referred to as " cooking to a clear bead ") and the melting point was constant within a degree or two. The products were then compared.

TABLE V

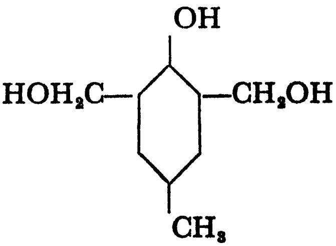
	M.Pt. °C	*A.V.*
17% p-Cresol dialcohol	97/108	130
27% Benzoyl ester of p-cresol dialcohol	92/99	135
25% Benzyl ether ,, ,, ,,	80/90	125
30% Triacetate ,, ,, ,,	83/90	120

All gave clear solutions in white spirit. The benzoyl derivative decomposed slightly during the reaction and gave some benzoic acid hence the slightly higher acid value.

These experiments show that the derivatives have not the same power of raising the melting point of the rosin as the original p-cresol dialcohol, and this is because the phenolic OH groups are the activating groups in the phenol alcohol molecules, and in the derivatives these have been partly or completely eliminated.

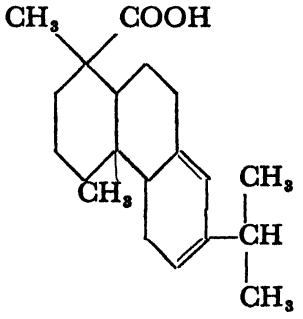
The Nature of the Resin Molecule.

Let us consider the type of resin obtained when rosin is condensed with a typical phenol dialcohol, namely p-cresol dialcohol (formula 1) and then esterified with glycerine. Actually no one



(1)

has elucidated this problem, but many theories have been put forward, some unfortunately by people who have never worked with these resins. We will content ourselves with the general type of reaction which can take place.



(II)

Now, rosin consists mainly of abietic acid (formula II) and the reactive groups in this molecule are the acidic carboxyl group, –COOH, and the two conjugated double bonds, so that for simplicity, we can represent rosin by a diagrammatic formula (formula III)

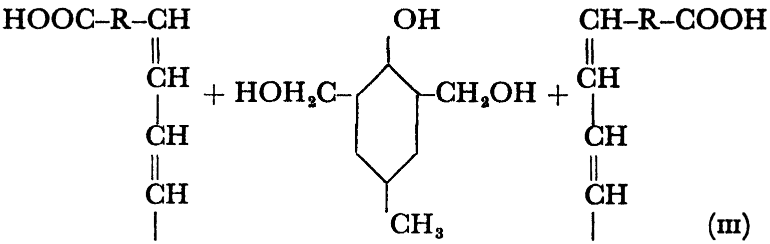
$$-CH=CH-CH=CH-R-COOH \qquad \text{(III)}$$

which will be used to explain the next few reactions.

The first reaction to consider is esterification arising from reaction of the alcohol groups in p-cresol dialcohol, and the rosin acid, but this does not occur as the acid value would be expected to fall and we have seen in Experiments 20, 21 and 22 that the acid value of the reaction products is that which would be expected from mere mixtures of the two reactants.

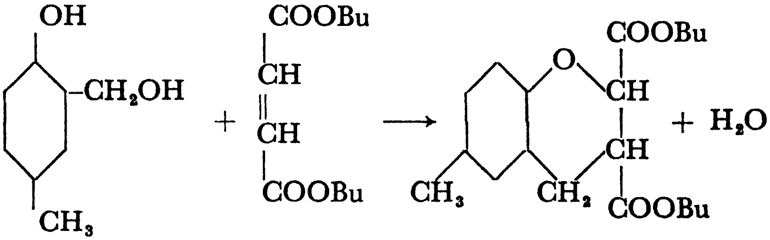
It would therefore appear that the cresol dialcohol reacts with the rosin at the double bonds.

Now, if we again consider Experiments 20–22 it will be seen that somewhere between 20 and 30% addition of p-cresol dialcohol to rosin the products are insoluble. If these experiments are repeated more carefully it will be found that the product of addition of 25% p-cresol dialcohol is still soluble in white spirit so that the limit can be narrowed down to within 25–30% of cresol dialcohol. Let us assume that the material which is not completely soluble in white spirit is caused by p-cresol dialcohol in excess of the maximum amount which combines with rosin. If we take all these factors into account, together with the fact that gum rosin usually contains a few per cent of neutral oils then a reasonable figure to take for the limiting amount of p-cresol dialcohol which will combine is 28 parts per 100 parts of rosin; which is equivalent to 168 parts of p-cresol dialcohol per 600 gms. of rosin, namely 1 gram molecule of dialcohol and 2 gram molecules of rosin acids.



(III)

So we have to consider the addition of one methylol group of the dialcohol to the pair of conjugated double bonds in the rosin molecule. Possibly the most likely reaction is that which has been described recently by K. Hultzsch, a member of the research staff of the firm which originally pioneered these resins. He worked with simple compounds containing these types of groups, namely p-cresol monoalcohol (formula IV) and dibutyl maleate (formula V) and he found that complicated reaction products which could be formulated as (formula VI) below were formed.



(IV) (V) (VI)

It is therefore very likely that the p-cresol dialcohol adds on to rosin by means of reaction between the methylol and phenolic OH group and the double bond system in the rosin acid.

In order to show that the resin obtained by heating rosin with a resole is a compound, and not a mixture of the two substances the following experiment may be carried out.

EXPERIMENT 30. *Vacuum Distillation of Rosin and Resin Acids.*

The apparatus best suited for vacuum distillation of resins boiling at high temperatures is illustrated in *Fig. 8.* It consists essentially of two distillation flasks A and B with exceptionally long necks, joined together by sealing the arms. The long necks prevent the rubber bungs becoming overheated, softening and contaminating the material distilling and it is for the same reason that the orthodox method of joining the two distilling flasks (*Fig. 7*) using a bung is avoided.

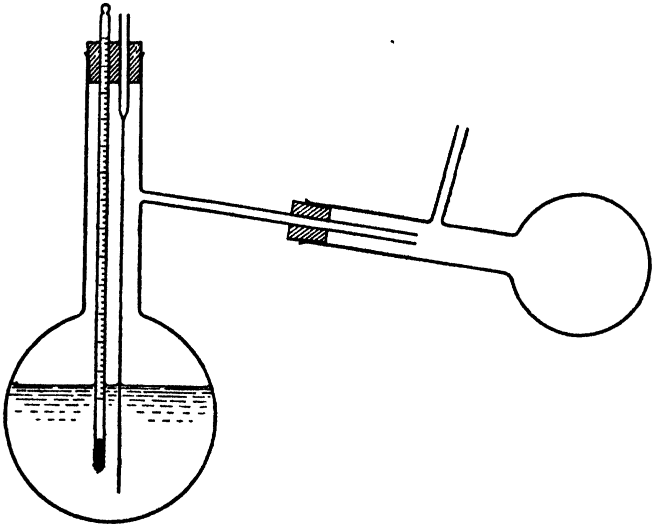


Fig. 7

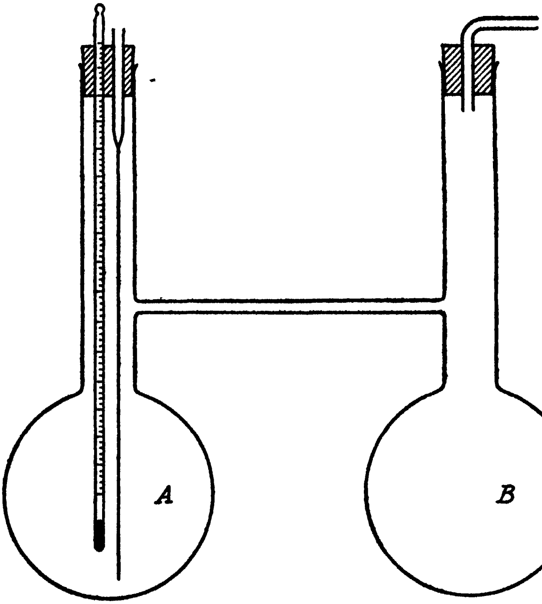


Fig. 8

A weighed amount of rosin is filled into one of the flasks (A). This is then melted by gently warming the flask to about 100°C. and then the flask is stoppered using a good sound rubber bung fitted with two holes, one to carry a thermometer dipping into the resin and the other to carry a bubbler to prevent bumping. The bubbler is made by heating a short length of glass tubing in a blowpipe flame until it is sufficiently hot to pull into a fine capillary. These bubblers allow a slight leak of air into the flask during distillation and so prevent overheating and subsequent bumping. The reason why the thermometer is immersed in the rosin and not placed in the vapour is that with all resin experiments it is the temperature of the resin which is important and this is usually an undistillable residue.

The neck of the second flask (B) is fitted with a rubber bung containing a glass tube and this is joined through a trap to a good vacuum pump. A pump capable of giving a vacuum of 10 mm. of mercury is sufficient and a water pump fed from a good constant source of high pressure water is satisfactory. The flasks are clamped to retort stands, flask A being over a gauze, and the vacuum distillation is commenced. It is best to use two burners for the distillation, one below the gauze supplying most of the heat, but the other should be used cautiously flicking the flame around the top of the flask to break up the foam which occurs when rosin or similar compounds are heated under reduced pressure.

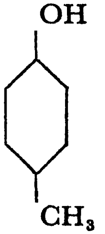
It will be found that the bulk of the rosin will distil in vacuum at temperatures under 250°C. if a vacuum of 10 mm. or less can be maintained. The yield of distillate and residue can be determined by pouring them into weighed dishes and reweighing, and the residue will be found to be less than 5% of the original rosin.

If now the above experiment is repeated, using however the product of reaction of 20 parts of p-cresol dialcohol and 100 parts of rosin, from Experiment 21, then it will be found that a large proportion of this compound is undistillable even at temperatures approaching 300°C., in fact not more than about 20% of the compound distils. This would therefore seem to indicate that a new compound of much higher boiling point has been formed.

CHAPTER VII

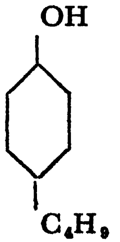
OTHER OIL-SOLUBLE PHENOLIC RESINS

THE alkyl or aryl phenolic resins, sometimes called " 100% phenolic resins " and occasionally " oil reactive phenolic resins," are a particular class of phenol formaldehyde resins which have been made oil-soluble by modifying the phenol molecule before reacting it with formaldehyde. The type of phenol used is called a substituted phenol, because the modification is made by substituting certain organic radicles for one or more of the hydrogen atoms in the nucleus. The term " alkyl " denotes that the radicle is made up of a chain of carbon atoms, while " aryl " is used when the substituent radicle is of aromatic origin. The cresols are the simplest substituted phenols, the substituent group being in this case the methyl group.

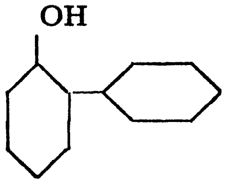


p-cresol (I)

These cresols are generally obtained from coal tar, but other substituted phenols are made synthetically. The phenols commonly used are t-butylphenol (formula II) amylphenol, octylphenol, etc., but certain arylphenols are also used, o-phenylphenol (formula III), for example, but as the reactions and properties are all very much alike the simpler alkyl phenols will be described.



(II)



(III)

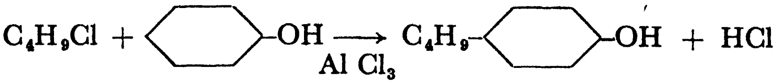
It has been shown that when the substituent group contains four or more carbon atoms then the formaldehyde reaction products are oil-soluble ; also, as the size of the groups increase, then the difference between the acid condensed novolacs and basic condensed resoles diminishes, and this will be demonstrated in experiments 32 and 33.

Preparation of Substituted Phenols.

The substituted phenols are mainly imported from America, but some attempts have been made to make them in this country.

There are four possible methods of preparation.

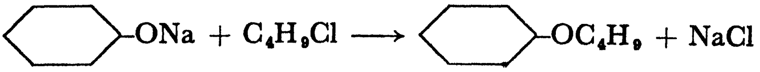
(1) By the Friedel Craft reaction. This is a common reaction for adding groups on to the benzene ring. In this case phenol is heated with an alkyl chloride in the presence of anhydrous aluminium trichloride, which is a catalyst, and the reaction can be expressed as



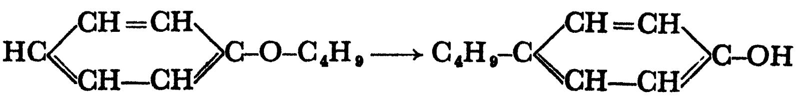
This method, however, is not generally preferred as anhydrous aluminium chloride is not easy to handle, and cleaner and simpler methods are available.

(2) By preparing phenol ethers and heating these at high temperatures, thereby causing isomerism, which means a rearrangement of the groups in the molecule.

The phenol ethers are made by reacting a solution of the phenol in caustic soda with the alkyl chloride. This reaction has been described in Chapter V, Experiment 17, using benzyl chloride, but with butyl chloride it can be represented as

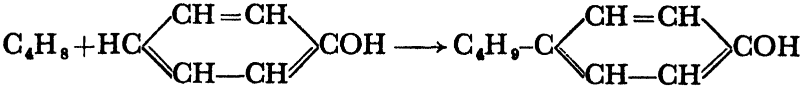


On heating this ether, at temperatures around 200°C. the butyl radicle exchanges positions with a hydrogen atom on the nucleus, *i.e.*,

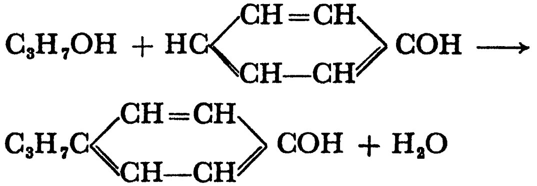


This method is novel but does not give good yields.

(3) One method in general use involves the addition of olefin hydrocarbon to the phenol, using small amounts of acid as catalyst. The olefin hydrocarbons, *i.e.*, isobutylene and di-isobutylene, are available in abundance in America, being products of the petroleum industry, and the method is represented by the equation



(4) The last method to be described is that used in England and on the Continent and consists in condensing phenol with an alcohol in the presence of large quantities of strong acid. Water is eliminated. The reaction is :—



This may be demonstrated by the following experiment.

Experiment 31. *Preparation of Isopropyl Phenol.*

Phenol	94 gms. (1 gm. mol.)
Isopropyl alcohol	60 gms. (1 gm. mol.)
Sulphuric acid	190 gms.

The phenol was dissolved in the isopropyl alcohol in a 500 cc. round bottom flask. The acid was then added slowly, shaking the flask to mix it in, and cooling it at the same time. When all the acid was added the flask was fitted with a reflux condenser and heated at 60°C. for 5 hours, using a water bath. The product should separate into layers but if it does not it can be made to do so by adding it to about half its volume of water (caution) and boiling for 1–2 hours to decompose sulphonic acids which may be formed. After cooling, the oily layer is separated from the lower layer of sulphuric acid, then washed twice with water and finally distilled in vacuum, the fraction B.Pt. 105/120°/15 mm. being collected.

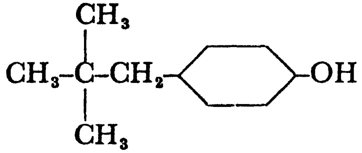
Yield—100 gms., *i.e.*, 73%.

The product is a colourless liquid with a phenolic smell and soluble in water.

Preparation of Resins from Substituted Phenols.

The substituted phenols may be condensed with formaldehyde, using either acid or alkaline catalysts. Actually, when acid catalysts are used the reaction proceeds very much in the same way as it does with ordinary phenol, but with alkaline catalysts the method usually favoured is to carry out the condensation in the presence of a large amount of alkali—sufficient to dissolve the substituted phenol—and because of this large excess of alkali, the condensation must proceed at a low temperature. As the substituted phenols usually preferred are those substituted in the ortho- or para-position, they have only two reactive positions, and can form only dialcohols. They are therefore not vigorously reactive and behave as mildly as o- or p-cresol which has already been demonstrated in Chapter IV. In fact the presence of an organic radicle in the phenol nucleus tends to make any phenol less vigorous in its reaction with formaldehyde.

Experimental. Condensation of Formaldehyde with p-tert-Amyl Phenol.



para-tertiary-amyl phenol

Experiment 32. *Alkaline Condensation.*

Tert.amylphenol	164 gms. (1 gm. mol.)
10% caustic soda	400 gms.
37% formaldehyde	160 gms. (2 gm. mols.)

The amylphenol was dissolved in the caustic soda, cooled to 40°C. and then the formaldehyde added, mixing well. The mixture was then heated in a flask fitted with a reflux condenser, at 60°–65°C. for 8–10 hours, by which time there was no further smell of formaldehyde. On cooling, the mixture was acidified by the addition of 90% of the amount of dilute hydrochloric acid required to neutralise the caustic soda, at the same time bubbling a slow stream of carbon dioxide into the solution to complete the decomposition of the sodium salts of the phenol. An oily product was obtained which was separated from the aqueous layer, then washed twice with water, and finally dehydrated by heating to 150°C., keeping it at this temperature until a sample taken out on to a cold glass plate was clear and solidified to a brittle resin.

The product was a pale solid resin—m.pt. 60/66°C.

Experiment 33. *Acid Condensation.*

Tert.amylphenol	164 gms. (1 gm. mol.)
37% formaldehyde	80 gms. (1 gm. mol.)
concentrated hydrochloric acid	5 cc.

This mixture was heated under reflux for 8–10 hours, then allowed to settle, and the product was well washed with water. It was finally dehydrated by heating to 150°C. The product was an extremely clear and pale resin, very hard, m.pt. 91/99°C.

Both these resins were soluble in benzene and alcohols but were insoluble in white spirit. They could be dissolved in linseed oil and in China wood oil by heating to relatively low temperatures. The best method of carrying out this test is to heat about 4 gms. of resin with 8 gms. of oil in a test tube, stirring with the thermometer. It will be seen that both resins will dissolve in the oil. The best varnishes, however, are those made from the alkaline condensed resins and in this case a reaction is believed to take place between the resin and the oil, especially when wood oil is used, and this is indicated by the vigorous foaming which occurs when heating the mixture to 240°C. The reaction is very likely similar to that which occurs between the phenol or cresol resoles and rosin during the preparation of rosin modified phenolic resin since in both cases we have present a phenol alcohol and a compound containing conjugated double bonds, in this particular case, wood oil, which is the triglyceride ester of eleaostearic acid

$$CH_3(CH_2)_3CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}(CH_2)_7COOH$$

These substituted phenol resins yellow very much less than the ordinary phenolics, and varnishes made from them are even more resistant to discoloration than those made from rosin modified phenolics.

These resins will also react with rosin or ester gum to form rosin modified phenolic resins of very particular interest, and these are again particularly good for colour retention.

EXPERIMENTS 34–37. *Addition of Various Substituted Phenol Resins to Ester Gums.*

Four experiments were carried out using in each case 300 gms. of ester gum and

(Experiment 34)—100 gms. of p-tert.amylphenol dialcohol (33%)
(Experiment 35)—100 gms. of o-phenylphenol dialcohol (33%)
(Experiment 36)— 84 gms. of p-cresol dialcohol (28%)
(Experiment 37)— 75 gms. of cresol resole from Experiment 15 (25%)

The ester gum was melted at 150°C. and stirred, and the dialcohol added in small portions to avoid excessive foaming. The mixture became so stiff that the temperature had to be raised to 170°C. in order to complete the addition. The temperature was then raised slowly to 240°C. and kept there until the resin was clear.

Results.

Expt.	*Phenolic derivative used*	*% Synthetic*	*M. Pt. of Final Resin*	*Solubility* 1:1 *in White Spirit*
34	Tert.amylphenol dialcohol	33%	100/110°C	Soluble
35	o-Phenylphenol dialcohol	33%	95/105°C	Not completely soluble
36	p-Cresol dialcohol	28%	129/143°C	Insoluble
37	Cresol resole	25%	108/118°C	Slightly soluble

It can be seen that the larger phenol molecules induce the dialcohol to combine more easily with ester gum giving products fairly soluble in white spirit. The melting points of the products are also appreciably lower than those from the lower substituted resins.

CHAPTER VIII

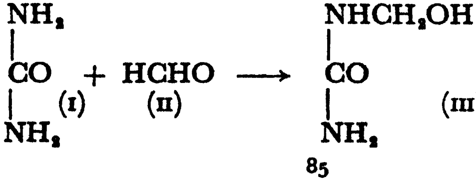
AMINO-RESINS

Urea Formaldehyde Resins.

