

Phenolic-Formal Resins

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Synopsis

A new method of curing phenolic novolac resins by means of cyclic formals under the catalytic influence of strong acids is given. It was proved that the formals react with the novolac molecules to form a highly crosslinked resite structure. As a practical consequence of this novel curing process it is possible to use the new resins at low or contact pressures in molding operations. The physical properties of the end products in general resemble those of the standard phenolic casting resins.

I. INTRODUCTION

The condensation products of phenols and formaldehyde are, in connection with their different properties and applications, generally classified as two important types: the resole or one-stage and the novolac or two-stage resins. The resoless have, in general, a truly thermosetting character, while in the case of the novolacs the crosslinking reaction must be effected with the aid of a hardening agent which supplies the additional methylene bridges. From a practical point of view, hexamethylenetetramine is a very useful compound for this purpose and is therefore almost exclusively applied.

In the technical manufacture of the phenoplasts the resoless are the basic material for the production of casting resins, adhesives, and laminated articles. The novolacs play a role as important raw materials for the production of industrial molding powders. In connection with the forming of volatile by-products during the setting process, the application of heat and pressure is an important feature in the final stage of the production of phenolic articles. This is particularly true for the fabrication of end products from molding powders, where high temperatures and pressures are necessary in order to get satisfactory results.

The liquid resole resins, on the other hand, are in general processed at lower temperatures and are sometimes used at rather low or contact pressure. However, an important drawback of these low pressure resins is the rather long curing time required at the lower temperature range. Additional disadvantages of the resoless are restricted shelf life and the time-consuming process involved in removal of solvent, which is often present to facilitate the impregnating or casting applications.

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In comparison with the more versatile polyester and epoxy resins the phenolics encounter, as condensation polymers, many more difficulties in the low pressure field. We now wish to report a new method of curing novolac resins in a short time by means of liquid reactive compounds, which enable working under extremely low pressures at moderate temperature.

The basic feature is the application of cyclic formals as a new class of hardening agents. The process can be distinguished into two different steps. First a novolac resin is prepared in the conventional way by reacting phenol and formaldehyde at about equal molar proportions; a slight excess of phenol is always maintained in order to avoid premature crosslinking. After a satisfactory resinification and dehydration the now hard and brittle novolac is dissolved in or intimately mixed with a certain amount of a cyclic formal. This mixture or solution has practically unlimited storage life. A very important point is that it is possible to vary the viscosity at a certain temperature within wide limits. The viscosity depends mainly on the concentration and nature of the formal and the degree of resinification of the novolac resin.

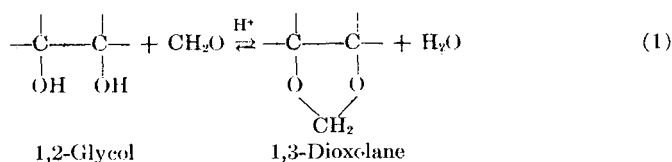
When a small amount of a strong acid is added to the resin mixture, the formal is cleft by a protolytic attack. Active components are released, which, at the low pH of the medium, will react immediately with the free active positions of the phenolic novolac. The result is a rather rapid gelation and curing of the composition, or a stepwise transition from liquid A-stage resin via a rubbery B-stage to the final hard resite or C-stage resin.

By further investigation of the reaction mechanism of the curing reaction, it has become evident that the function of the cyclic formal is not restricted to the simple delivery of formaldehyde as a hardening agent. By means of an acetone extraction method we could prove that the formals or splitting products thereof are practically entirely integrated in the cured resin.

II. CYCLIC FORMALS AS CURING COMPOUNDS

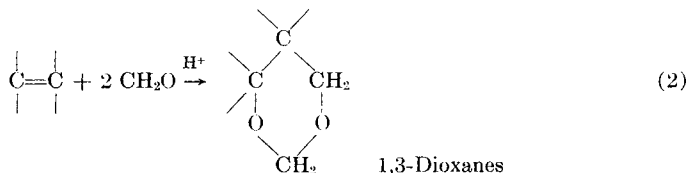
A. Formation of the Cyclic Formals

As basic material we used the cyclic formals of 1,2-glycols and 1,3-glycols, which are respectively called 1,3-dioxolanes and 1,3-dioxanes. In general they are made quite easily by reacting about equal molar quantities of formaldehyde and the glycol concerned under the influence of a small amount of strong inorganic acid.¹ As an example, the acetalization reaction of formaldehyde with 1,2-glycols can be represented as shown in eq. (1).