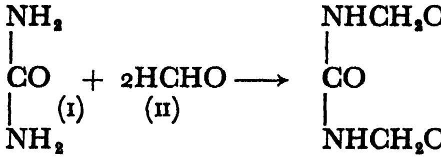
UREA formaldehyde resins, which are condensation products of urea and formaldehyde, are, like the phenol formaldehyde resins, thermosetting, but there the similarity ends. Unlike the phenolic resins they are water-white in colour and show no tendency to discolour on heating or exposure to sunlight. They are therefore extremely useful in moulding powders or industrial finishes where pure white or lightfast pastel shades are required. They are possibly best known to the public in the form of moulded picnic ware and as finishes for refrigerators. They are also used as adhesives and the so-called "allwood aircraft," *e.g.*, the Mosquitos, were generally glued with urea formaldehyde resins. These resins however have some defects. Although very hard they are also very brittle and require plasticising. Their water-resistance is very much poorer than the corresponding phenolic resins, and they do not withstand heating to such high temperatures as the phenolics.

The first thing to remember when making urea resins is that very careful control of the acidity or alkalinity of the resin is absolutely necessary.

If urea (I) and formaldehyde (II) are mixed together and allowed to condense at ordinary or slightly elevated temperatures, in the presence of a trace of alkali, then, depending on the relative proportions of the reactants, either monomethylol urea (III) or dimethylol urea (IV) is obtained, or mixtures of these compounds, and there the reaction practically ceases, larger molecules only being produced should the temperature be allowed to rise appreciably.



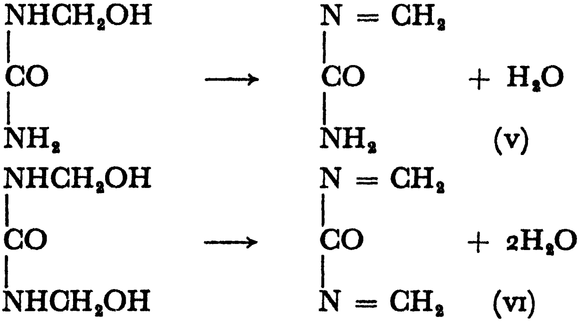
$$\begin{array}{l} NH_2 \\ | \\ CO \\ | \quad (I) \\ NH_2 \end{array} + \begin{array}{c} \\ \\ HCHO \\ (II) \\ \\ \end{array} \longrightarrow \begin{array}{l} NHCH_2OH \\ | \\ CO \\ | \\ NH_2 \end{array} \quad (III)$$



$$\begin{array}{l} NH_2 \\ | \\ CO \\ | \\ NH_2 \end{array} \underset{(i)}{} + \underset{(ii)}{2HCHO} \longrightarrow \begin{array}{l} NHCH_2OH \\ | \\ CO \\ | \\ NHCH_2OH \end{array} \quad (iv)$$

These compounds are both crystalline compounds of fixed melting point. If, however, urea and formaldehyde are reacted together in the presence of a small amount of strong acid, hydrochloric acid for example, a white solid is rapidly formed—Goldschmidt's compound—which is of indeterminate composition, and is insoluble in all common solvents and infusible. Both the methylol ureas and Goldschmidt's compound are useless in such forms for plastics, adhesives or lacquers.

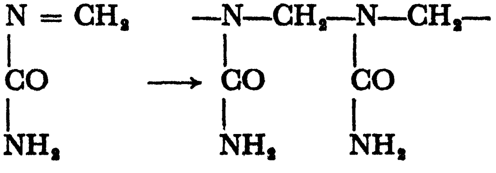
If the products of alkaline condensation are further heated under slightly acid conditions, then resinous compounds are obtained, and if the acid conditions are sufficiently mild the white insoluble products are not obtained immediately. The resin-forming reaction is not completely understood but is probably explained by the intermediate formation of mono-methylene urea (v) and di-methylene urea (vi)



$$\begin{array}{l} NHCH_2OH \\ | \\ CO \\ | \\ NH_2 \end{array} \longrightarrow \begin{array}{l} N = CH_2 \\ | \\ CO \\ | \\ NH_2 \end{array} + H_2O \quad (v)$$

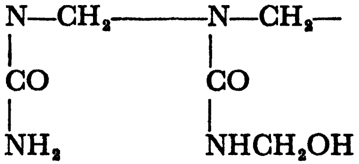
$$\begin{array}{l} NHCH_2OH \\ | \\ CO \\ | \\ NHCH_2OH \end{array} \longrightarrow \begin{array}{l} N = CH_2 \\ | \\ CO \\ | \\ N = CH_2 \end{array} + 2H_2O \quad (vi)$$

These methylene ureas containing unsaturated linkages are capable of further polymerising through these double bonds. Thus mono methylene urea can polymerise to give molecules like (vii) and dimethylene urea can give similar but more complex products.



$$\begin{array}{l} N = CH_2 \\ | \\ CO \\ | \\ NH_2 \end{array} \longrightarrow \begin{array}{llll} -N- & CH_2- & N- & CH_2- \\ \;| & & \;| & \\ CO & & CO & \\ \;| & & \;| & \\ NH_2 & & NH_2 & \end{array} \quad (vii)$$

Moreover, if the methylol ureas (III) and (IV) do not completely dehydrate to the corresponding methylene ureas, compounds like (VIII) are possible.



$$\begin{array}{ll} \mathrm{N{-}CH_2{-}{-}{-}{-}} & \mathrm{N{-}CH_2{-}} \\ | & | \\ \mathrm{CO} & \mathrm{CO} \\ | & | \\ \mathrm{NH_2} & \mathrm{NHCH_2OH} \end{array}$$

(VIII)

The reactions explained so far are those likely to occur during the production of moulding powders, adhesives and many aqueous stoving finishes such as those used on textiles, paper, etc.

F/U Ratio.

A factor which is of great importance in urea resin manufacture is the f/u ratio. This is very much like the f/p ratio, already described in Chapter IV, and can be explained as

$$f/u = \frac{\textit{No. of gram molecules of formaldehyde.}}{\textit{No. of gram molecules of urea used.}}$$

The f/u ratio of any unknown urea formaldehyde resin can be simply calculated from an analysis of the resin. If the resin is analysed quantitatively for carbon and nitrogen content by any of the analytical methods described in organic text books then the ratio %Carbon/%Nitrogen can be used to calculate the f/u ratio. This can be demonstrated by the following table.

TABLE VI

	%C	*H*	*N*	*O*	*C/N*
Formaldehyde	40·0	6·7	—	53·3	—
Urea	20·0	6·7	46·7	26·6	0·42
Monomethylol urea	26·7	6·7	31·1	35·6	0·86
Dimethylol urea	30·0	6·7	23·3	40·0	1·29

The ratio C/N can be plotted against f/u and will be found to be a straight line relationship, *Diagram III*, and consequently for any given analysis the f/u ratio of the original resin can be determined. Unfortunately the f/p ratio of phenolic resins cannot be determined by such a simple method.

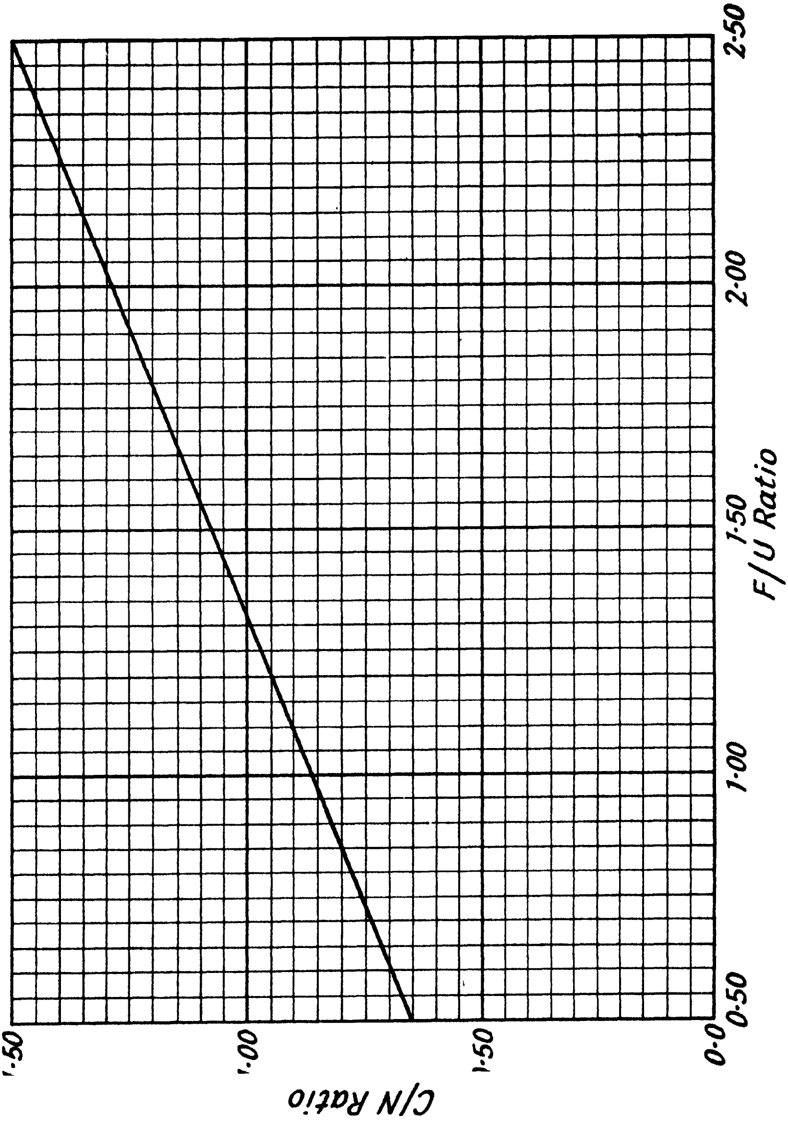


Diagram III

Hydrogen Ion Concentration.

The hydrogen ion concentration of urea resin solutions is often referred to and is of great importance with these resins, but it is not intended to go into a complicated explanation of the term here. Those who are interested should refer to any standard textbook on inorganic or physical chemistry. For our purpose it is sufficient to know that the hydrogen ion concentration is a method of measuring the degree of acidity or alkalinity of a solution. Usually this strength is referred to by quoting it as a figure called the pH, and a neutral solution has a pH of 7, an acid solution a pH between 0–7, and an alkaline solution a pH of 7–14. The pH can be measured only when water is present. Scientific instrument makers have designed electrical instruments for measuring these pH's accurately, but an alternative method, which gives fairly accurate results, is the use of a coloured indicator solution called a universal indicator. This solution is usually supplied in a bottle, with instructions for using it on the label. Briefly, about 5 cc. of the aqueous solution are placed in a clean test tube and 2–3 drops of the universal indicator added. The solution will change colour according to its pH. A red colour indicates a pH of 4–4·5, green is for pH's around 7, *i.e.*, neutral, and a blue colour indicates a pH of 8–10. There are intermediate shades corresponding to the degree of acidity or alkalinity. Sometimes a calibrated shade card is supplied with the indicator. When the pH of a non-aqueous solution has to be measured the usual method is to shake a few cc. of the resin solution with about 5 cc. of saturated brine, which has been previously neutralised to pH 7, then settle, pipette off the aqueous layer into a fresh test tube, add the indicator and proceed as before. Occasionally, where the samples to be tested are soluble in alcohol, they may be tested by adding the indicator to a solution of the sample in previously neutralised alcohol.

Factors Influencing Urea Resins.

It has already been mentioned that the two main factors influencing the preparation of the resins are f/u ratio and pH.

In general f/u ratios greater than 1 are always used as these are the types which would give complex three dimensional molecules when fully cured.

Experiment 38. *Effect of pH and f/u ratio on Urea Formaldehyde Condensations.*

Into each of three test tubes were weighed 5 gms. of urea. Then 6, 9 and 12 cc. of 37% formaldehyde respectively were added to each test tube. This corresponded to f/u ratios of 1:1, 1·5:1 and 2:1. A second similar set of test tubes was also prepared. By vigorous shaking the formaldehyde rapidly dissolved the urea, and the temperature of the mixtures fell to about 8°C. Two drops of universal indicator were added to each of the test tubes, the pH of the solutions was 6·0. This acidity is due to the trace of free formic acid present in all formaldehyde solutions.

To the first set of test tubes was added 0·2 cc. of N/2 sulphuric acid, the pH was then 4·0–4·5. To the second set of test tubes was added 0·2 cc. of N/2 alkali, and the pH of these mixtures was thereby raised to 8·0. The test tubes were allowed to stand in a rack in a bath at 35°C. and the results are tabulated below.

Table VII

Expt.	*Urea*	*Formaldehyde*	*f/u*	*pH*	*Observations*
A	5 gms.	6 cc.	1·0	4·5	Hard white insoluble mass formed in 4–5 minutes
B	5 gms.	9 cc.	1·5	4·5	
C	5 gms.	12 cc.	2·0	4·0	Hard white mass formed in 10 minutes
D	5 gms.	6 cc.	1·0	8·5	Crystals deposited after 24 hours
E	5 gms.	9 cc.	1·5	8·0	Mass of crystals deposited after 7 hours
F	5 gms.	12 cc.	2·0	8·0	Mass of crystals deposited after 6 hours. These crystals dissolve in hot butanol

The conclusions to be drawn from these experiments are:—

(1) Acid condition favour rapid formation of hard insoluble white compound. Increase in f/u ratio slows up the formation of this compound.

(2) Soluble white crystals are formed under alkaline conditions. With a high f/u ratio these appear in a few hours but as the f/u ratio is reduced they take longer to appear.

Briefly,

	Low f/u	*High f/u*
Strong acid	Rapid formation of insoluble material.	Slower formation.
Alkali	Slower deposition of soluble crystals.	Rapid deposition.

Aqueous Resins.

If mild acid conditions are used, that is, adjusting the pH of the solution to about 6·5—remember, pH 7·0 is neutral point—and keeping it at that figure during reaction if necessary by addition of alkali, then resin formation can be carried out at high temperatures, and very stable resins are obtained with high f/u ratios, but again a reduction in the f/u ratio to 1·3 or 1·5 makes the resin more reactive and it rapidly becomes insoluble and infusible. The resins made by this mild acid process are best used as adhesives. They can be made if necessary with a long storage life which is required, for example, when adhesives have to be exported, yet by simply increasing the acidity by adding strong acids the resin can be made to set. This is done just prior to use. Acid hardeners are used, these in their simplest forms are solutions of acid or ammonium chloride, and by varying the strength or quantity different setting times can be obtained.

Apparatus for Making Urea Resins.

As will already have been appreciated, both in the laboratory and in the works, the type of apparatus necessary for making urea formaldehyde resins is essentially the same as with phenolic resins with the provision that it must be kept scrupulously clean and, in the case of works plant, be made of suitable metal which will not contaminate the product. Stainless steel or glass lined vessels are usually employed. In the works a unit similar to that in *Fig 5* is used, and in the laboratory units for refluxing, *Fig. 2*, vacuum distilling, *Fig. 3*, and separating, *Fig.* |9, are all that are necessary.

EXPERIMENT 39. *Preparation of Aqueous Urea Formaldehyde Resins.*

Urea	60 gms.
Formaldehyde	180 gms.

Mix the urea and formaldehyde together and adjust the pH to 7·0 by the addition of a few drops of dilute ammonia solution. Boil the mixture under reflux. If a few drops of universal indicator have been added to the solution the pH of the solution can be observed during the reaction. The solution slowly goes acid during boiling but after 45 minutes refluxing the pH is only 6·6. The solution is made neutral by the addition of a trace of alkali, then water is removed by vacuum distillation at 60°C. until a yield of 170 gms. of resin is obtained.

The resin is a mobile syrup, with only a faint trace of cloudiness. It is insoluble in xylol, and does not mix with ethyl acetate. This resin can be used as an adhesive. To 10 gms. of resin were added 2·5 cc. N/2 sulphuric acid. After mixing some of the resin was spread on to two pieces of wood which were then clamped together for 10 minutes. A firm joint was obtained. The resin without addition of acid had a stability of several months, the resin with the acid hardener had formed a gell in five minutes.

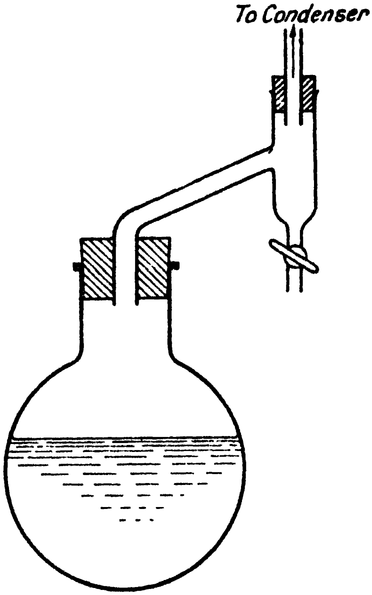


Fig. 9

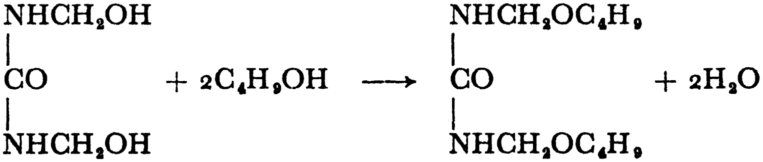
These resins of high f/u ratio cannot be used for moulding powders for two reasons. The water-resistance is low and on moulding they tend to liberate the excess formaldehyde as a gas. The resultant moulding has patches which are marked by these gas bubbles, with consequent disfiguration. Consequently, resins of lower f/u ratio, about 1·3–1·5 are used and these have to be made at low temperatures under alkaline conditions, *i.e.*, pH 7·5–8·0. As these syrups have a very low stability they are stabilised by the addition of traces of stabilisers while they are being used as impregnating materials for the paper or wood flour normally used as fillers for this type of moulding powders.

Neither of the two types of resin described so far are of much use for surface coatings. They are incompatible with other resins and plasticisers and insoluble in many of the common lacquer solvents. Stoved films are weak and brittle, readily affected by atmospheric conditions, and there is a tendency to blister and craze. In general, adhesion to metal is poor. As these resins are thermosetting resins they could at first only be expected to be used as stoving finishes for metal, and it is not wise to use water as a solvent in such cases as this might cause initial corrosion to develop, which would then spread further on exposure of the finished articles.

These defects have been largely attributed to the presence of free hydroxy groups in the resin molecule arising from the methylol ureas, *i.e.*, examine formula (VIII), and can be largely overcome by the introduction of a similar type of resin in which the major portion of these hydroxy groups have been etherified by suitable alcohols, *e.g.*, butanol.

Again, for stability, high f/u ratios are preferred and dimethylol urea is usually the starting point for these resins.

If dimethylol urea is reacted with butanol, preferably under slightly acid conditions, etherification occurs, and compounds similar to (IX) are produced.



$$\begin{array}{l}\mathrm{NHCH_2OH}\\ |\\ \mathrm{CO}\\ |\\ \mathrm{NHCH_2OH}\end{array} + 2\mathrm{C_4H_9OH} \longrightarrow \begin{array}{l}\mathrm{NHCH_2OC_4H_9}\\ |\\ \mathrm{CO}\\ |\\ \mathrm{NHCH_2OC_4H_9}\end{array} + 2\mathrm{H_2O}$$

(IX)

By means of this etherification, even if it is incomplete, the number of free hydroxy groups in the resin is considerably reduced, and it becomes more soluble in organic solvents, particularly of the hydrocarbon type such as are commonly used in the paint and lacquer industry. Moreover the tendency to resinify rapidly by first forming methylene ureas is reduced, and the result is a more easily controlled reaction.

The resins which result from this etherification are usually soluble in alcohols and aromatic hydrocarbons, and they can be stoved (*i.e.*, heat-hardened) at quite low temperatures to give continuous films free from blemish, which as would be expected are extremely pale in colour and do not discolour. These films however are hard, but brittle, and they are also poor in gloss. Consequently they are usually plasticised, and alkyd resins (Chapter IX) are generally preferred for this purpose. They not only plasticise the urea resin but add appreciably to its gloss. Alkyd resins alone make very attractive stoving finishes but the addition of urea resins to them imparts improved colour and tends to give harder films. Moreover, they accelerate the rate of curing of the film enormously.

There are several alternative methods of making these lacquer urea resins but fundamentally they are all the same. First, urea and formaldehyde are reacted together under conditions which favour the formation of dimethylol urea. Then butanol is added and traces of mild acids. After a short condensation, taking care to avoid the formation of insoluble products (Note, if they form they cannot be made to redissolve again) the water in the formaldehyde is removed, usually by vacuum distillation at 60°C., but an alternative method is to add salt to the reaction mixture, cool and settle. The mixture forms two layers, the lower one saturated brine, containing the water from the formaldehyde and the upper layer consisting of a butanol solution of resin which can be separated.

In either case a butanol solution of resin is formed which has to be further heated in order to complete the etherification, and to thicken the resin. This is carried out by slow distillation and during this process water of reaction is removed.

Other methods involve the heating of urea, formaldehyde and butanol together at the start. Again, as urea resins are usually used in conjunction with alkyds there are processes where these resins are incorporated in the reaction mixture, but such a process has many disadvantages.

EXPERIMENT 40. *Preparation of Urea Formaldehyde Resin suitable for Lacquers.*

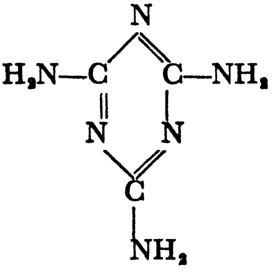
Urea	60 gms.
37% Formaldehyde	170 gms.
Butanol	70 gms.

The urea and formaldehyde were mixed together and 2 cc. of N/2 caustic soda added in order to adjust the pH to 8·5. Then the butanol was added and the mixture heated under reflux for 20 minutes. The solution was cooled, diluted with 120 cc. of butanol, and 20 gms. of salt added. After shaking well and settling the mixture formed two layers. The mixture was separated and 130 cc. of brine were removed. The solution of resin in butanol was distilled under vacuum at 60°C. until no more water distilled. By this means a further 15 cc. of water were obtained and 67 cc. of butanol. The resin at this stage was clear—except for some free salt which could be filtered off—and gave a clear film on stoving for 15 minutes at 125°C. A further 100 cc. of butanol were added to the resin and 1 cc. of N/2 NaOH to adjust the pH to 6·5, and it was then heated under reflux with a separator (*Fig. 9*). On heating the solution butanol and any water formed in the mixture vaporise together, but on condensing in the condenser and dropping into the separator they form two layers as water and butanol are only partially soluble in one another. The lower is water which is the heavier, and the upper layer butanol which can be returned to the flask. By this means water is removed from the system, and as it accumulates it can be drawn off from the bottom of the separator. When it is desired to concentrate the solution butanol can be drawn off as well. After heating for one hour a further 25 cc. of water and 150 cc. of butanol were found to have been removed. The solution after filtering free from deposited salt was clear. It gave good homogeneous films on stoving and was compatible with a xylol solution of a castor oil alkyd. (*Experiment 43.*)

Melamine Formaldehyde Resins.

A very important development towards the end of the 1930's was the introduction of a new class of thermosetting resins based on Melamine.

Melamine (formula x) is formed from dicyandiamide and is indirectly a product of the now extensive acetylene and calcium

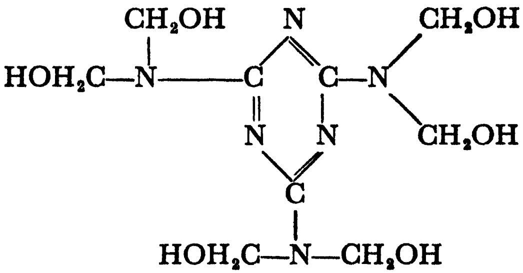


(x)

carbide industry. It is a white crystalline solid, melting at 354°C., and is sparingly soluble in water, *i.e.*,

at 100°C. approximately 5%
at 20°C. approximately 0·5%

Chemically it is a tri-amino compound, and possesses certain groups similar to those in the urea molecule (formula I); consequently it would be expected to react with formaldehyde to form resinous compounds of a similar nature. That is so. Melamine dissolves readily in formaldehyde solutions when heated and forms crystalline compounds. The most stable derivative is hexamethylol melamine (formula XI)



(XI)

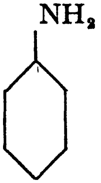
This compound, the addition compound of one molecule of melamine and six molecules of formaldehyde, may be likened to dimethylol urea (formula IV). It is formed if melamine is allowed to stand several hours or is heated with an excess of formalin. It is obvious that intermediate compounds in which one, two, etc., molecules of formaldehyde combine with one molecule of melamine are possible but only the tri- and hexa-methylol melamines have been isolated.

The reactions involved in the manufacture of resins from melamine and formaldehyde are similar to those already described under the heading of urea resins but are more complex. The same strict control of hydrogen ion concentration—pH—is necessary and high formaldehyde/melamine ratios are required if stable resins are required. Resin syrups can be made similar to the aqueous urea formaldehyde resins, but these are too unstable due to their reactivity to be of use alone. Melamine is, however, introduced in small amounts in urea formaldehyde adhesives and moulding powders to improve the properties of these compounds.

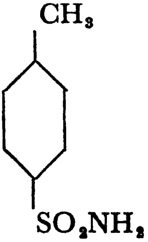
Pure melamine formaldehyde resins suitable for use in lacquers can however be made by the usual methods of etherification, using butanol or other suitable monohydric alcohols. As has already been described this etherification process is a method for reducing the number of potentially reactive methylol groups in the molecule and the tendency to resinify is decreased. Melamine resins have many advantages over the urea formaldehyde resins. They are more reactive and therefore give products which harden more rapidly; this is a two-fold advantage, at the same temperature they harden more rapidly than urea resins and the curing or stoving time is therefore reduced, alternatively they harden in the same time at lower temperatures. The symmetrical nature of the molecule, coupled with the high melting point of the original melamine, tend to make these products more stable to heat, and actually they may be used at temperatures 80°C. above the maximum possible temperature which can be used with urea resins without decomposing. They yield products which are harder and more water resistant than urea resins, and finally the lacquer resins are more readily soluble in lacquer solvents and in certain plasticisers and drying oils. Melamine formaldehyde resins for example are compatible with linseed oil, whereas urea resins are not. All these properties make these resins very attractive and give them a wider field than is possible with urea resins.

Other Amino Resins.

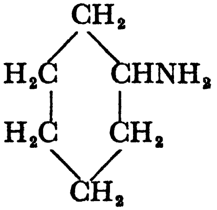
A wide range of resins is possible with other compounds containing amino groups. Thus aniline (formula XII), p-toluene sulphonamide (formula XIII) and other sulphonamides, together with such substances as cyclohexylamine (formula XIV) all form resinous condensation products with formaldehyde.



(XII)

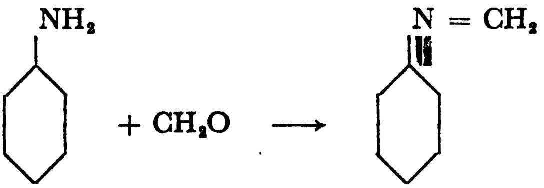


(XIII)



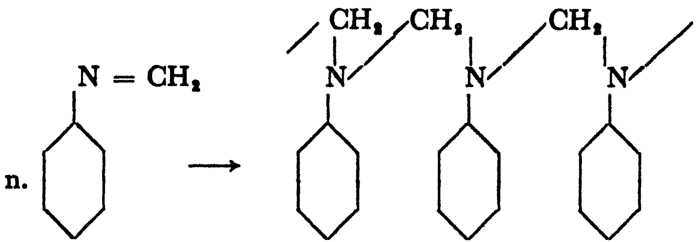
(XIV)

The aniline formaldehyde resins are readily formed in acid or neutral conditions. The reaction has not been studied exten-



(XV)

sively but it is likely that the compound (formula XV) is first formed and this further polymerises giving (XVI).



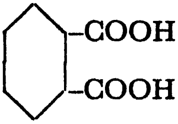
(XVI)

These resins are thermoplastic. The aniline formaldehyde resins are used in the preparation of moulding powders and laminated paper and fabric board, of particular use in the electrical industry. The resins based on sulphonamides are slowly finding uses as surface coatings, usually in conjunction with other resins.

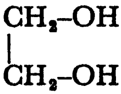
CHAPTER IX

ALKYD RESINS

ALKYD resins, or "glyptals" as they are sometimes called, are essentially condensation products of polybasic acids and polyhydric alcohols, but these products are sometimes modified by introducing simpler acids and alcohols, or incorporating oils and other resins. A polybasic acid is an acid with more than one acid grouping in the molecule, *e.g.*, phthalic acid (formula I), and a polyhydric alcohol is an alcohol with more than one alcohol grouping. The simplest example is glycol (formula II). We have already described how alcohols and acids react together to form esters (which are neutral) and water, so one might expect compounds like phthalic acid and glycol to form neutral esters, in fact a cyclic ester glycol phthalate (formula III) should be possible.

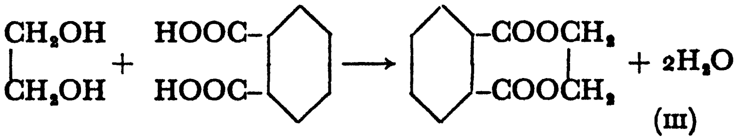


(I)



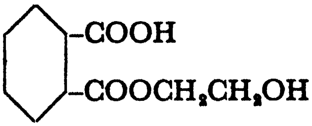
$$\begin{array}{l} CH_2\text{–}OH \\ | \\ CH_2\text{–}OH \end{array}$$

(II)

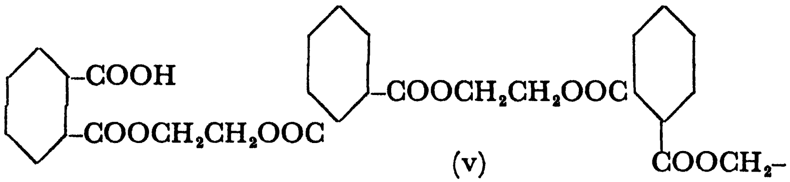


(III)

This simple reaction never occurs. Actually the first product of reaction is a half ester, glycol monophthalate (formula IV) and the acid carboxyl and alcoholic hydroxy groups are too far apart to link up readily. In a system containing millions of such molecules it is easier for the carboxyl group of one molecule to collide and react with a hydroxy group in another molecule and by this means long chain resin molecules (formula V) can be built up.

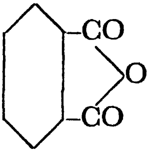


(IV)



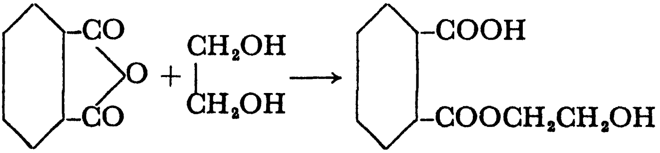
(v)

Although phthalic acid has been mentioned in these first examples it is rarely used. Phthalic anhydride (formula VI), the acid anhydride of phthalic acid, is the common raw material for alkyds. Phthalic anhydride is readily made by oxidising naphthalene, which is derived from coal tar, using air and a vanadium pentoxide catalyst.



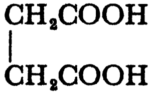
(VI)

It is very cheap, and has the advantage that less water is evolved in the reaction when it is used than in the case of the acid itself, the initial formation of the half ester being accomplished without water splitting out.



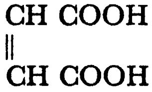
(v)

Of course other acids and alcohols may be used, *e.g.*, succinic acid (formula VII), maleic acid (formula VIII), and glycerol (formula IX) and pentaerithritol (formula X)



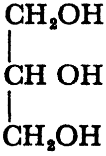
$$\begin{array}{l} \mathrm{CH_2COOH} \\ | \\ \mathrm{CH_2COOH} \end{array}$$

(VII)



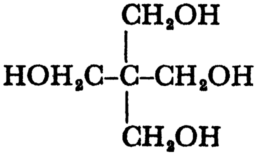
$$\begin{array}{l} \mathrm{CH\ COOH} \\ \| \\ \mathrm{CH\ COOH} \end{array}$$

(VIII)



$$\begin{array}{l} \mathrm{CH_2OH} \\ | \\ \mathrm{CH\ OH} \\ | \\ \mathrm{CH_2OH} \end{array}$$

(IX)



$$\begin{array}{c} \mathrm{CH_2OH} \\ | \\ \mathrm{HOH_2C{-}C{-}CH_2OH} \\ | \\ \mathrm{CH_2OH} \end{array}$$

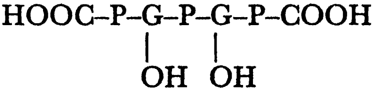
(X)

and the most common alkyds are those derived from phthalic anhydride and glycerol and usually modified by partial substitution with monobasic acids and monohydric alcohols. For simplicity in writing complicated formula we will therefore represent phthalic acid as HOOC–P–COOH, and glycol and glycerol as HO–G–OH, and $\mathrm{HO{-}\underset{\underset{OH}{|}}{G}{-}OH}$ respectively, whereupon formula (v) above might be written HOOC–P–G–P–G–P–G–OH, ignoring the central carbon oxygen linkages.

Thermoplastic and Thermohardening Resins.

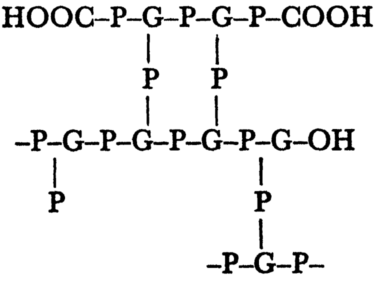
In resin chemistry it has been found that where reacting chemicals each has at least two reacting groups in the molecule long chain resinous molecules can be built up. This has been demonstrated in the case of phthalic acid and glycol above. When there are only two reactive groups in each molecule and no more, then a long chain, or linear molecule is formed and these resinous compounds are thermoplastic. (*See* page 143). That is, they are softened by heating.

If, however, one or both of the reacting compounds have more than two reactive groupings, as, for example, when phthalic anhydride and glycerine are used, then the first products of reaction are linear, that is, they form long slender chains, *e.g.*,



$$\mathrm{HOOC{-}P{-}\underset{\underset{OH}{|}}{G}{-}P{-}\underset{\underset{OH}{|}}{G}{-}P{-}COOH}\qquad\text{(xi)}$$

but these molecules may be cross-linked to other similar molecules by esterification of free hydroxy groups either by phthalic acid itself, or by means of resin molecules with terminal acid groups and compounds similar to (formula xii) are formed.



$$\begin{array}{ccccccccc}
 & & \mathrm{HOOC{-}P{-}} & \mathrm{G} & \mathrm{{-}P{-}} & \mathrm{G} & \mathrm{{-}P{-}COOH} & & \\
 & & & | & & | & & & \\
 & & & \mathrm{P} & & \mathrm{P} & & & \\
 & & & | & & | & & & \\
\mathrm{{-}P{-}} & \mathrm{G} & \mathrm{{-}P{-}} & \mathrm{G} & \mathrm{{-}P{-}} & \mathrm{G} & \mathrm{{-}P{-}} & \mathrm{G} & \mathrm{{-}OH} \\
 & | & & & & & & | & \\
 & \mathrm{P} & & & & & & \mathrm{P} & \\
 & & & & & & & | & \\
 & & & & & & \mathrm{{-}P{-}} & \mathrm{G} & \mathrm{{-}P{-}}
\end{array}\qquad\text{(xii)}$$

These cross linked molecules are no longer linear in form but three dimensional, and are infusible and insoluble. Therefore, these resins are said to be thermohardening, or heat convertible.

Following the Course of the Resin Reaction.

(*a*) *Acid Value.* The resins, as we have explained, are ester resins, and as the resins are formed a reduction in the acid value of the mixture is to be expected. Actually the acid value of the product never reaches zero. As can be seen by referring to any of the formulæ for the resins given above, there is always a free acid group attached to some part of the molecule, but resins with acid values of 5, or 10, sometimes 25, are very common in commercial modified resins, and this is very good considering that the acid value of the phthalic anhydride before reaction is 757. (*See* definition of acid value on page 157).

Let us react one gram molecule of phthalic anhydride (148 gms.) and one gram molecule of glycol (62 gms.) together at about 150–180°C. The acid value of the mixture, if no reaction occurs at all, can be calculated.

148 gms. of phthalic anhydride	A.V. 757	112000
62 gms. of glycol	A.V. 0	0
210 gms. of mixture, average acid value		$\frac{112000}{210}$ 533 units.

If, however, a half ester is formed then we have a compound (IV) with only one acid group, *i.e.*, equivalent to only one gram molecule of potash, and the acid value is $\frac{56000}{210}$ or 267 units.

Similarly, the acid value of the chain molecule of 3 unit length (V) can be calculated to be approximately 98. As this chain length increases so the A.V. correspondingly decreases. So one method of following the course of these resins is to measure the acid value which falls in much the same way as in the case of ester gums.

(*b*) *Solubility.* Another property of the resin which gives an indication of the way the reaction is proceeding is its solubility. If we consider the simplest case, the glycol-phthalic anhydride resin described above, both these compounds are soluble in water, alcohol and acetone and so is the half ester (IV). But as the resinification proceeds the solubility decreases and the product becomes insoluble in water but still soluble in alcohol and acetone, and later insoluble in alcohol, but soluble in acetone. This solubility test is therefore a method of controlling the course of the reaction. For more complex resins other solvents, or mixtures of solvents, may have to be used.

(*c*) *Viscosity.* The viscosity of a resin is a means of determining quantitatively its fluidity, and various methods of measuring this property are mentioned on page 154. The viscosity is affected by the size of the molecules ; small molecules are very mobile but as they increase in size and become heavier, they lose this mobility and this is shown by an increase in the viscosity of the resin. So again the course of the resin reaction may be controlled by viscosity measurements, which usually increase as shown in *Diagram IV.*

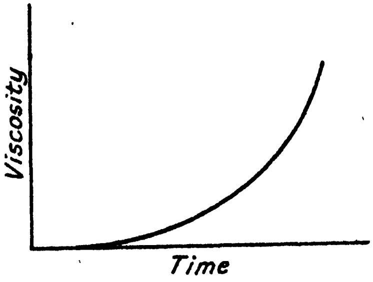


Diagram IV

EXPERIMENT 41. *Preparation of Glycol-Phthalic-Anhydride Resin.*

Phthalic Anhydride	148 gms. (1 gm. mol.)
Glycol	62 gms. (1 gm. mol.)

These materials are heated together in a 500 cc. round bottom flask fitted with a cork containing a thermometer and a glass bend (*Fig. 1*). Mixing may be easily carried out by occasionally shaking the flask. The flask should be clamped to a retort stand over a ring holding a gauze. Raise the temperature slowly to 135°C. then take away the burner. Note the exothermic reaction which takes the temperature up to about 150°C. Then continue heating and maintain the temperature at about 175–180°C. Take samples immediately the exothermic reaction ceases, at about 150°C., and also at hourly intervals and measure the acid value and the solubility in solvents. You will notice how at first a sample of resin dissolves easily in an equal weight of methylated spirits, and that this solution can be diluted to about 1:10 by adding more methylated spirits before cloudiness appears. Later the solubility becomes 1:5, and finally 1:1, and then the resin becomes insoluble in alcohol and acetone has to be used. It should be noted that solutions are always cooled to room temperature before examining for cloudiness. Notice also how the resin gets appreciably more viscous. The acid value will fall rapidly too, until at the point where the product is no longer soluble in alcohol the resin has an acid value of about 80.

EXPERIMENT 42. *Preparation of Glycerol-Phthalic-Anhydride Resin.*

Phthalic Anhydride	148 gms. (1 gm. mol.)
Glycerine	62 gms. (2/3 gm. mols.)

These materials are heated together in exactly the same way as described in Experiment 41. Again note the exothermic reaction at about 140°C. Measure the acid value and change in solubility periodically. Notice how the resin becomes insoluble and practically gelled at an acid value of about 140 although equivalent amounts of glycerine and phthalic anhydride are present. It is important also to notice how the phthalic anhydride tends to sublime out of the resin during the cooking. White crystals will be found on all parts of the apparatus above the level of the resin.

Oil Modified Alkyds.

The straight glyptals described above have found little use commercially except in the electrical industries, mainly as adhesives for lamps and valves. They have not found any application in the plastics and surface coating industry excepting as constituents of certain nitrocellulose and cellulose acetate compositions, but by suitable modification with vegetable oils and other resins they have been converted into useful surface coating resins; in fact prior to 1940 this type probably represented the largest tonnage of synthetic resin used in the paint and varnish industry.

In appearance these alkyds are usually soft viscous resins and in some ways they may be regarded as being similar to the resin oil complex formed when making natural gum varnishes; they only need thinning with solvent and the addition of driers, where necessary, before use. They are made with oil lengths ranging from about 30% to 80%. Those with 30% to 50% oil are called "short oil" alkyds, or alkyds of "short oil length," with 50% to 65% oil they are of "medium oil length," and those with 65% to 80% oil are "long oil" alkyds. These resins are all somewhat darker and can be made with much lower acid values than the unmodified glyptals. In general, it will be found that the acid values of short oil resins become constant at a higher value than those of longer oil length resins. This can be easily understood when it is remembered that glyceryl-phthalate resins, regardless of the amount of glycerol and phthalic anhydride reach a fairly constant and high acid value before gelation. An oil modified resin is essentially such a resin diluted with oil, which usually has an acid value of only 1–2 units, and consequently the more oil incorporated, the lower the acid value. Commercial alkyd resins are usually marketed with acid values of the following order:—

Short oil alkyds	A.V. 25
Medium oil alkyds	A.V. 15–25
Long oil alkyds	A.V. under 15

The solubilities of such resins also vary considerably. Thus all are soluble in aromatic hydrocarbons and mixtures of aromatic hydrocarbons and butanol, but usually the long oil alkyds alone are soluble in white spirit.