The equilibrium can be shifted to the right by removal of the lower boiling dioxolane compound from the reaction mixture. After a suitable separation from the condensation water, the 1,3-dioxolanes can be obtained in high yields. The 1,3- or *m*-dioxanes can be prepared in the same way from 1,3-glycols, but other syntheses are also possible.

As a modification of the Prins reaction, a cyclization of the primary formed products, often leads to the formation of 1,3-dioxanes in large amounts.² A typical example is the synthesis of 4-phenyl-1,3-dioxane from styrene.³ The addition reactions can in general be given as shown eq. (2).



By these two important methods a very broad range of cyclic formals can be made, if necessary even fairly easily on a large scale, because of the accessibility and costs of the raw materials.

The lower members are liquids with rather low boiling points and a high solvent power for phenolic resins. The formals of higher molecular weight and those derived from polyfunctional hydroxy compounds, for instance pentaerythritol, sorbitol etc., are mostly solid at room temperature.

B. Novolac-Formal Mixtures

The phenolic novolac resins are miscible in all proportions with the cyclic formals. The consistency of the mixtures at room temperature can vary from solid to a viscous fluid, depending upon several factors, the most important of which are the nature and concentration of the formal. The solvent power of the formals decreases in general with increasing molecular weight, and the mixtures based on dioxolanes have often a lower viscosity than the corresponding 1,3-dioxanes. In connection with the high viscosity of the novolac solutions, the mixing process can be accelerated by heating and stirring both components at about 100°C. In Figure 1 the concentration dependence of viscosity at room temperature is given on a logarithmic scale for two dioxolanes which act as solvents for the same phenol novolac; in Figure 2 the viscosity-temperature relationship is plotted for two different types of formals, viz. 1,3-dioxolane and 4-phenyl-1,3-dioxane.

The concentration of both formals in the latter case is about 47 mole-% and the percentages formal by weight are, respectively, 40% and 60%. One clearly sees in Figure 2 the much higher solvent power of the dioxolane. This is also again demonstrated when equal weight percentages of the two types are compared as in Table I.

A very important property with respect to the practical application is the storage life of the resin mixtures. In the case of the conventional resoles it