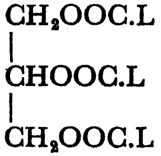
Alkyds from non-drying oils are of no use in air-drying varnishes, but they are extremely useful as plasticising resins for cellulose lacquers, or urea thermosetting resins.

Oils.

It is worth while now discussing the various types of vegetable oils used to modify alkyd resins. These can be divided into two main classes, drying and non-drying oils, although, of course, there are oils intermediate between these classes, called semi-drying oils. Linseed, perilla, tung and dehydrated castor oil are examples of common drying oils, while typical non-drying oils are castor and olive oils.

When painted out as a film on a non-porous surface, *i.e.*, a glass or metal plate, the drying oils dry to a tough film in a few days, and this can be speeded up to a few hours by the addition of a small amount of soluble lead, cobalt or manganese salts (called driers), but the non-drying oils remain persistently tacky.

All these oils are alike in so far as they are esters of glycerine and fatty acids, the acids usually consisting of a chain containing 18 carbon atoms. The oils may be represented diagrammatically as:—



$$\begin{array}{l}CH_2OOC.L\\ |\\ CHOOC.L\\ |\\ CH_2OOC.L\end{array} \qquad \text{(xiii)}$$

where L . COOH is the oil fatty acid.

Most oils are a mixture of glycerides of different acids but certain acids predominate in each oil and these are :—

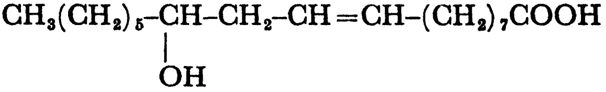
Elaeostearic acid	(xiv)	in tung oil
Linoleic and	(xv)	found in varying proportions in linseed and perilla oils
Linolenic acids	(xvi)	
Oleic acid	(xvii)	in olive oil
Ricinoleic acid	(xviii)	in castor oil
Linoleic acid		in dehydrated castor oil

$CH_3(CH_2)_3\text{-}CH{=}CH\text{-}CH{=}CH\text{-}CH{=}CH(CH_2)_7COOH$ (xiv)

$CH_3(CH_2)_4CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}(CH)_7COOH$ (xv)

$CH_3(CH_2CH{=}CH)_3(CH_2)_7COOH$ (xvi)

$CH_3(CH_2)_7\text{-}CH{=}CH\text{-}(CH_2)_7COOH$ (xvii)

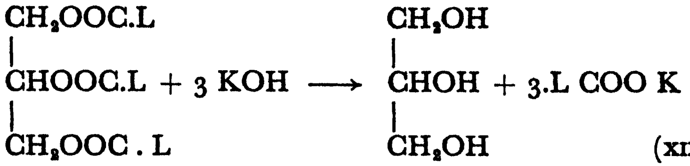


$$CH_3(CH_2)_5\text{-}\underset{\substack{|\\ OH}}{CH}\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_7COOH \qquad \text{(xviii)}$$

Of course, acids which contain a chain of 18 carbon atoms and one or more double bonds can exist in many isomeric forms, so these formulæ are only representative.

Actually, olive oil is never used in this country for making resins but most of the common vegetable oils contain a small amount of oleic acid. The oils from C_{18} fatty acids with one double bond do not dry, but where the fatty acid contains two or more double bonds drying does occur. Where the double bonds are conjugated, as in tung oil and dehydrated castor oil, special properties are achieved ; superior speed of drying and water resistance, for example.

The oils may be broken down into fatty acids and glycerine by two main methods. One is saponification, and this is carried out by heating the oil with an aqueous or alcoholic solution of caustic alkali, potash for example. By this means the potassium salts of the fatty acids are formed (formula xix).



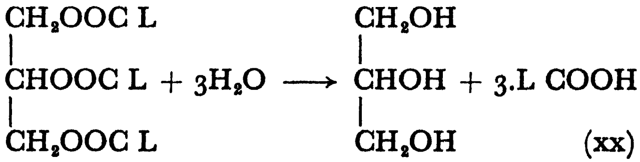
$$\begin{array}{lcl} CH_2OOC.L & & CH_2OH \\ | & & | \\ CHOOC.L + 3\ KOH & \longrightarrow & CHOH + 3.L\ COO\ K \\ | & & | \\ CH_2OOC\ .\ L & & CH_2OH \end{array}$$

(xix)

By acidification of these salts with acid the fatty acids are liberated, and can be separated, washed with water and dried or distilled.

$$L\ COO\ K + HCl \longrightarrow KCl + L\ COOH$$

The other method is called oil splitting and is a direct method involving the use of high pressure steam with a catalyst.



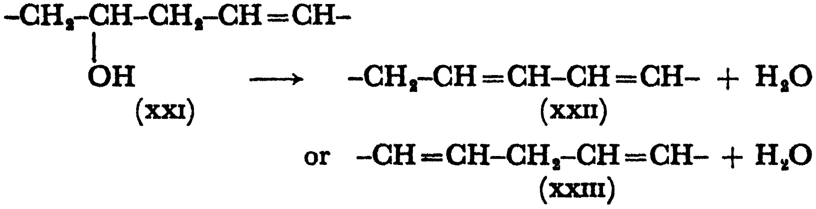
$$\begin{array}{lcl} CH_2OOC\ L & & CH_2OH \\ | & & | \\ CHOOC\ L + 3H_2O & \longrightarrow & CHOH + 3.L\ COOH \\ | & & | \\ CH_2OOC\ L & & CH_2OH \end{array}$$

(xx)

The potassium and sodium salts of the fatty acids are soaps, and at one time glycerine was a by-product of the soap industry. Nowadays the demand for glycerine is so great that fatty acids are a by-product of the glycerine industry.

The fatty acids can, of course, be re-esterified to form an oil again.

Dehydrated castor oil is a special " synthetic " oil. By heating castor oil, which as we have seen is non-drying, at temperatures of about 280°C., and preferably in the presence of a catalyst, *e.g.*, sulphuric or phosphoric acid, or activated clay, phthalic anhydride, etc., the hydroxyl group of each ricinoleic acid molecule, together with a hydrogen atom from an adjacent CH_2 group, are split off in the form of water and an additional double bond is formed in the molecule thus making a drying oil with two double bonds per acid portion of the molecule.



$$\begin{array}{lcl} -CH_2-\underset{\displaystyle OH}{\underset{|}{C}H}-CH_2-CH{=}CH- & \longrightarrow & -CH_2-CH{=}CH-CH{=}CH- + H_2O \\ \text{(xxi)} & & \text{(xxii)} \\ & \text{or} & -CH{=}CH-CH_2-CH{=}CH- + H_2O \\ & & \text{(xxiii)} \end{array}$$

As the process involves the removal of water, *i.e.*, dehydration, the oil is called dehydrated castor oil. The oil is of the linseed oil type but dries more rapidly, is more water resistant and has better colour and colour retention than linseed oil.

Stand Oils ("Bodied" Oils).

Oils may be thickened or bodied by heating at high temperatures. Thus, if linseed oil, tung oil or dehydrated castor oil is heated at about 250°–290°C. for some time a considerable thickening occurs. This is very evident with tung oil, which gells in about 10 minutes at 290°C., but dehydrated castor oil can be heated safely for a few hours at this temperature, and linseed oil for very many hours. The reaction, which is controlled by measuring the increase in viscosity, is essentially a polymerisation reaction involving linkage of fatty acid molecules at the double bonds. The fatty acids in these oils all possess two or more double bonds in the molecule, and as has been shown in Chapter I, molecules containing double bonds are capable of linking to one another through these bonds. In the paint and varnish industry thickened oils, however lightly they have been bodied, are preferred to the raw oils as they give more tough and durable paint films. Consequently, when oils are used in alkyd manufacture they are usually bodied at some stage in the manufacture, and it is as well to remember that any increase in viscosity of the resin during the process is contributed to by the thickening of the oil as well as the progress of the glyptal reaction.

Laboratory Apparatus for the Manufacture of Alkyds.

At this point it would probably be as well to describe suitable types of apparatus for preparing alkyd resins in the laboratory. Many of the experiments which have already been described, or are about to be described, can be carried out very simply in a beaker, or in a wide mouthed flask, or even in a metal tumbler, stirring with a thermometer, but it will be noticed that dark products invariably result and also there is a considerable loss of phthalic anhydride which sublimes out of the flask and coats all the surrounding area with gummy white crystals. Where a series of comparative experiments involving quantitative measurements are to be made, such as using a standard formula but comparing in it the effect of changing the oil, *e.g.*, use of linseed or perilla, raw or boiled oil, etc., then some better form of apparatus is needed. A reasonable scale for preliminary sorting experiments would involve flasks of one litre capacity and batches of about 600 gms. One type of apparatus is shown in *Fig. 10.* It consists of a three-neck flask. In one of the narrow necks is corked a thermometer, and in the other narrow neck is fitted a wide outlet tube which is carried to a condenser. In the central wide neck is fitted a cork carrying a stirrer gland or seal, and also a bent tube to blow carbon dioxide over the surface of the resins. Samples of the resin may quite easily be taken by removing the thermometer. The flask can be heated by means of an oil or solder bath or directly over a gauze.

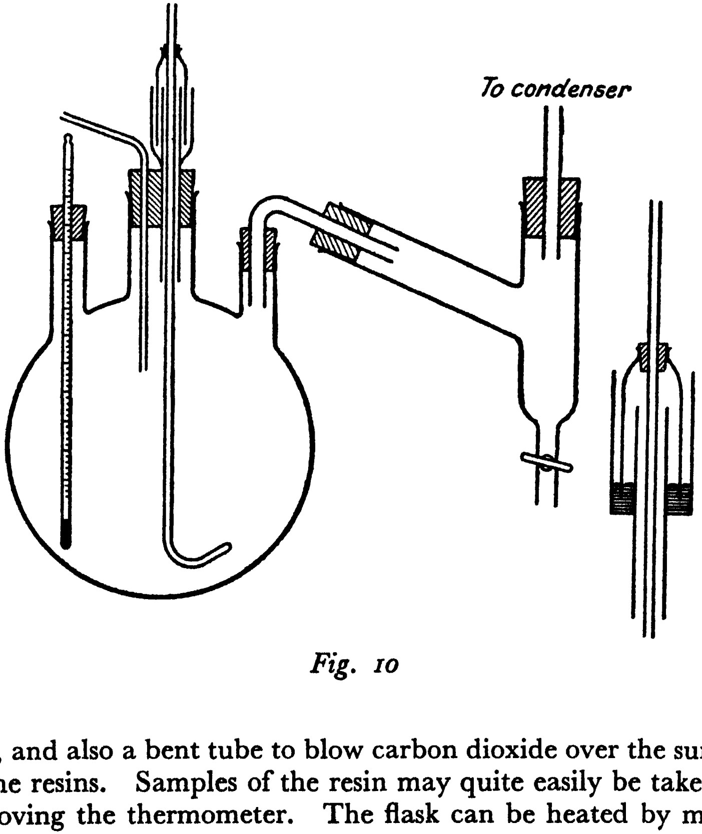


Fig. 10

Mercury can be used in the stirrer seal but it is a better idea to use a small amount of the oil which is being used as modifier for the alkyd. In the same way it is preferable to use glycol, glycerol or linseed oil in any bubbling device used to measure the rate of blowing carbon dioxide into the batch. Sulphuric acid is normally employed in these bubblers, but if by chance a small amount was blown into the hot resin, or alternatively hot resin was sucked back into the acid a serious accident could occur

Another form of apparatus using a wide neck one-litre bolt head flask is shown in *Fig. 11.* It is self explanatory. The great point to remember is that the outlet tube should be as wide as possible as it is very easily blocked by phthalic anhydride.

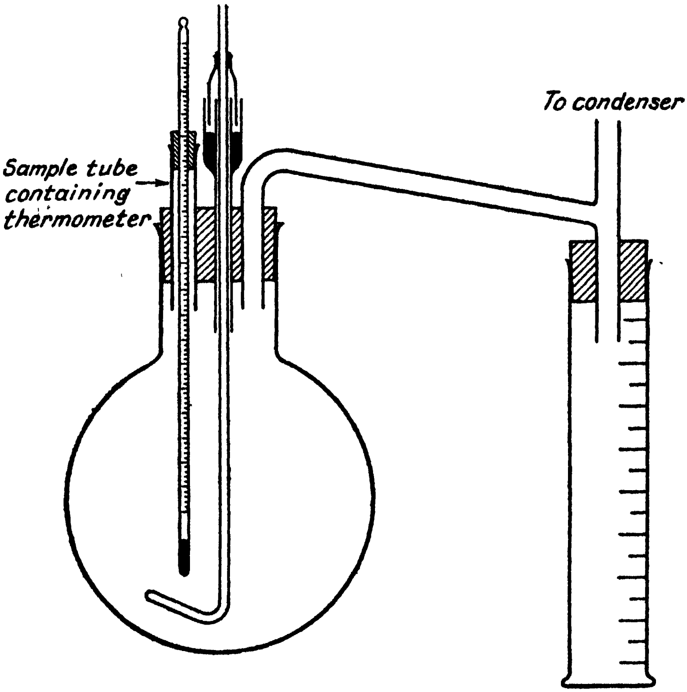


Fig. 11

In actual practice, after the first initial experiments, it is not generally necessary to have the elaborate condensing apparatus which is shown. For most experiments a measurement of the quantity of distillate is unnecessary, and if experiments are carried out under a hood with a fume extractor there are no unpleasant fumes, so the apparatus can be simplified by having an outlet tube with a tin can standing beneath to catch any drippings.

For larger experiments it is preferable to use a metal reaction vessel. Most of the makers of synthetic resin plant manufacture small laboratory plant for such purpose, usually of about ½ to 1 gallon capacity, but a very simple and inexpensive unit is shown in *Fig. 12*. This vessel, made in stainless steel or aluminium consists of a cylindrical pot with a dished bottom which can be heated directly by gas, or in an oil bath. It has the advantage that if it is necessary to cool quickly the hot oil bath can be rapidly lifted away and if necessary replaced by a cold oil bath.

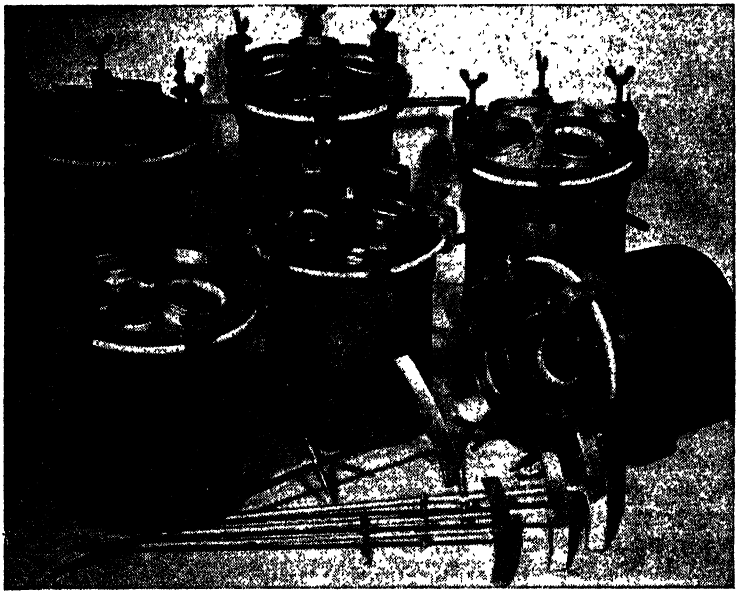


Fig. 12

(By courtesy of the London Aluminium Company and A. Holden & Sons Ltd., Birmingham)

The lid of the pot is secured by six small G clamps which make it very easily detachable for emptying, charging, and cleaning. The lid is fitted with two sight glasses: one is illuminated by means of a small lamp, the other is for inspection. Also in the lid are a series of holes, mostly of about ¾-in. diameter, which may be used to secure thermometers, outlet tubes or reflux condensers, stirrer glands, etc., but one is of 2 inches diameter and serves as a charging hole or sampling hole if necessary.

As a stirrer gland the glass seals may be used, or alternatively a metal gland such as is supplied by the makers of Quickfit apparatus can be used.

This type of apparatus has some disadvantages but all are outweighed by the ease and simplicity of use.

Preparation of Oil Modified Alkyds.

If castor oil, glycerine and phthalic anhydride are heated together they very soon form a homogeneous mixture which in time becomes resinous. If, however, the castor oil is replaced by a drying oil, then, regardless of whatever reaction temperature is used, the mixture remains in two layers, a lower layer of unmodified glyptal which polymerises rapidly, finally gelling, and an upper layer of drying oil which never cooks into the resin. In other words, castor oil modified resins may be made by heating all the reactants together, but drying oil resins cannot be made by such a simple method. The reason for the ease with which raw castor oil can be incorporated into these alkyd resins, is the presence of the hydroxyl " OH " groups in the molecule. (*See* page 4).

EXPERIMENT 43. *Manufacture of Castor Oil Modified Alkyds.*

Castor oil	200 gms.
Phthalic anhydride	148 gms.
Glycerine	92 gms.

Heat the mixture together in a 500 cc. round bottom flask, stirring with a thermometer, or use the apparatus in *Fig. 10* and double the charge. Maintain the temperature at 200°C. Notice the various stages in alkyd resin making. At first the mixture is " hot cloudy," then on further heating it becomes " hot clear." Take a small sample—a drop on the end of the thermometer—and place it on a cold glass plate and allow it to cool. The mixture is " cold cloudy." On further heating the mixture becomes " cold clear," but again, if a small sample is taken in a test tube and dissolved in xylol, say 1:1, the solution is " cloudy". Finally, after further heating, the product gives a *clear solution* in xylol and can be further thickened by continued esterification to give a product suitable for use in surface coatings.

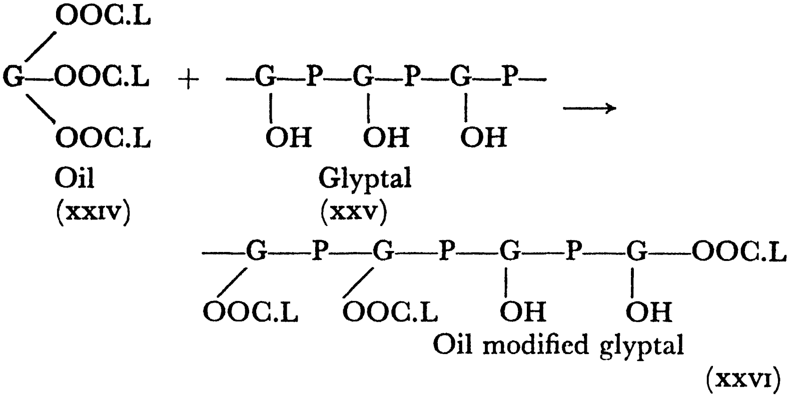
EXPERIMENT 44. *Attempted Manufacture of Linseed Oil Modified Alkyds.*

Linseed oil	200 gms.
Phthalic anhydride	148 gms.
Glycerine	92 gms.

Use the same apparatus for this experiment as was used for Experiment 40. Keep the temperature at about 200°C. It will be noticed that as soon as stirring is stopped the mass separates into two layers, an upper layer of oil and a lower layer of unmodified glyptal. If heating is prolonged, regardless of the temperature the lower layer gells before it becomes completely miscible with the oil.

Methods of Making Drying Oil Modified Alkyds.

Let us consider diagrammatically what we want to do. Using our simplified formulæ we can write the scheme as



Oil (XXIV)

Glyptal (XXV)

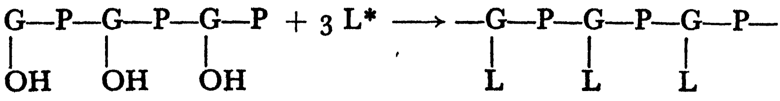
Oil modified glyptal (XXVI)

Such a simple straightforward reaction is not possible. We have seen in Experiment 41 that on heating oil and glyptal together neither a solution of one in the other nor a combination is obtained. There are, however, ingenious methods of overcoming these difficulties and these are called :—

(1) The Fatty Acid Process and
(2) The Monoglyceride Process.

The Fatty Acid Process.

As its name implies this process involves the splitting of the drying oil into glycerine and drying oil fatty acids by either of the methods already described. The split fatty acids are available commercially. If glycerine, phthalic anhydride and drying oil fatty acids are heated together at temperatures around 180–220°C. a homogeneous product results. The quantity of glycerine is of course adjusted to allow for the additional acidity of the fatty acid. The resin making process can be represented as :—



$$\underset{\text{OH}}{\text{G}}\text{—P—}\underset{\text{OH}}{\text{G}}\text{—P—}\underset{\text{OH}}{\text{G}}\text{—P} + 3\,\text{L}^{*} \longrightarrow \text{—}\underset{\text{L}}{\text{G}}\text{—P—}\underset{\text{L}}{\text{G}}\text{—P—}\underset{\text{L}}{\text{G}}\text{—P—}$$

(XXVII) (XXVIII)

---

* L representing a fatty acid molecule.

Although a satisfactory product can be made by heating all the reacting materials together, an alternative method is to heat only the glycerol and phthalic anhydride together to form a clear but soft resin, then add the fatty acid to the hot glyptal and cook it in. (Experiment 45.)

With all these fatty acid modified glyptals the oil length of the resin can be increased by cooking more oil into the resin. The oil should be added hot, and in small portions. It is usual to wait until the resin is hot and cold clear, then to add a small portion of oil and maintain the temperature or even raise it until the product is again cold clear, then add further amount of oil.

EXPERIMENT 45. *Preparation of Fatty Acid Modified Alkyds.*

Phthalic anhydride	148 gms.
Glycerine	106 gms.
Linseed oil fatty acids	235 gms.

The glycerine and phthalic anhydride were heated together at 230°C. for about 15 minutes, *i.e.*, sufficient time to convert them into a resinous product. Meanwhile the fatty acids were warmed separately to about 100°C., then added slowly to the glyptal resin with vigorous stirring. After completing the addition the temperature is maintained at 230–235°C. for several hours until the resin is soluble in xylol and acid value of the resin is below 20. The product is a dark viscous resin. It is interesting to follow the rise in viscosity of a resin like this during manufacture, dissolving the resin in xylol, making the solution of 50% solids content, and measuring the viscosity by one of the methods described in method 4, page 154. Note the rise in viscosity as esterification proceeds.

EXPERIMENT 46. *Alternative Method.*

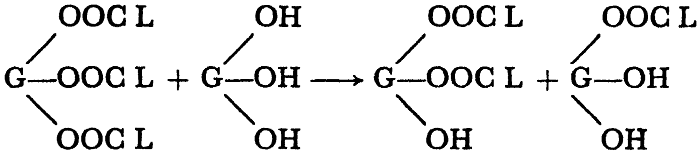
Phthalic anhydride	148 gms.
Glycerine	92 gms.
Linseed oil fatty acids	130 gms.
Linseed oil	36 gms.
Medium viscosity linseed stand oil	72 gms.

The phthalic anhydride, glycerine and fatty acids were heated together at 170°C. for 1 hour, then the linseed oil was slowly added. When a homogeneous mixture which was hot and cold clear was obtained the linseed stand oil was added and the temperature raised slowly to 210–220°C. At the end of 3 hours the resin was cold clear and had an acid value of 60, and after 6 hours heating the acid value was 29. After 12 hours heating the acid value was constant at 23, and the viscosity of the resin was increasing considerably, it was therefore cooled quickly by immersing the flask in a cold oil bath.

The Monoglyceride Process.

In this process the oil and glycerine are first reacted together to form new addition compounds and these can then be treated with phthalic anhydride to form homogeneous resins.

If a vegetable oil, which is an ester of glycerol and long chain fatty acids, is heated with more glycerol under reflux, at temperatures around 250–300°C., a redistribution of the fatty acids in the glycerol molecules occurs and this process is called "alcoholysis." The reaction may be represented diagrammatically as :—



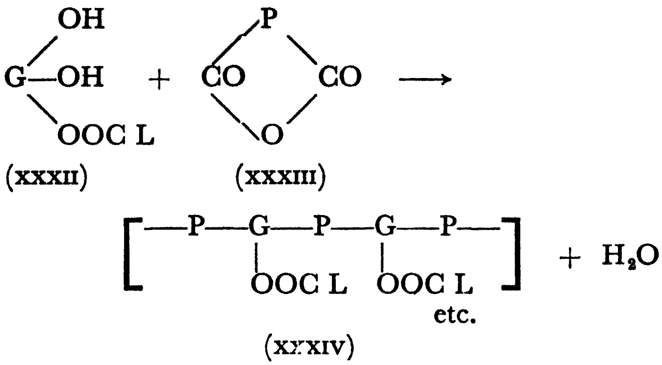
Oil Glycerine

(xxix) (xxx) (xxxi)

Usually a catalyst is used to assist the reaction. Traces of alkali or alkali metals are suitable catalysts. The new compounds are partial esters of glycerine, and are commonly, though incorrectly, referred to as diglyceride (formula xxx) and monoglyceride (formula xxxi) respectively.

If drying oils are being used, the completion of this reaction to a stage suitable for alkyd manufacture can be determined by the solubility of the product in alcohol, *e.g.*, 74 o.p. methylated spirits. Glycerine, and also the partial esters of glycerine are all soluble in alcohol but drying oils are not. If therefore a sample of the mixture is taken during the very early stages of the reaction and dissolved in methylated spirits, say 1:2, then the solution will be cloudy and will rapidly separate into two layers, one the drying oil, and the other a methylated spirit solution of glycerine. When, however, the reaction is completed the product is completely soluble in methylated spirits.

If at this stage the temperature is dropped to 200–250C°, and phthalic anhydride added as foaming allows, then a homogeneous product is obtained which passes through the various stages of "hot clear," "cold clear," etc., and can be esterified and condensed until it has the properties required of it. The reaction is :—



(xxxii) (xxxiii) (xxxiv)

Experimental.

Experiment 47. *Preparation of Drying Oil Alkyds from the Drying Oil.*

Alkali refined linseed oil	450 gms.
Glycerine	92 gms.
Phthalic anhydride	148 gms.

The linseed oil and glycerine were heated together in a 1000 cc. three neck flask fitted with a thermometer, a stirrer and a long air condenser for refluxing. The temperature was raised rapidly to 270–290°C. and kept there, while the mixture was rapidly stirred. After 3 hours a sample from the batch was cooled in a test tube and was disssolved in twice its volume of 74 o.p. methylated spirit. It gave a clear solution.

The product was then allowed to cool to about 180°C. and the phthalic anhydride added slowly. When this addition was completed and the anhydride was completely melted, the resin was slowly heated to 250°C. and kept at that temperature. When foaming occurred this could be controlled to a certain degree by slowing or stopping the stirrer. After 4 hours the heating was stopped and the resin allowed to cool. It was a dark amber colour and had an acid value of 18. It was a soft, viscous, pourable resin about the consistency of a thick stand oil.

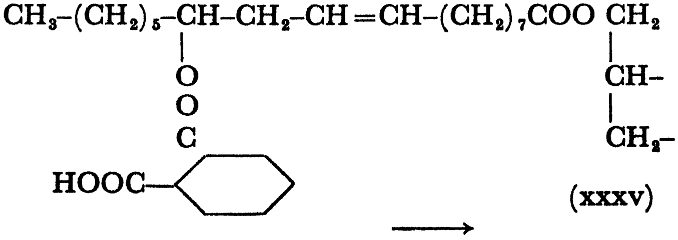
The Fatty Acid *versus* The Monoglyceride Process.

There are advantages and disadvantages in both processes but, in general, the monoglyceride process is the better process. In its favour it can be said that it overcomes the necessity of splitting oils into fatty acids, and is therefore cheaper. It is also a cleaner process, as fatty acids are usually soft curdy materials which are not pleasant to handle. A point which has sometimes been made against fatty acids is that they are likely to become contaminated during transit or on storage by material from the containers, *i.e.*, metal from drums, and this leads to severe discolouration during resin making, and even when they have been packed in wooden casks contamination has been known to occur as a result of painting on the cask, near the bung hole. This contamination does not occur with oils. On the other hand, fatty acids can be more readily distilled than oils, and separated into quicker and slower drying fractions, and this does enable novel resins to be made. Finally, the monoglyceride process cannot be used with those oils which are very reactive on heating. Thus, tung oil gells in about 10 minutes at 280–290°C. and consequently could not be converted into monoglycerides by the normal process.

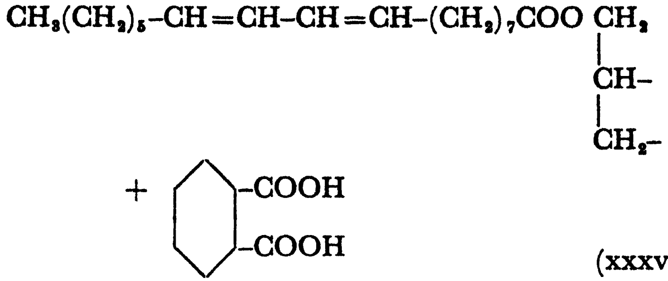
Dehydrated Castor Oil Alkyd Resins.

The preparation of dehydrated castor oil alkyds is well worth a short study, not necessarily because these resins possess any outstanding properties, but because they allow the student to observe several reactions occurring simultaneously, and emphasize the need for careful control of reaction conditions. Of course, in all resin manufacturing processes there are several reactions going on at the same time, but usually they are not so easily observed or controlled.

Dehydrated castor oil alkyds can be made either by the fatty acid or by the monoglyceride process, using already prepared dehydrated castor oil. We are not concerned here with either of these processes. There is an alternative method in which the castor oil is dehydrated during the resin making process. It has already been explained how castor oil can be dehydrated and converted into a drying oil by heating at high temperature, namely 270°C. or over, and using an acid catalyst. For example, with phthalic anhydride a half ester would first be formed (formula xxxv) (castor oil is an alcohol) and this would at the high temperature split up to give a dehydrated oil (formula xxxvi) and phthalic acid, and the cycle is then continued by the phthalic acid combining with more castor oil to form a fresh ester and consequent liberation of more water.



(xxxv)



$$CH_3(CH_2)_5\text{-}CH{=}CH\text{-}CH{=}CH\text{-}(CH_2)_7COO\,CH_2\text{-}CH\text{-}CH_2\text{-} + C_6H_4(COOH)_2$$

(xxxvi)

In this way the water is split from castor oil and thus its " OH " group removed.

An unmodified glyptal resin behaves in a similar way, inter-esterifying with the raw castor oil with the elimination of water ; then this at a high temperature splits again in a manner somewhat similar to the above. Now, if castor oil, phthalic anhydride and glycerine are heated together at temperatures around 180–220°C. homogeneous resins are produced of different degrees of condensation of low or high viscosity, but all are non-drying. Typical viscosity curves are shown in *Diagram V, A, B, and C.* The increase in viscosity is due to large molecules being formed, by esterification, and possibly to a certain extent by "inter-esterification," that is, exchange of radicles between various glycerol molecules, and the simplest unit could be represented as :—

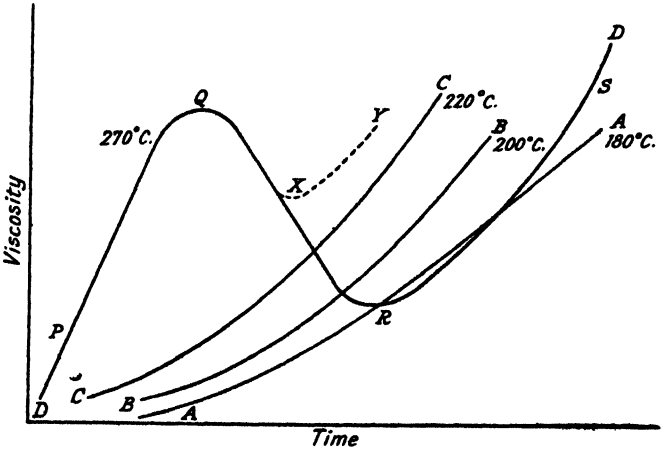
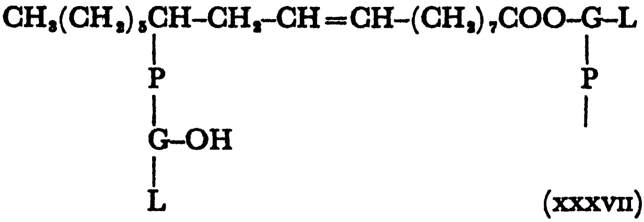


Diagram V



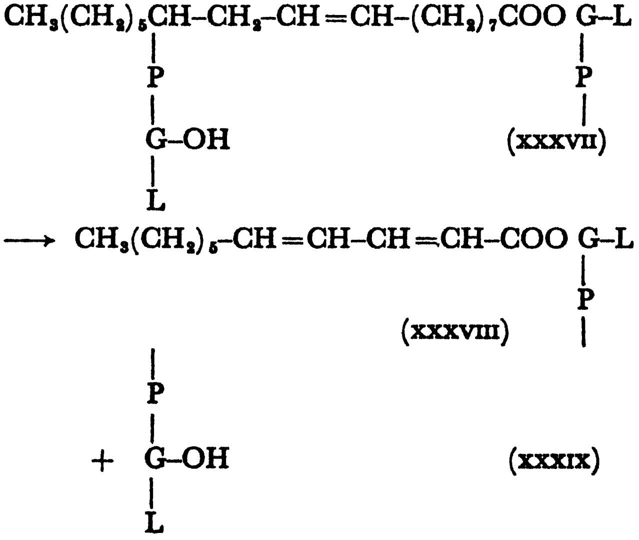
$$\mathrm{CH_3(CH_2)_5\underset{\substack{|\\ P\\ |\\ G{-}OH\\ |\\ L}}{C}H{-}CH_2{-}CH{=}CH{-}(CH_2)_7COO{-}\underset{\substack{|\\ P\\ |}}{G}{-}L}$$

(xxxvii)

In this (formula xxxvii) one fatty acid molecule has been shown in full, and the others have been represented by L's, but do not forget that additional glyptal molecules can be attached to these other fatty acids by the same method of linkage as shown in formula (xxxv).

If the temperature at which this resin is being made is raised to 270°C. and kept at that temperature, or a higher temperature, then the viscosity curve (*Diagram 5*, *Curve D*), follows a sine curve, and that will now be explained.

The first part of the curve, PQ, represents the rise in viscosity of a castor oil alkyd due to formation of large molecules. The curve can be taken as an extension of the series of curves A, B, C, at 180, 200, and 220°C. But when the temperature of 270°C. is reached and maintained, dehydration commences and this involves the splitting of larger molecules to form smaller molecules (formula xxxviii) and (formula xxxix) with the consequent drop in the viscosity of the resin—QR.



$$\mathrm{CH_3(CH_2)_5\underset{\substack{|\\ P\\ |\\ G{-}OH\\ |\\ L}}{C}H{-}CH_2{-}CH{=}CH{-}(CH_2)_7COO\ \underset{\substack{|\\ P\\ |}}{G}{-}L} \quad \text{(xxxvii)}$$

$$\longrightarrow \mathrm{CH_3(CH_2)_5{-}CH{=}CH{-}CH{=}CH{-}COO\ \underset{\substack{|\\ P\\ |}}{G}{-}L} \quad \text{(xxxviii)}$$

$$+\ \mathrm{\overset{\substack{|\\ P\\ |}}{G}{-}OH \atop {|\atop L}} \quad \text{(xxxix)}$$

The process of splitting, re-esterification with loss of water and again splitting continues with the production of the dehydrated oil radicle until dehydration of the castor oil is virtually completed. The fall of the viscosity curve now ceases, and begins to rise again (RS) due to two factors : (I) the linkage of the molecules again in a straightforward alkyd resin forming reaction, and (II) the polymerisation of the oil molecules through the double bonds with resulting stand oil formation.

The parts of curve D are therefore :—

PQ	Rise in viscosity curve due to formation of large castor oil—phthalic anhydride—glycerine molecules while temperature is raised to 270C°.
QR	Fall of viscosity as castor oil is dehydrated with consequent splitting of molecules.
RS	Rise in viscosity again due to further esterification and polymerisation through double bonds.

If the temperature has been kept constant at, say, 270°C., then the minimum in the viscosity curve R denotes the end of the dehydration reaction. It is important that this point should be measured accurately. If for any reason this point is overshot and the high temperature is maintained for any length of time thickening occurs at such a rate that it is difficult to control the resin to finish at any fixed viscosity and, moreover, gelation may occur. On the other hand, if the temperature is dropped before this point is reached the dehydration reaction is halted and we are left with a drying oil alkyd containing a portion of non-drying oil, which will be a serious defect. So the control of the reaction by accurate viscosity measurements is important. Control of temperature measurements is also important. Let us consider a batch of resin where the temperature is being kept at 270°C. and the viscosity begins to fall from Q to R. If, after a short time denoted by the point V, the temperature is allowed to drop to 240°C, then dehydration ceases, the fall of viscosity ceases, the increase due to straight alkyd reactions, similar to PQ begins, and a curve XY is obtained with a false minimum at X. The curve may indicate a minimum but the resin is by no means dehydrated.

EXPERIMENT 48. *Preparation of Dehydrated Castor Oil Alkyd.*

Castor oil	300 gms.
Glycerine	75 gms.
Phthalic anhydride	148 gms.

Heat this mixture together and raise the temperature in one hour to 270–275°C. Keep at 270°C. for 3 hours, then cool and empty. At half-hourly intervals after the start of the experiment take 20–30 gm. samples in beakers and cool them rapidly by standing in cold water. Then make up accurately 50% solutions in xylol and measure the viscosities accurately at 25°C. Plot the curve. A curve similar to Curve D will be obtained.

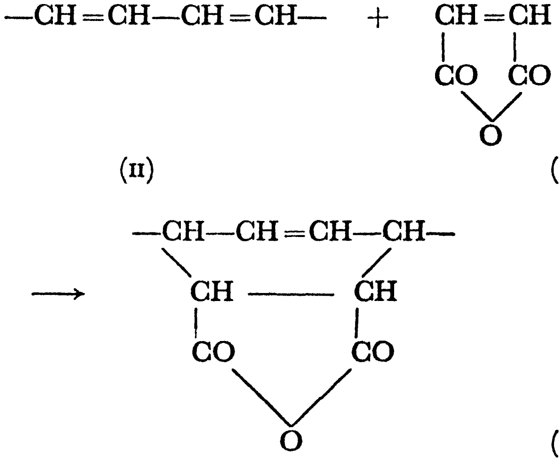
Pour films of the resin solutions on to glass plates and allow them to stand for several days. Notice how samples taken after the minimum viscosity was reached dry tack free whereas the earlier samples remain tacky.

CHAPTER X

MALEIC ANHYDRIDE RESINS

In the 1920's a great deal of work was carried out in developing a reaction which though not new was just being exploited. This reaction is known as the Diels Alder reaction, after the names of the two most prominent investigators, but sometimes it is called the " Diene Synthesis," and it is an extremely useful means of synthesising new compounds.

There are many forms of the reaction but that which is most popular with synthetic resin chemists involves the addition of maleic anhydride (formula I) to compounds possessing a conjugated system of double bonds (formula II), the addition occurring by means of linkage through the double bonds.



(II) (I)

(III)

This reaction has been made use of in many ways. For instance, it is the means of synthesising the anhydrides of new compounds which are essentially new dibasic acids. According to the size of the molecule containing the conjugated system these new dibasic acids can have quite large molecular weights, and they can be used for the manufacture of alkyd resins with properties quite distinct from the normal phthalic anhydride alkyds described in Chapter IX.

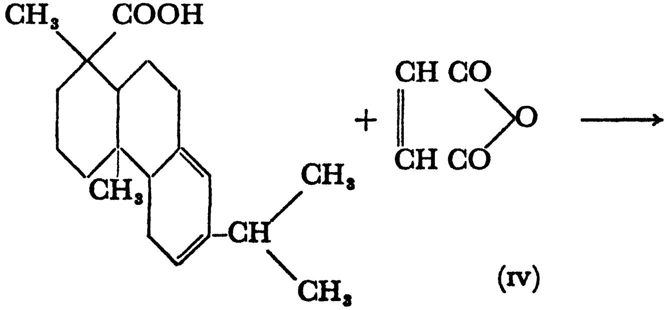
One advantage of this reaction is that it allows quite cheap, and sometimes useless, commodities to be converted into new raw materials for the resin industry. Thus, oils including lubricating oil sludges, terpenes, colophony and coal-tar products have all been successfully converted into raw materials for alkyd resin manufacture. The reaction is very simply carried out: it merely consists in heating the compound with maleic anhydride either alone or in solution for several hours at 150°C. In some cases the reactions are spontaneous and exothermic, consequently no extreme application of heat is needed

The rosin modified maleic resins are probably the best known and will be described here.