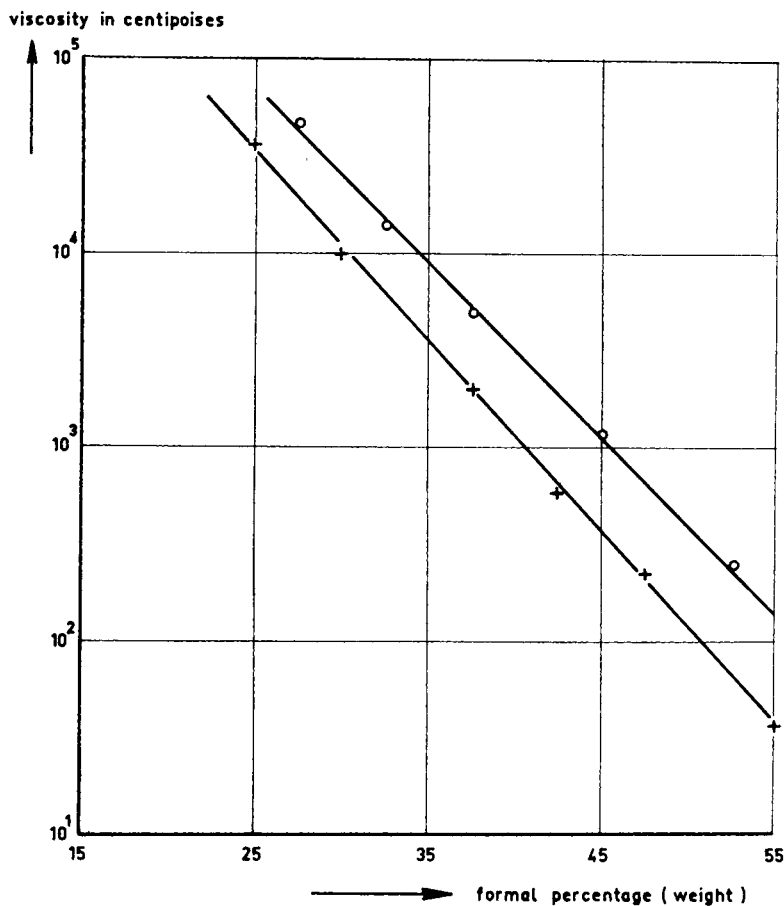


Fig. 1. Viscosity-concentration relationship of two novolac-formal mixtures at 20°C.: (+) 1,3-dioxolane; (O) 4-methyldioxolane.

is a well-known fact that those resins gradually increase in viscosity as a consequence of the presence of reactive methylol groups.

In order to investigate the stability of the new phenolic-formal systems at intervals over a period of two years we measured the viscosity of two

TABLE I
Viscosities and Plastic Behavior of Two Formal-Novolac Mixtures at Room Temperature

Concentration, wt.-%	Consistency	
	Novolac with 1,3-dioxolane	Novolac with 4-phenyl-1,3-dioxane
60	80 cpoise (pourable)	20,000 cpoise (viscous syrup)
50	400 cpoise (pourable)	Very viscous paste
40	1,000 cpoise (pourable)	Stiff paste
30	10,000 cpoise (pourable)	Rubbery to stiff
20	Very viscous paste	Hard, brittle resin

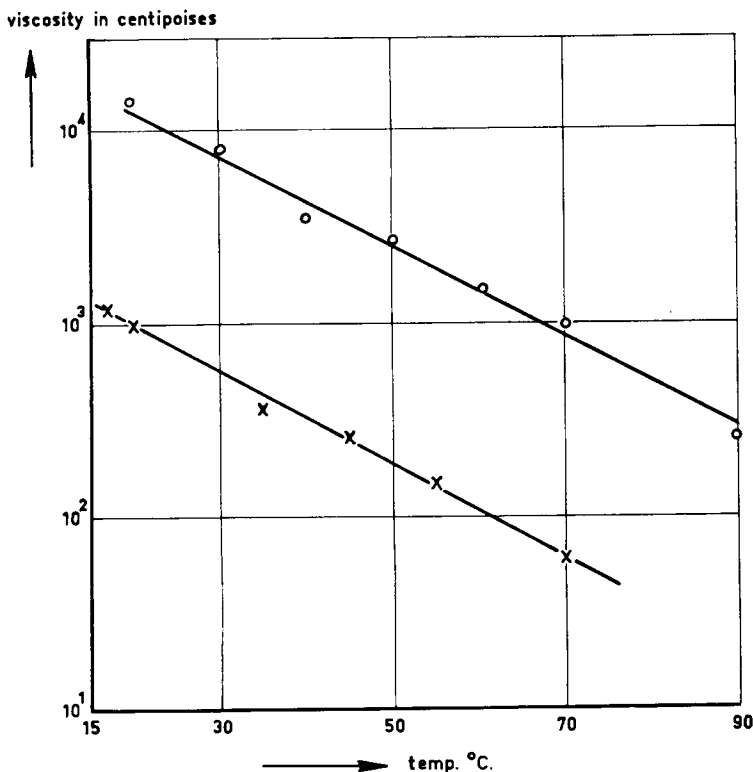


Fig. 2. Correlation of the viscosity with temperature for two different novolac-formal mixtures: (O) 4-phenyl-1,3-dioxane; (X) 1,3-dioxane. Formal concentration 47 mole-% formal.

TABLE II
Change in Viscosity of Two Novolac-Formal Mixtures Stored at Room Temperature

Storage time, months	Viscosity, cpoise	
	Mixture A 30% 1,3-dioxolane	Mixture B 30% 4-CH ₃ -1,3-dioxolane
0	14,000	21,500
1	13,500	19,000
2	13,500	21,500
3	18,500	26,000
4	21,500	32,000
5	22,000	31,000
6	24,000	34,000
10	26,000	36,000
15	27,000	37,000
21	31,000	39,000
24	33,000	42,000

samples, which contain rather active formal and were stored at ordinary temperatures (15–25°C.). The measurements were performed with a Brookfield rotation viscometer. The results are given in Table II.