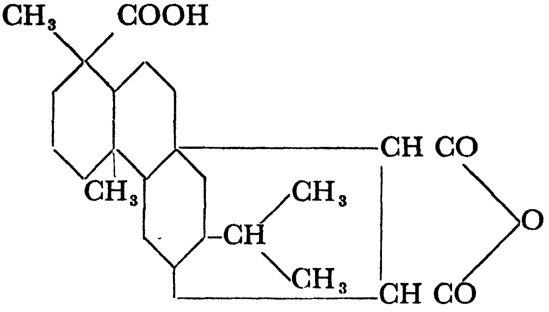
In appearance these resins are somewhat like the rosin modified phenolic resins described in Chapter VI; they are made with the same low acid value, approximately the same melting points, and the colours compare with the palest of the phenolic resins. They are also used in somewhat similar ways, as both types of resins can be cooked into oils. Their outstanding property, however, is that they allow very pale oil varnishes to be made which are extremely useful for the production of white and other pale coloured paints, and they have very little tendency to discolour. They were probably developed at an opportune time, the rosin modified phenolic resins after a long struggle had shown their superiority over natural gum varnishes for certain purposes, but all these finishes suffered from after yellowing, particularly on exposure to sunlight. The rosin modified maleic resins were quick to fill the gap.

The Rosin Maleic Anhydride Adduct.

As has been explained in Chapter III, rosin consists essentially of a mixture of abietic acids of which the common formula is (formula IV).



(IV)



(v)

This acid possesses a conjugated system of double bonds and consequently reacts with maleic anhydride, giving an addition compound (formula v). If equimolecular proportions of the two reactants are heated together at 170°C. for about 3 hours the reaction proceeds almost to completion. The product is a resinous solid somewhat like rosin in appearance but harder and darker. The adduct is actually a crystalline compound and can be obtained as such by recrystallising the resinous product using glacial acetic acid as the solvent. (*Experiment 49*). It has a melting point of 227°C. It should be noted that this compound is the partial anhydride of a tribasic acid.

Ester Products of Rosin and Maleic Anhydride.

As with other types of resins made from rosin and its derivatives, the acid value of these resins has to be reduced and this is usually done by esterification with glycerine. But the rosin-maleic anhydride product is tribasic and glycerol is trihydric so the ester product of these two compounds would be so complex it would become insoluble and infusible. In order to overcome this a certain amount of monobasic acid in the form of free rosin is introduced into the mixture. Actually when making the resins much less maleic anhydride than is theoretically needed is used, 14% maleic anhydride calculated on the rosin is the most which is ever used, while the theoretical amount which will combine is about 33%.

There are two main methods of making these resins. According to one process the rosin is first heated at 150–170°C. for a short time with maleic anhydride, then glycerine is added and the temperature raised slowly to 250°C and kept there for several hours. If necessary, the reaction may be speeded up by applying vacuum. The resin is heated until it has the correct acid value, a constant melting point, and it fulfils certain solubility tests in solvents and oils, then it is emptied and allowed to cool.

In an alternative process the maleic anhydride is first reacted with glycerine at a low temperature forming a product somewhat like the straight glyptal resins. This product is water white in colour and soluble in water. This is then added to the rosin which is kept at about 150°C. during the addition, and after the addition is completed the temperature is raised and kept at 250°C. and the reaction carried out in the same way as in the first method.

The second method has two advantages over the first, it tends to save glycerine and give paler products.

When glycerine is added to very hot resin, as is the case in the first method, there is a tendency for a portion of it to volatilise and be carried away with the water vapour which is a product of the reaction unless a very efficient refluxing and condensing system capable of separating the glycerine and water is used. This causes losses which are overcome by the second process, as in that case the glycerol and maleic anhydride are reacted together at much lower temperatures to form condensation products which are non-volatile and these can be added to molten rosin without any risk of glycerol volatilising.

The preliminary formation of these glycerol maleate resins can cause an appreciable difference in the colour of the final rosin modified resin and this is very important in products which are to be used for the finest colours. As the intermediate product is a mobile liquid it can be strained free from the particles of foreign matter which have been known to contaminate maleic anhydride, particles of paper from paper bags, bits of string, small pieces of metal, etc., all of which would have contributed to the darkening of the resin if heated with rosin to high temperatures.

Although these resins are a form of alkyd they may also be regarded as ester gums into which glycerol/maleic anhydride resin has been incorporated. The maleic anhydride contents of these resins vary in practice from about 7–14%, and as this content is raised between these limits the resins become harder, of higher melting point, and less soluble in solvents and oils. *See* table on next page.

TABLE VIII

Resin	*% Maleic Anhydride*	*Melting point°C.*	*Solubility*	*Miscibility with oil*
A	7	82/90	Easily soluble in ethyl acetate, benzene and white spirit. Solutions can be diluted.	Solutions in white spirit 1 : 1 may be mixed with medium linseed stand oil giving clear solutions.
B	8	87/96		
C	9·5	93/102		
D	11–12	101/114	Soluble in white spirit 1 : 1, dilution not good.	Solutions will not mix in cold with linseed stand oil. Oil must be cooked into resin in portions at 250°C.
E	14	108/119		

It will be noticed that the harder resins are soluble in linseed stand oil only with difficulty and the general method of cooking is to cook one part of resin with one part of oil at 250°C. until the mixture gives a clear drop on a cold glass plate, then to increase the oil length by cooking any additional oil in small portions waiting between each addition until the mixture is cold clear.

The colour of these resins is interesting. The addition of maleic anhydride to the resin gives a resin which is noticeably darker than the palest rosin products—ester gum, etc.—regardless of the precautions taken, and this colour deepens somewhat as the amount of maleic anhydride increases. But regardless of this, those resins with the highest amount of maleic anhydride give products which not only are sufficiently pale for most good class white finishes but also possess the best resistance to discolouration.

Experimental.

EXPERIMENT 49. *Preparation of Rosin-Maleic Anhydride Addition Product.*

Rosin	100 gms.
Maleic anhydride	33 gms.

The rosin was melted in a 500 cc. beaker and raised to 140°C. The maleic anhydride was then added slowly and stirred in. The temperature raised to 170°C and kept there for 2–3 hours. The resin was then poured out into a tray and allowed to cool, then broken up into small pieces, and dissolved in 200 gms. of glacial acetic acid by heating in a flask fitted with a reflux condenser. On allowing to cool the addition product crystallised out in fine cream coloured crystals. The crystals were filtered from the liquor using a vacuum filtering apparatus and were washed with a little clean acetic acid. The crystals were pressed as dry as possible on the filter funnel using a heavy glass stopper, and then they were dried in a vacuum desiccator containing caustic soda pellets. After about 24 hours in the desiccator the product is substantially free from acetic acid. The yield of crystals is high. M.Pt. 224–227°C.

EXPERIMENT 50. *Condensation of Maleic Anhydride with Rosin and Glycerol.*

Rosin	200 gms.
Maleic anhydride	15 gms.
Glycerine	35 gms.

The rosin was melted in an atmosphere of carbon dioxide and heated to 130°C. The maleic anhydride was added slowly with stirring. After the addition the temperature was raised to 170°C. and kept there for 2 hours. The product was a pale clear resin, acid value 201, m.pt. 77–85°C., and was soluble in white spirit and alcohol. At this stage the glycerine was added, the temperature raised to 250°C. and kept at that temperature for 6 hours. The resin was then emptied.

The final product was a pale clear resin, soluble in ethyl acetate, benzene and white spirit. A.V. 27, M.Pt. 81–90°C.

EXPERIMENT 51. *Preparation of Glyceryl Maleate Intermediate.*

Glycerine	100 gms.
Maleic anhydride	65 gms.

The mixture was heated at 125°C. with occasional stirring for about 2 hours. The product was a viscous liquid soluble in water.

EXPERIMENT 52. *Condensation of Glycerol-Maleate with Rosin.*

Rosin	500 gms.
Glycerol maleate (*See Expt. 51*).	100 gms.

The rosin was melted and the temperature kept at 150°C. The glycerine maleic anhydride resin was then added slowly with stirring. Reaction began immediately but there was practically no frothing. The temperature was gradually raised to 250°C over a period of about 4 hours, and kept at this temperature until the acid value was less than 20, and the melting point constant (another 5 hours).

The product was a very brittle resin which cracked very readily on cooling. A.V. 19·9, M.Pt. 100–113°C.

The resin was soluble in white spirit, but not in alcohol.

CHAPTER XI

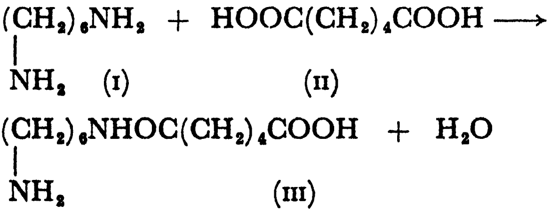
POLYAMIDE RESINS

In Chapter IX we have dealt with a class of resins known as Alkyds, which may be considered as polyesters. Just as the more simple of these are produced by reaction of polybasic acids with polyhydric alcohols, so in a similar manner can resins be made by the reaction of polybasic acids and poly amino compounds. These are called polyamide resins, of which Nylon is an example. Nylon is a trade name but has become a generic name given to all synthetic polyamides.

A polyamine is a compound containing more than one amino group. The commonest example in the resin industry is hexamethylene diamine (formula I).

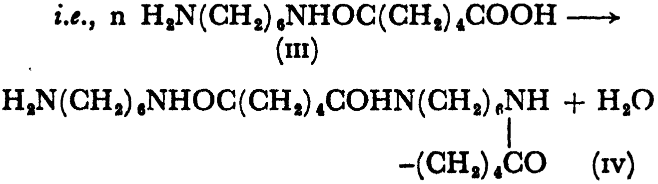
$$\mathrm{H_2N{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}NH_2} \quad (\mathrm{I})$$

If hexamethylene diamine (formula I) and a dibasic acid, *e.g.*, adipic acid (formula II) are heated together at a high temperature, water is eliminated, and the first product of reaction is (formula III),



$$\begin{array}{lll}\mathrm{(CH_2)_6NH_2} & + \ \mathrm{HOOC(CH_2)_4COOH} \longrightarrow & \\ | & & \\ \mathrm{NH_2} \quad (\mathrm{I}) & \qquad (\mathrm{II}) & \\ \mathrm{(CH_2)_6NHOC(CH_2)_4COOH} & + \ \mathrm{H_2O} & \\ | & & \\ \mathrm{NH_2} & \qquad (\mathrm{III}) & \end{array}$$

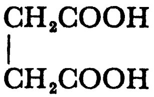
i.e., a compound containing two different reactive groups is formed. Molecules of this compound can in turn combine with one another to form long chain polyamides,



$$\begin{array}{l} i.e.,\ \mathrm{n\ H_2N(CH_2)_6NHOC(CH_2)_4COOH} \longrightarrow \\ \qquad\qquad\qquad (\mathrm{III}) \\ \mathrm{H_2N(CH_2)_6NHOC(CH_2)_4COHN(CH_2)_6NH} + \mathrm{H_2O} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad | \\ \qquad\qquad\qquad\qquad\qquad\quad \mathrm{-(CH_2)_4CO} \quad (\mathrm{IV}) \end{array}$$

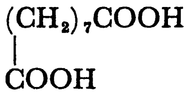
It is obvious that a large number of quite different types of polyamides can be made by varying the nature of the original diamine or dibasic acid used. Thus tri, tetra, or penta-methylene diamine (formulæ v, vi, vii) or succinic (formula viii), azelaic (formula ix) or sebacic acid (formula x) are typical examples of many compounds which can be used.

$H_2N(CH_2)_3NH_2$ (v) $H_2N(CH_2)_4NH_2$ (vi) $H_2N(CH_2)_5NH_2$ (vii)



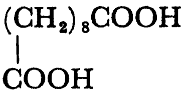
$$\begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array}$$

(viii)



$$\begin{array}{l} (CH_2)_7COOH \\ | \\ COOH \end{array}$$

(ix)



$$\begin{array}{l} (CH_2)_8COOH \\ | \\ COOH \end{array}$$

(x)

The properties of the polyamides resulting from these various reactants will, of course, vary somewhat but the general properties of the class remain the same.

It is obvious from (formula iii) that it is not absolutely necessary to have diamines and dibasic acids to initiate the polyamide condensation. The simplest example of a polyamide condensation is one in which the starting material is an amino acid, *i.e.*, a compound containing one amino and one carboxyl group, *e.g.*, 5 amino caproic acid (formula xi).

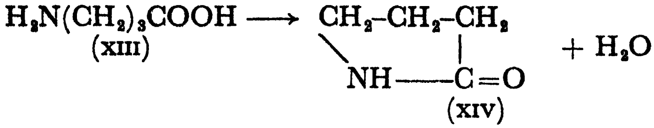
$$H_2N(CH_2)_5COOH \qquad \text{(xi)}$$

If this is heated, water is lost and a polyamide is formed which is claimed to have a molecular weight of about 1200, *i.e.*, it consists of a chain of at least 8 units of amino-caproic acid.

$$\underset{\text{(xi)}}{nH_2N(CH_2)_5COOH} \longrightarrow$$

$$\underset{\text{(xii)}}{H_2N(CH_2)_5CO\ HN(CH_2)_5CO\ HN(CH_2)_5\text{-}} + nH_2O$$

Carothers, who specialised in this work on polyamides, pointed out that these long chain compounds are formed only when the reacting compound has more than six atoms in the chain, otherwise cyclic compounds are possible. In the above example (formula xi) the members are the NH_2 group, the (CH_2) groups, and the oxygen link. Thus, if amino butyric acid (formula xiii) is used a ring compound—a lactam (formula xiv)—is formed in preference to a chain compound and this is monomeric.



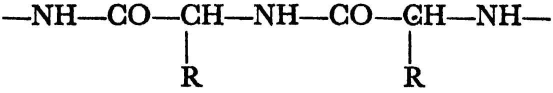
This is a five-membered ring compound. Five and six-membered ring compounds are very stable arrangements of atoms and form in preference to chain compounds under any conditions which favour such a reaction. Seven-membered rings are less likely, but in the example quoted above, using amino caproic acid, the product of reaction consists of about 70% polyamide and 30% of lactam. Eight-membered ring compounds are rare.

As has already been mentioned, the general method of preparation of polyamide resins is to heat a mixture of diamine and dibasic acid together in a still. Temperatures of 200–280°C. are frequently used, and reaction conditions vary from the use of high pressure or reduced pressure. By further reaction under more drastic conditions super polyamides are formed. These are of course of much higher molecular weight.

The Nylons are usually designated by numbers, 66, 610, etc., which refer to the number of carbon atoms in the chains of the reacting molecules. The first figure refers to the number of carbon atoms in the diamine and the second figure, or pair of figures, refers to the number of carbon atoms in the molecule of the dibasic acid, *i.e.*, 66 indicates hexamethylene diamine (6 C atoms) and adipic acid (6 C atoms). 610 Nylon indicates hexamethylene diamine (6 C atoms) and sebacic acid (10 C atoms). In general these resins are thermoplastic, of high softening point ; the commonest grade of Nylon, 66, melts at about 270°C. So far they have been of little use in the surface coating industry. They are very insoluble ; the best solvents are cresols or phenol, which are not pleasant to handle as solvents, but the Nylons give very hard, tough films. In general, they are used in filament form and as threads for stockings and fabrics.

To form these monofils, Nylon is melted and forced through a die into water where it solidifies. At this stage the long chain molecules are arranged haphazardly and the filaments lack strength and elasticity. By a process of cold drawing, in which the filament is stretched to about four times its length, the molecules are orientated and pulled closer together in parallel formation, and an attraction is set up between the chains, thereby increasing the strength of the films.

In their chemical structure these polyamides resemble natural products such as silk, hair and gut. The natural fibres are essentially proteins and possess a general structure :—



$$-\mathrm{NH}-\mathrm{CO}-\underset{\substack{|\\ \mathrm{R}}}{\mathrm{CH}}-\mathrm{NH}-\mathrm{CO}-\underset{\substack{|\\ \mathrm{R}}}{\mathrm{CH}}-\mathrm{NH}- \qquad \text{(xv)}$$

and in the case of silk R is a methyl, CH_3 group. Compare formula (xv) with formula (xii), a typical polyamide.

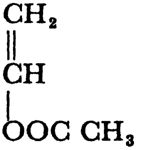
The Nylon plastics are of particular interest as they are an example of the results of an enormous programme of systematic research carried out by a large team of chemists and engineers employed by a large firm, the Du Pont de Nemours organisation in America, with a definite object in mind, to prepare synthetic fibres which could replace silk, and thus make the American markets independent of the Japanese silk trade. The programme of work, which took ten years, was successful.

CHAPTER XII

ETHENOID RESINS

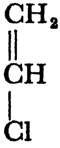
Vinyl Resins.

VINYL resins is the general name given to a class of polymer resins derived from simple monomers all of which contain the vinyl grouping $CH_2=CH-$. Examples of common monomers are vinyl acetate (formula I), vinyl chloride (formula II), acrylic acid (formula III), and styrene or, as it is sometimes called, vinyl benzene (formula IV).



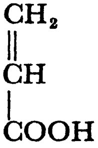
$CH_2=CH-OOC\,CH_3$

(I)



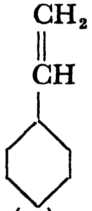
$CH_2=CH-Cl$

(II)



$CH_2=CH-COOH$

(III)



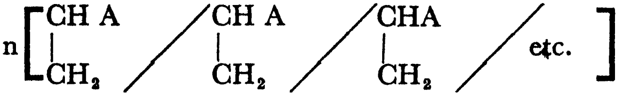
(IV)

Notice that the common formula for all these compounds is $CH_2=CH-A$, where A is some radicle which is different in each case. The nomenclature of these resins is a little irrational, as those workers who specialise in styrene or acrylic acid resins sometimes regard these as a class distinct from the vinyl resins, while other workers classify resins derived from such compounds as vinylidene chloride (formula V) as vinyl resins, but although these latter are not true vinyls the mechanism of the polymerisation resin forming reaction is very similar.

$$CH_2=CCl_2 \qquad (V)$$

The vinyl resins are made from the relative monomeric compounds by the process of polymerisation (page 18). In the presence of certain catalysts, which are generally peroxides, and by the action of light or heat, the molecules of the monomers are made to link together through the double bonds to form larger chain molecules of very high molecular weight *i.e.*, $n.m.(CH_2{=}CH\ A) \longrightarrow n(CH_2{=}CH\ A)m$

or



$$n\left[\begin{array}{c}CH\ A\\ |\\ CH_2\end{array} \diagup \begin{array}{c}CH\ A\\ |\\ CH_2\end{array} \diagup \begin{array}{c}CHA\\ |\\ CH_2\end{array} \diagup \text{etc.}\right]$$

There are no by-products of the reaction. The monomers used in these reactions are generally gases or low boiling mobile liquids ; the polymers obtained are viscous syrups or hard solids, according to the conditions of the reaction. The molecular weights of the polymers indicate that a single molecule of polymer is made up of several thousand molecules of the monomer linked together. All these polymer resins are thermoplastic resins, which is to be expected according to the present day ideas of resin chemistry. (*See* page 143). So far, these resins have found only a very limited use in surface coatings but they are very popular in the plastics industry and are developing a very big field there. Generally speaking, lacquer chemists avoid thermoplastic resins, since most of them, when plasticised to give a flexible film, have very low softening points—and remember a surface exposed to hot sun for some hours can attain a temperature of the order of 80–90°C.—and all are very difficult to get into solution. These polymers of high molecular weight are generally insoluble in the common solvents or soluble only to the extent of 1–2%, and consequently only strong solvents, which are generally expensive, and frequently of overpowering odour, have to be used. Even with these strong solvents the solutions are extremely viscous, and in order to get solutions suitable for brushing, spraying, rollercoating, or dipping, the usual methods of applying a lacquer, the solutions have to be thinned to extremely low solids content. This is again a drawback. Apart from the fact that such solutions usually give extremely thin films which are not sufficiently protective and have to be built up by adding several successive coats, the process is costly as all the expensive solvent is being evaporated into the air, unless the drying is carried out under controlled conditions and the solvent vapours are condensed and recovered. (This process is used fairly extensively in the cloth and paper coating industries.)

So, except where their special properties outweigh these disadvantages, these resins are avoided in the lacquer industry, but as a class they are of comparatively recent development and no doubt during the next few years remarkable improvements can be expected.

The properties of the vinyl resins are influenced to a great extent by the nature of the substituent groups. Thus the percentage of chlorine in vinyl chloride is very high, approximately 56%, and it is well known that organic compounds containing such large amounts of chlorine are practically inert chemically, non-inflammable, and possess strong anti-bacterial properties. Polyvinyl chloride (commonly referred to as P.V.C.) has such properties. If plasticised wisely, with plasticisers of similar properties, it gives products which are resistant to acids and alkalis, which do not support combustion, and are resistant to termites. Similarly, there is a big difference in the properties of polyvinyl acetate and polystyrene, where the substituent groups are an acetate and a hydrocarbon radicle respectively. The acetate group ionises, is a weak conductor and consequently this resin is of little use as a dielectric, but styrene is made up of atoms and radicles none of which ionises and consequently the electrical properties of polystyrene make it pre-eminent among synthetic resins as a dielectric.

Preparation of Vinyl Resins.

The vinyl resins are products of the carbide industry; practically all the monomers are obtained from acetylene (formula VI) as a starting material. Thus, vinyl chloride and vinyl acetate are prepared by reaction of acetylene with hydrochloric acid and acetic acid (formula VII) respectively.

$$\underset{\text{(VI)}}{CH\equiv CH + HCl} \longrightarrow CH_2{=}CHCl$$

$$\underset{\text{(VII)}}{CH\equiv CH + H\,OOC\,CH_3} \longrightarrow CH_2{=}CH\,OOC\,CH_3$$

The processes of manufacture vary according to the monomer used. Thus, vinyl chloride is a gas and consequently it is usual to polymerise it by heating in sealed vessels, under pressure, while vinyl acetate and styrene are mobile liquids of relatively high boiling point. The latter boils at 146°C., so it is possible to handle these monomers in ordinary vessels fitted with reflux condensers.

As has already been mentioned, a catalyst is generally used, and the best catalysts are those capable of liberating oxygen. The most popular catalyst is benzoyl peroxide, but sodium peroxide, hydrogen peroxide, and sodium perborate are others which have been suggested. The quantity of catalyst used is small, usually of the order of 0·1 %, and a popular theory regarding the mechanism of this catalytic action is that pure monomers polymerise quite readily, but traces of impurities inhibit the polymerisation, and the small amount of catalyst added is sufficient to oxidise any inhibitive impurities present. Such a theory is supported by the fact that monomers which are to be stored for any length of time are usually treated with a small percentage of an inhibitor, usually a reducing agent, and hydroquinone is the substance in general use. This has to be removed from the monomer just before use, and is usually accomplished by washing the monomer with caustic soda solution. Polymers of varying molecular size are made by varying the quantity of catalyst and the temperature of the reaction, and rapid polymerisation produces polymers of low molecular weight, and vice versa.

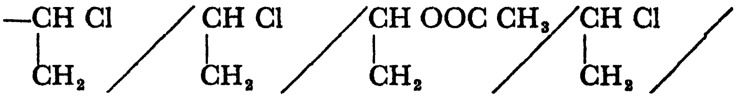
Another well-founded theory of the action of these catalysts is based on the electron structure of unsaturated compounds. Readers interested in this should consult a text book on Organic Electronic Theory.

EXPERIMENT 53. *Polymerisation of Styrene.*

The styrene must first be freed from hydroquinone. Take 50 cc. of styrene in a separating funnel and add 20 cc. of N/1 caustic soda solution. Stopper the funnel and shake vigorously, then allow to settle. The lower layer of caustic soda solution is brown. Separate it and discard. Wash repeatedly with caustic soda solution until it is no longer discoloured. Then wash twice with distilled water and finally dry by adding anhydrous sodium sulphate. Filter the styrene. To 20 cc. of styrene in a test tube add 0·5 cc. of 100 vol. hydrogen peroxide. Shake well; then stand in a warm place, *i.e.*, on top of a laboratory oven, and leave for three days. The styrene will be found to have thickened to a quite viscous syrup.

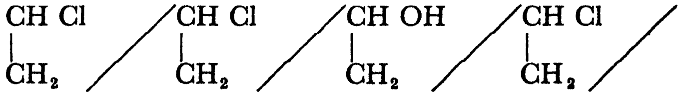
Interpolymerisation.

A wide range of quite novel compounds are obtained by the process of interpolymerisation, that is, polymerisation of a mixture of compounds. These compounds are not simple mixtures of the various polymers but new polymers in which chemical combination has occurred. Thus, one popular polymer is the vinyl chloride-vinyl acetate combination which could be represented as



In fact it is probable that greater quantities of this type of co-polymer are consumed at the present time than of the straight polyvinyl chloride.

There is actually no limit to the various combinations which can be obtained in such a manner. Thus, not only can various proportions of the respective monomers be used, and reaction conditions favouring polymers of either low or high molecular weight, but also other modifications can be introduced by simple chemical reactions. By careful saponification of the above mixed polymer it should be possible to convert it into a vinyl chloride-vinyl alcohol inter polymer, *i.e.*,



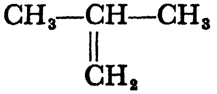
and other interesting reactions can be carried out.

Polythene and Polyisobutylene.

The vinyl group is probably the best known of the ethenoid series of resins but a unique class of plastic material is that produced by the polymerisation of ethylene (formula VIII) and isobutylene (formula IX).

$$H_2C{=}CH_2$$

(VIII)



$$CH_3\text{—}\underset{\substack{\| \\ CH_2}}{CH}\text{—}CH_3$$

(IX)

In the chapter on Polyamide resins we have seen how a large American firm, Du Pont de Nemours, initiated a large-scale, long-term research programme, costing a large sum of money, with a definite commercial aim, namely the production of a synthetic fibre to replace silk, and this was achieved after many years of patient, organised and systematic work. The product was Nylon.

Unlike their American counterparts, the British firm of I.C.I., in the early 1930's, conceived the idea of studying the mechanism of simple chemical reactions under quite extraordinary conditions unattainable in the ordinary laboratory. They chose conditions of extremely high pressure, about 2000 atmospheres or more, and high temperatures. Such a programme was attempted purely from an academic point of view, to investigate the unexplored fields of chemical reactions, and with no immediate object of financial gain, although it is obvious that such an investigation would prove costly and take many years to carry out.

Among the reactions investigated was that in which ethylene gas was heated under conditions of high temperature and very high pressures. During these experiments a resinous material, which could only have been obtained by some reaction of the ethylene, was obtained in small yield. By systematic research processes were evolved by which this product, polyethylene or polythene as it was soon called, could be obtained in large yields. The reaction is another example of polymerisation, through the unsaturated linkage, *i.e.*,

$$nCH_2{=}CH_2 \longrightarrow -CH_2-CH_2-CH_2-CH_2-CH_2-$$

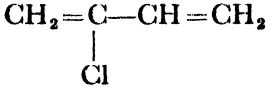
Polyethylene is a white translucent solid. It is made in various grades, according to the degree of polymerisation, and each grade has a different softening point. Each grade, however, unlike ordinary resins, has a fairly sharp softening point. These materials are extremely useful substances, particularly in the plastics industry. They are completely unaffected by water, solvents below 70°C., acids, alkalis or other chemical reagents, moreover, as a result of their hydrocarbon structure they possess extremely valuable electrical properties which make them indispensable in the field of high frequency electrical work.

Polyisobutylene is made by a similar process using isobutylene in place of ethylene. It is a much softer resin than polyethylene and is used to plasticise the latter material.

Synthetic Rubbers.

Although not strictly within the scope of this book, this chapter can only be concluded by referring to those synthetic resins which are of the synthetic rubber class, *e.g.*, Neoprene and the Buna rubbers. These are also products of the polymerisation reaction.

Neoprene is the name given to a rubber-like material produced by the polymerisation of a substance called chloroprene (formula x).



$$CH_2{=}\underset{\displaystyle Cl}{\underset{|}{C}}{-}CH{=}CH_2$$

(x)

Notice that in structure this compound resembles vinyl chloride (formula II), but with the introduction of another group with an unsaturated linkage. As a result the product of polymerisation still contains a certain number of unsaturated linkages which have not reacted, and in this way these products resemble rubber structure, and like rubber they are capable of further reaction, particularly with sulphur, *i.e.*, the process of vulcanisation.

The Buna rubbers are products of polymerisation of butadiene (formula XI) or interpolymers of butadiene and other monomers, for example styrene (formula IV), or acronitrite (formula XII).

$$CH_2{=}CH{-}CH{=}CH_2 \qquad \text{(XI)}$$

$$CH_2{=}CH\ CN \qquad \text{(XII)}$$

CHAPTER XIII

KIENLE'S FUNCTIONALITY THEORY OF RESIN FORMATION

By now the reader will probably be confused by the different types of resin which have been described. He will realise that these are only a selection of the many resins which can be synthesised from an apparent miscellany of raw materials by means of many of the common reactions of organic chemistry, and some of the uncommon ones, too, and using all manner of apparatus. And each resin is a complex mixture of molecules of varying size and shape.

Out of all these apparently chaotic mixtures of organic products could not some semblance of order be discovered? From time to time various workers have attempted to formulate theories to be used as a basis for the study of this immense problem of resinification. One of the soundest of the early theories suggested that resin formation occurred through the use of compounds containing certain distinctive groups which were called "resinophores." An obvious example of a resinophore is the group $-CH{=}CH_2$, and the formation of polymers from monomers containing such groups has been described in Chapter XII (page 132). There were, however, certain limitations to this theory which make it impossible to cover all types of reactions involving the formation of large molecules. The work of Carothers on Superpolyamides, and Kienle on Polyesters, however, led to new ideas and it was Kienle who first proposed regular principles underlying the formation of synthetic polymers. He did not immediately seek peculiarities in the reacting compounds but first looked for differences in the reactions causing the formation of resins in place of pure compounds, realising that definite structural reasons must exist to explain why the products of some reactions are pure liquids or solids of definite boiling or melting point and the products of other reactions are indeterminate resins of undefined softening point.

Now, in order that a reaction may occur between two molecules those molecules must each possess " points of reactivity " or reactive groups, sometimes called functional groups, and reacting compounds must have more than one such group in each molecule in order that condensation or polymerisation may occur. That is the basis of the theory of functionalities. A table is given below indicating the functionalities of some of the more common resin-forming materials, with explanations in those cases in which the number of functionalities is not obvious.

Thus, if acetic acid (formula I) with one reactive carboxyl group, is heated with ethyl alcohol (formula II), with only one reactive hydroxyl group, under certain conditions, an ester, ethyl acetate (formula III) is formed, which is a pure compound of fixed boiling point, and shows no tendency to resinify.

$$\underset{(\mathrm{I})}{CH_3COOH} + \underset{(\mathrm{II})}{C_2H_5OH} \longrightarrow \underset{(\mathrm{III})}{CH_3COOC_2H_5} + H_2O$$

But if phthalic acid (formula IV) and glycol (formula V), which each contains two functional groups, are reacted together, resin formation occurs and long chain molecules are formed.

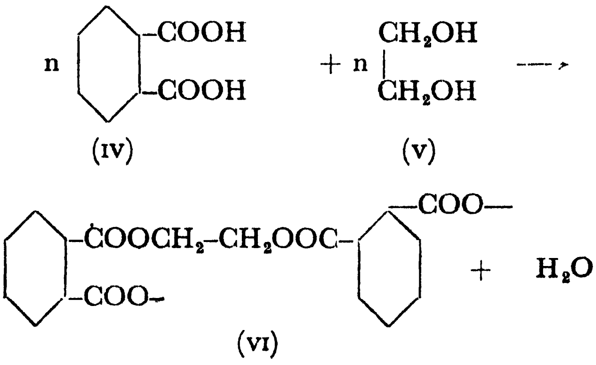
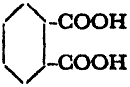
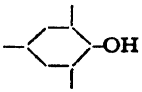
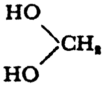
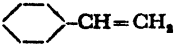
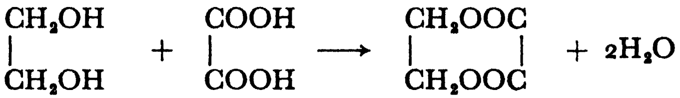


TABLE IX

Substance.	*Formula.*	*Functional Groups.*	*No.*
Glycol	CH_2OH | CH_2OH	OH	2
Glycerol	CH_2OH | $CH{-}OH$ | CH_2OH	OH	3
Phthalic acid		COOH	2
Adipic acid	CH_2CH_2COOH | CH_2CH_2COOH	COOH	2
Hexamethylene diamine	$H_2N(CH_2)_6NH_2$	NH_2	2
Urea	$H_2N.CO.NH_2$	NH_2	2
Phenol			3
Formaldehyde	H CHO or sometimes regarded as the hydrate H CHO, H_2O or 	OH	2
Styrene		$-CH{=}CH_2$ or $-\underset{\mid}{C}H-\underset{\mid}{C}H_2$	2
Dimethylene urea	$N{=}CH_2$ | CO | $N{=}CH_2$	$-\underset{\mid}{N}{=}\underset{\mid}{C}H_2$	4
Maleic acid	$CH.COOH$ ‖ $CH.COOH$	COOH $-CH{=}CH-$ or $\underset{\mid}{C}H-\underset{\mid}{C}H$	2 2

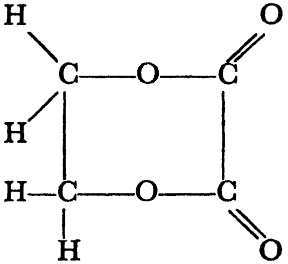
Carothers has shown that an exception can be made to this rule. When the size of the molecules is such that the product of initial reaction can form five or six membered rings, then cyclic compounds result, but otherwise resinous molecules are formed. An example of a cyclic compound is the product of reaction of glycol (formula v) and oxalic acid (formula vii).



$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + \begin{array}{l} COOH \\ | \\ COOH \end{array} \longrightarrow \begin{array}{l} CH_2OOC \\ |\qquad\quad | \\ CH_2OOC \end{array} + 2H_2O$$

(v) (viii) (viii)

which can be written



(ix)

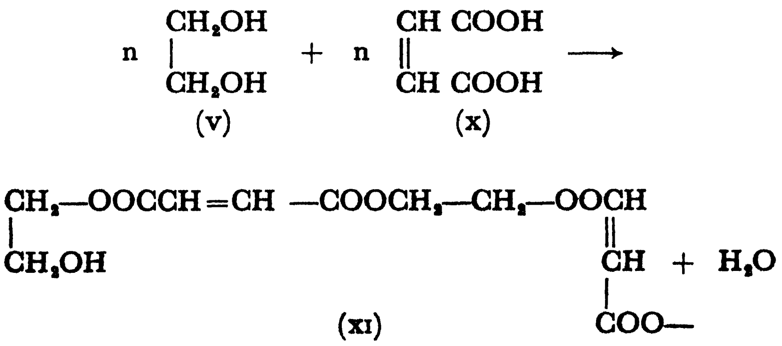
But apart from this exception the rule holds.

It is generally assumed that resins in which the molecules are made up of long chains of atoms, *i.e.*, molecules arising from a reaction of 2 : 2 functionality, are thermoplastic, or heat non-convertible. If, however, one of the reacting compounds has a functionality greater than 2, *i.e.*, glycerol has three hydroxy groups and is therefore of functionality 3, then two of the groups can be used to form the chain molecules but the third cannot take any part in such a chain reaction but can cause cross linking between the chain molecules, and the products of such reactions, which are large molecules of more complicated structure, are thermosetting or heat convertible. This is illustrated in Table X.

TABLE X

Reacting Molecules.	*Reaction.*	*Formation.*	*Chains.*	*Mol. Wt.*	*Type of Resin.*
Styrene	2·2	By heat	Long	V.high	non-convertible
Formaldehyde	2·2	"	"	"	
Glycol-Phthalic Anhy.	2·2	Elimn. of water	"	"	
Glycerol-Phthalic Anhy.	3·2	"	Short twining	Moderate	Heat convertible
Cyclopentadiene	2·2	By heat	Long	V.high	Non-convertible
Phenol Formaldehyde					
Acid Condensation	2·2	Elimn. of water	Long	Moderate	Non-convertible
Alkali condn.	3·2	"	Short twining	"	Convertible

Kienle, while working with alkyd resins, realised that particular cases exist where compounds contain more than one type of functional group, and in certain reactions only a portion of these groups take part in the primary reaction, the remaining groups remaining inactive until a later secondary reaction. A typical case is the formation of glycol maleate resins using glycol (formula v) and maleic anhydride. Maleic acid (formula x), has essentially two carboxyl groups, and is therefore bifunctional; it also possesses an unsaturated linkage –CH=CH–, and is again bifunctional in that respect. The initial reaction between glycol and maleic anhydride on heating at 150 to 170°C. for a long period is the formation of a polyester (formula XI), *i.e.*:



$$n\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array} + n\begin{array}{l}CH\ COOH\\ \|\\ CH\ COOH\end{array} \longrightarrow$$

$$\begin{array}{l}(v) \qquad (x)\end{array}$$

$$\begin{array}{lll}CH_2\text{—}OOCCH=CH\ \text{—}COOCH_2\text{—}CH_2\text{—}OOCH & & \\ | \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \| & & \\ CH_2OH \qquad\qquad\qquad\qquad\qquad\qquad\quad CH & + & H_2O \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | & & \\ \qquad\qquad\qquad (xi) \qquad\qquad\qquad\qquad COO\text{—} & & \end{array}$$

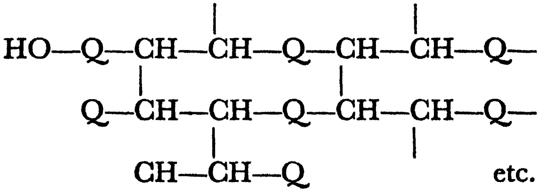
The formula (XI) can be written

$$HO\text{—}Q\text{—}CH{=}CH\text{—}Q\text{—}CH{=}CH\text{—}Q\text{—} \qquad \text{(XII)}$$

where Q represents $-CH_2CH_2OOC-$ or $OOC-CH_2CH_2COO-$

Now, such a compound (formula XII) still contains secondary reactive groups which so far have been inactive, but can be made to take part in a resin forming reaction.

Thus, if these resinous compounds are heated at higher temperatures, *i.e.*, 250°C., cross linking between the chain molecules occurs through these groups and compounds such as

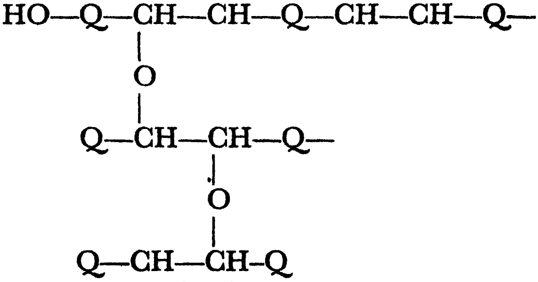


$$\begin{array}{ccccccccc} & & & \mid & & & & \mid & \\ HO\text{—}Q\text{—} & CH & \text{—} & CH & \text{—}Q\text{—} & CH & \text{—} & CH & \text{—}Q\text{—} \\ & \mid & & & & \mid & & & \\ Q\text{—} & CH & \text{—} & CH & \text{—}Q\text{—} & CH & \text{—} & CH & \text{—}Q\text{—} \\ & & & \mid & & & & \mid & \\ & CH & \text{—} & CH & \text{—}Q & & & & \text{etc.} \end{array}$$

(XIII)

can be built up.

Alternatively these chain compounds can be made to link together by means of oxygen linkages. In the presence of traces of cobalt catalysts, the $CH{=}CH$ become activated to oxygen and form new complex molecules, probably of this nature—



$$\begin{array}{ccccc} HO\text{—}Q\text{—} & CH & \text{—} & CH & \text{—}Q\text{—}CH\text{—}CH\text{—}Q\text{—} \\ & \mid & & & \\ & O & & & \\ & \mid & & & \\ Q\text{—} & CH & \text{—} & CH & \text{—}Q\text{—} \\ & & & \mid & \\ & & & O & \\ & & & \mid & \\ Q\text{—} & CH & \text{—} & CH & \text{-}Q \end{array}$$

(XIV)

Other examples of this secondary reaction can be seen in the drying oil modified alkyds which were described in Chapter IX.

As a result of his work on glyptals, Kienle has advanced three postulates of resin formation.

I. Organic molecules of high molecular weight are formed only when the interacting molecules are polyreactive, *i.e.*, have more than one centre of reactivity.

II. The interlocking of the molecules proceeds according to chance contact of any two individual reaction points which possess the proper degree of activation to bring about reactivity.

III. The relative size and shape of the reacting molecules, and position of the reacting points largely determine the physical properties of the resulting polymeride, *e.g.*, hardness, flexibility and heat convertibility.

Table X supports the first postulate.

The preparation of glycol maleate resins described above is an example of the second postulate, particularly the latter phrase, and examples demonstrating the third postulate can readily be seen in the description of the effect of substituents in various ethenoid polymers. (*See* page 134).

CHAPTER XIV

NOTE WRITING

It can be said with truth that science has progressed largely by the writing and reading of reports. The readers of this book will belong chiefly to that class which helps to provide the material for such reports. It is therefore very important that each should realise the necessity and desirability of keeping adequate records of all work carried out in a neat and orderly manner. This applies both to records of experimental work and to analytical tests.

Notebooks.

There is a tendency sometimes to keep records on scraps of paper. These invariably get mislaid, or alternatively are copied incorrectly, consequently the experimenter should provide himself with a *bound* notebook. Loose leaf notebooks should not be used, as again there is a tendency to take pages out, or to use sheets of paper on the bench with the idea later on of filing them, and again the chance of losing the page is ever present.

It is a good idea to have the pages numbered. Again this overcomes to some extent the removal of pages which have been spoilt or show bad or inaccurate work. The good assistant realises at an early date that it is not worth while covering up mistakes or faulty work. Only by allowing older or more experienced people to examine his work can his mistakes be discovered and corrected. The criticism—even if it is caustic—is helpful. The " cover-up man " is not wanted in the industry, and once found is always open to suspicion.

Records of Testing.

A great deal of routine testing is carried out in any resin department. The testing of raw materials, of resins during manufacture, and of final products, is of great importance. Such tests as solid contents of solutions, viscosity, etc., are every-day occurrences. Proper record should be kept. Remember that although a test may be memorised on the day it is carried out, it is frequently necessary to refer back to work carried out many months before. The person who is referring back may not always be the one who did the original work, hence the need for preciseness and clarity. Take for example the examination of a paint exposure panel. These are frequently exposed for several years. The examiner of the panel after such a period of years is often not the same person who formulated the finish, or who applied it, and unless there is a permanent record of the formula and method of application available in clear, concise terms understandable by anybody, that long term exposure test has been useless, and it cannot be repeated in a few days.

When any test has to be carried out the date, name and number of the sample, and nature of the test should be recorded clearly on the top of a page or a portion of a page, then any weighings, titrations or remarks should follow in such a way that one can *read* the method and follow the nature of the test. The following examples taken from actual practice illustrate the good and bad record keeper.

Bad.	Varnish 111/1.	Viscosity 55 secs.
Good.	10/4/45.	
	Varnish 111/1.	Viscosity, No. 4 Ford Cup/20°C. 55 secs.

Notice how the nature of the apparatus, and the temperature of the determination, both of which affect the results considerably, have been clearly stated.

Consider determining the solids content of a solution. In many laboratories there are several methods in use usually differing as regards the temperatures and length of time of the determination. Thus, different conditions are normally used to determine the solids content of cellulose lacquers and high stoving phenolics. Now consider the following extracts from notebooks.

Bad.	49·5622		13·7542
	57·1820		15·9276
	7·5168	37·95	2·1728
	52·4160	2·853	1·0568
	49·5622	$\frac{2{\cdot}854 \times 100}{7{\cdot}52}$	48·6%
	2·8538		

Good. 10/4/45.

Solids Content of Sample 111/1, 2 hours at 150°C.

	(I)	(II)
Wt. of dish	13·7542	21·3106
Wt. of dish + resin	15·9270	23·3270
Wt. of Resin	2·1728	2·0170
Wt. of dish + residue	14·8110	22·2900
Wt. of Residue	1·0568	0·9800
Solids content	48·6%	48·5%

It is possible to work out what the bad recorder was doing, but only just, and how many mistakes did he make? Such a state of affairs indicates an untidy mind, and such a mind is usually not a scientific one. Some laboratories have their own books of analytical methods. In such cases where several methods exist for one test the method number is sufficient explanation, *i.e.*,

Acid value of linseed oil No. 14 (Method 1a) 7·4.

The degree of accuracy of various tests is not fully understood by young operators. They should know, however, that it is useless to report any solid content, viscosity, acid value or other routine test on an oil or resin to more than one place of decimals. I have known iodine values of 179·432, solid contents of 33·958% and viscosity measurements of 13·342 cps.—the latter determination arising by dividing a time of 55 secs. by a calibration factor for a viscosity apparatus—but all these are absurd.

Records of Experiments.

Here again the operator must keep neat and accurate records of his work. New discoveries are made only by careful observation and recording of changes. The simplest method of keeping records is to rule up a page as below. Date, nature of apparatus, and charge should be entered at the top, and then frequent observations of time, temperature, remarks, and tests should be made. Observations are usually made at fixed times, but if something untoward occurs between these times it should be recorded. Consider the report sheet of the resin which should have been condensed at 220°C. It read—

Time	*Temperature*	*Remarks*
—	—	
—	—	
10.00	220°C.	Steady reaction
10.30	218°C.	,, ,,
11.00	223°C.	,, ,,
—	—	

when in reality this is what the log should have recorded.

Time	*Temperature*	*Remarks*
—	—	
10.00	220°C.	
10.10	170°C.	Raise gas flame
10.25	212°C.	
10.30	218°C.	
10.40	247°C.	Flame lowered
10.45	233°C.	
11.00	223°C.	

If this had been part of the record of a non-drying castor oil alkyd it would have indicated how near it was to becoming a drying oil alkyd. In general it should be understood that a 10°C. deviation in temperature during the preparation of a synthetic resin usually has a profound effect upon the nature and properties of the product. In many cases smaller deviations can be even more critical.

Report Writing.

At some stage in a career a report has to be written, so a few notes on how to write a report may not be out of place.

In the first place, don't write a report unless it is necessary. Remember also that the writer of a report has been immersed in the subject for some time, while the reader has not had, and is probably not likely to have, the time to get fully acquainted with all the details of the subject, so the salient features should be brought out and the trifling details omitted. Finally, remember that people in authority read reports, so a good style of writing is to be recommended.

Generally, a series of short reports is better than one very long one ; they are easier to write and easier to read. Thus, a report on "Cyclopentadiene as a Raw Material for Synthetic Resins" could be split up into a series of reports such as—

"Resin Forming Reactions of Cyclopentadiene—Part I. Reaction with Maleic Anhydride."

"Resin Forming Reactions of Cyclopentadiene—Part II. Reaction with Formaldehyde."

and so on.

A report should be made up of :—

(*a*) *A Title. e.g.*, "Alkyd Resins—Effect of varying the glycerine/phthalic anhydride ratio."

(*b*) *An Introduction.* This should explain the reason for carrying out the work, it should refer to previous reports or published literature and indicate briefly the line of attack to be adopted.

(*c*) *Experimental.* This section should describe the main experiments in such a way that new workers can repeat the work if necessary. Results should be clearly shown.

(*d*) *Discussion of Results.* Here the results have to be explained and conclusions drawn.

(*e*) *Conclusions.* Any definite conclusions should be set forth here.

(*f*) *Recommendations.* This should explain very definitely what specific actions should be taken by various departments or sections of a works. It might include action to be taken by production, research, or even sales departments, etc.

In the case of extremely long reports a *summary* should also be included. This should follow, in précis form, the general lines of the whole report and should only include material which can be found in the report. It should be made up of a few simple statements of fact.

CHAPTER XV

ANALYTICAL METHODS

1. Acid Value.

THE acid value of a resin or oil is the number of milligrams of potassium hydroxide required to neutralise the free organic acids in 1 gram of the material.

The most general method in use is as follows :—

Weigh accurately, to 1/10th of a milligram, approximately 1 gram of the substance into a 100 cc. conical flask. Dissolve the resin in 20 cc. of a mixture of benzene and alcohol (approximately two parts of benzene and one part alcohol, neutralised using phenol phthalein as indicator). This solvent will dissolve most oils and resins, but when it does not alternative solvents may be used, *i.e.*, pure benzene, or pure alcohol, or any neutral solvent, acetone is sometimes used. The substance may be dissolved by warming or shaking, but if warming is used the solution must be cooled after all the resin is dissolved.

Add 5 drops of phenol phthalein indicator. Titrate the solution with alcoholic N/10 potassium hydroxide until the solution is just red.

Calculation.

$$\text{Acid value} = \frac{\text{No. of cc.} \times 56 \times \text{Factor of Caustic Potash}}{\text{Wt. of Substance}}$$

Example.

Wt. of resin taken 0·9810 gms.

Titration using N/10 KOH, F ·104, 13·1 cc.

$$\text{Acid value} = \frac{13{\cdot}1 \times 56 \times {\cdot}104}{{\cdot}981} = 77$$

A modification of this method is as follows :—

Five gms. of resin is weighed out on a works balance and dissolved in 50 cc. of benzene/alcohol solvent in a 250 cc. flask. A few drops of phenol phthalein solution are added and the solution is titrated with N/2 caustic soda solution. Note here that although caustic soda solutions are frequently used in place of caustic potash solutions the acid value is still given in mgms. of potash and

1 cc. N Caustic Soda ≡ 1 cc. of N Potash ≡ 56 mgms. KOH.

The acid value may be read from the following table. Using 5 gms. of substance and N/2 alkali, or

10 gms. of 50% solution and N/2 alkali, or
10 gms. of substance and N/1 alkali.

TABLE XI

cc.	*A.V.*	*cc.*	*A.V.*
0·1	0·6	2	11·2
0·2	1·1	3	16·8
0·3	1·7	4	22·4
0·4	2·2	5	28·0
0·5	2·8	6	33·6
0·6	3·4	7	39·2
0·7	3·9	8	44·8
0·8	4·5	9	50·4
0·9	5·0	10	56·0
1·0	5·6	20	112·0

2. Saponification Value.

The saponification value of a substance is a measure of the total acids, free and combined, in the substances and can be defined as the number of milligrams of potash required to saponify 1 gram of the substance.

Three gms. of the substance are weighed into a Geissler flask. The sample is dissolved in 30 cc. of a neutral benzol-alcohol mixture and 50 cc. of N/2 alcoholic KOH is added (100 cc. for some samples). The mixture is refluxed on the water bath for 8 hours.

It is preferable to use the same pipette for the alcoholic KOH on each occasion. Duplicate tests and a blank determination should be carried out. If several tests are carried out similtaneously then two blanks are done for every ten tests.

At the end of 8 hours, the flasks are cooled and the contents titrated with N/2 acid. Sulphuric acid is usually used.

Calculation.

$$\text{Sap. value} = \frac{(\text{No. of cc. } H_2SO_4 \text{ for Blank} - \text{cc. of } H_2SO_4 \text{ of sample}) \times 28{\cdot}05 \times \text{factor}}{\text{Wt. of sample in gms.}}$$

Should the sample be insoluble in benzol-alcohol, the solvent is dispensed with, and the alkali added directly.

3. Melting Point Determination.

Any standard laboratory melting point apparatus can be used. A typical example is shown in *Fig. 13*.

The apparatus should be heated by a flame 20 mm. high placed with the tip of the flame 50 mm. below the sulphuric acid bulb. The thermometer, graduated from 0–360°C. need not be certificated. The bulb of the thermometer should be 1 cm. above the bottom of the flask. The bath consists of 96% sulphuric acid with one crystal of potassium nitrate, or alternatively liquid paraffin can be used.

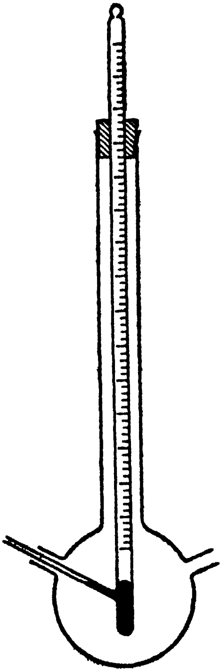


Fig. 13

Melting point tubes for resins are larger than the normal tubes used for organic compounds. They should have an internal diameter of 1–1·5 mm. The resin is finely ground in an agate mortar and the tube is filled to a depth of at least 8 mm., the powdered resin being well tapped down. The tubes are inserted in the bowl and held in place with the acid.

Two points are observed :—

(*a*) The Sinter-point, at which temperature the first signs of shrinkage are observed.
(*b*) The Fusion point, at which point fusion has clearly commenced.

The figure is given as M.Pt. 60/67°C., etc. The difference between the two figures increases as the temperature becomes higher.

4. Determination of Viscosity.

The viscosity of most resins is determined in solution form, and 50% solutions in toluene, or, in the case of alcohol soluble resins, in 74 o.p. methylated spirits, are the common solutions. These solutions must be made up very accurately as obviously a trace too much or too little solvent can make a considerable effect on the viscosity figure.

The temperature at which a viscosity determination is carried out is also extremely important as the temperature coefficient of viscosity is very high. The temperature normally used is 25°C. ± 0·1° but sometimes 20°C. ± 0·1° is used. It is immaterial which temperature is used provided it is recorded and kept standard throughout the laboratory. In well equipped laboratories a thermostatically controlled water bath is installed.

Two common methods of determining viscosity are the bubble tube and the Ostwald tube method. The latter is described in detail in B.S.S. 188.

Bubble Tube Method.—Standard glass tubes are used, 110 mm. long and 11 mm. internal diameter with one end sealed. The tubes are uniform in diameter. Two marks are etched on the tube, one 5 mm. and the other 15 mm. from the open end. The tube is filled with solution up to the lower mark, and is sealed with a cork pushed in so that the bottom of the cork just reached the upper mark on the tube. In this way a standard sized bubble is formed in the tube, 10 mm. deep. The tube is then immersed for 15 minutes in a water bath to bring the temperature to the correct figure for the measurement.

These tubes can be used in two ways :—

(*a*) Holding the tube vertical, invert it rapidly and measure the time for the bubble to rise to the top of the tube using a stop watch. Take the mean of three determinations and report the viscosity in seconds.

(*b*) The tube can be compared with a series of standard tubes containing oils of known viscosity. This is the principle of the Gardner Holdt method of measuring viscosity.

6. Determination of Phenol or Cresol in Water.

For this determination the strength of the solution for analysis should be about 1 gm./1000 gms. water. Test samples should be diluted to about this concentration. The following solutions are required :—

A. A solution of 6 gms. KBr in 1000 cc. of water.
B. A solution of 1·671 gms. $KBrO_3$ in 1000 cc. of water.
C. A solution of KI in water (10%).
D. A n/10 solution of sodium thiosulphate.

Method.—Fifty cc. of the sample are placed in a 500 cc. bottle fitted with a ground glass stopper possessing a dropping funnel with a stopcock. Add 50 cc. of each of solutions A and B, admitted direct into the bottle and not through the funnel. The stopper is replaced and 5 cc. of conc. H_2SO_4 are slowly admitted. The tap is closed and the bottle is gently shaken with a circular motion and then allowed to stand for 10–15 mins. Bromophenol forms as a precipitate. The bottle is cooled with ice or running water. When quite cold 10 cc. of the solution C is placed in the funnel, and slowly run in, the tap being closed immediately, and the bottle shaken. The iodine liberated is equivalent to the excess of bromine. After 2–3 mins. the stopper is withdrawn and rinsed into the bottle and the solution is then titrated against thiosulphate.

A blank determination, and also a duplicate are carried out.

Reactions.

1. $5\,KBr + KBrO_3 + 3\,H_2SO_4 \longrightarrow 6\,Br + 3\,K_2SO_4 + 3\,H_2O$
2. $C_6H_5OH + 6\,Br \longrightarrow C_6H_2Br_3OH + 3\,HBr$

1 mol. of phenol $\equiv$ 6 atoms of Br
1 atom of Br $\equiv$ 1 atom I $\equiv$ 1 mol. $Na_2S_2O_3$
1 mol. phenol $\equiv$ 6 mols. $Na_2S_2O_3$

Calculation.

y cc. of N/10 thio for blank.
z cc. of N/10 thio for test.

$$\text{Then percentage of phenol in water} = \frac{(y-z) \times \cdot 00157 \times 100}{50}$$
$$= \cdot 00314(y-z)$$

7. Determination of the Formaldehyde Content of Solutions.

Three gms. of the raw material (3 cc. = 3·3 gms. approx.) are quickly weighed into a 300 cc. stoppered conical flask and 50 cc. of N NaOH solution quickly added from a pipette. Approximately 50 cc. of 3% hydrogen peroxide solution is then added as rapidly as possible from a cylinder. The flask is then lightly stoppered and warmed either by hand, or by placing on the top of the drying oven. It is then allowed to stand for a time.

In the case of a 30–40% solution 2 hours is allowed.
In the case of a 10% or under solution 12 hours is allowed.

Reactions.

(*a*) $2\,HCHO + 2\,NaOH + H_2O_2 \longrightarrow 2\,H.COONa + H_2 + 2\,H_2O$
(*b*) $HCHO + NaOH + H_2O_2 \longrightarrow HCOONa + 2\,H_2O$

Both these reactions are equivalent.

The solution is now back titrated with N.HCl using litmus as in indicator. Two blanks are also carried out :—

1. The material may be acid. Therefore weigh out 3 gms. of the solution and titrate with N NaOH.
2. Another blank is run with 50 cc. of NaOH from the pipette and 50 cc. of H_2O_2, and treated as in the test.

Then if y = cc. of N.HCl used in blank 2.
z = sum of cc. of acid used in test and NaOH used in blank 1.

$$\text{Then \% formaldehyde} = \frac{(y-z) \times 0{\cdot}03002 \times 100}{\text{Wt. of sample.}}$$

A duplicate test should be carried out.

8. Determination of m-Cresol content of Crude Cresol.

Weigh 10 gms. of the sample (to ·001 gm.) into a 100 cc. conical flask and add 15 cc. of 96% H_2SO_4. Place in the oven at 90°C. for 1 hour.

Pour the sulphonated product into a 1-litre flask, invert the conical to drain and cool in cold water. When cold rinse the conical with part of 100 cc. HNO_3 (A.R. S.G. 1·4) from a

100 cc. cylinder and then pour back into the cylinder. Repeat the process 2–3 times and then pour the cylinder contents into the flask as rapidly as possible. Shake once quickly and then stand in cold water in the fume cupboard. A violent reaction starts and when completed the flask is heated on the water bath for 1 hour. Place 50 cc. of water in a 500 cc. beaker and pour the contents of the flask into it. Rinse the flask with a further 150 cc. of water, in portions, and then allow it to stand 3 hours. The crystals are then filtered through a weighed No. 3 Jena sintered glass filter. The beaker is washed with about 20 cc. N/1 nitric acid. The filter is then washed with a little 2 N nitric acid as tri-nitro *m*-cresol is slightly soluble in water. Place the filter in the oven for not more than 12 hours and weigh. The weight should then be confirmed by reweighing after 1 hour.

The glass filter should rest in a large crucible while drying.

$$\% \ m\text{-cresol} = \frac{10 \text{ Wt. of tri-nitro-cresol}}{\cdot 174 \times \text{Wt. of sample.}}$$

o- and *p*-cresols are oxidised to oxalic acid.

Note.

If the sample contains phenol, picric acid is obtained and the result is high. Phenol and xylenol are shown in the distillation test (B.P. 180–190° and 205–210°C.). If present in any appreciable amount omit the determination and report accordingly.

9. Determination of Free Phenols in Resins.

Grind up 100 gms. of the resin and steam distil in a small round bottom flask. Test the first drop of distillate with bromide water and if the test is positive continue until no more phenol (or cresol) distils. Make up the distillate to 1000 cc. and estimate the amount of phenol in solution.

10. Comparison of Reactivities of Heat-Hardening Phenolic Resins.

Two methods are in common use, the measurement of transformation temperature and of transformation time :—

Transformation Temperature.—An oil bath is maintained constant at 200°C. Into the oil bath is placed a test-tube, 6-in. long by 1-in. diameter, containing sufficient of the sample to fill the test tube to a depth of 1 inch. The resin is stirred with a thermometer until it begins to gell, and the temperature when this begins is noted. This is the transformation temperature. A substance with a low transformation temperature is more reactive than one with a higher transformation temperature.

Transformation Time.—An iron plate, approximately 6 inches square and 1-inch thick has a hole drilled in the centre ¼-inch diameter and ¾-inch deep. In this is placed a thermometer. At distances of 1½ inches from this central hole a set of depressions are made in the plate. These should be about ½-inch diameter and ⅛-inch deep. The plate is heated either by an electric heater or even gas flame and kept steady at 120°C. as measured on the thermometer in the central hole. Samples of resin are placed in the depressions and stirred with a piece of stout wire until they become unstirrable and begin to gell. The time for this to happen, measured in seconds, is the transformation time. This method is only reliable when comparing two or more resins. The resin with the shorter transformation time is the more reactive.

11. Solubility of Solid Resins in Solvents.

Crush the resin and weigh 5 gms. into a test tube. Add 5 gms. of solvent and warm in a water bath. Place a cork lightly on top of the test tube to prevent solvent evaporation. Shake gently from time to time to assist solution.

When all the resin is in solution cool well and report whether cold solution is sparkling clear or cloudy.

Report as :—Solution 1 : 1 white spirit. Clear or cloudy.
or Solution 1 : 1 ethyl acetate. Clear, etc.

A solution which becomes more cloudy on even moderate dilution indicates that the resin is insoluble. A slightly cloudy solution which remains slightly cloudy on dilution indicates cloudiness due to free glycerine in those cases in which glycerine has been used in the resin.

12. Dilution Test.

Take the solution prepared as above and add half its volume of similar solvent. Shake well and notice if clear or not. If clear add another measure of solvent and shake well. Continue until the solution is just cloudy. Report as : Dilution 1 : 5 etc. Just cloudy. *i.e.*, 1 part of resin to 5 parts of solvent, etc.

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