From the figures it can be concluded that the resin solutions are quite stable and that the formal react practically not at all with the novolac component under normal and neutral conditions. The apparent small increase in viscosity is probably chiefly caused by a slight, inevitable evaporation of the rather volatile formal, especially during the measurements.

C. Gelation and Curing of the Resin Mixtures

When a strong acid compound is added to a novolac-formal mixture, the original inert solution is transformed to a reactive two-component system. A reaction is started between the cyclic formal and the phenolic resin, which

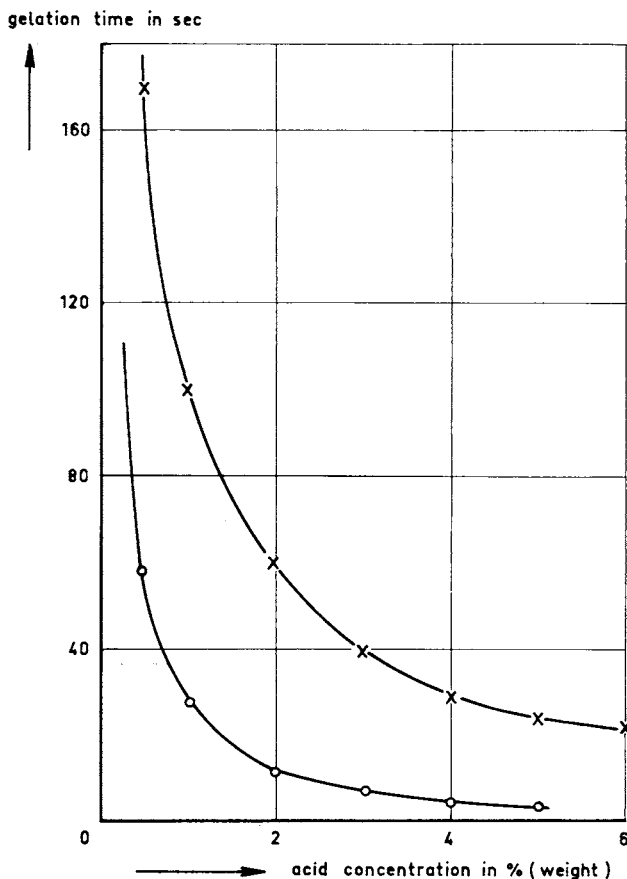


Fig. 3. Gelation time vs. acid concentration at 110°C.: (X) *p*-toluenesulfonic acid; (O) mixture of *o*- and *p*-phenolsulfonic acids. Resin composition: phenol-novolac and 4-phenyl-1,3-dioxane; formal-novolac ratio by weight 50:50.

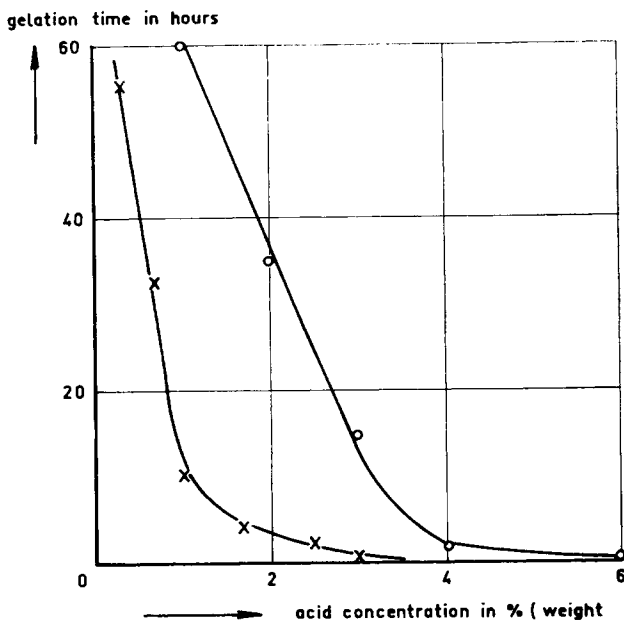


Fig. 4. Gelation time vs. acid concentration at 20°C.: (X) sulfuric acid 96%; (O) mixture of *o*- and *p*-phenolsulfonic acids. Resin composition: phenol-novolac and 1,3-dioxolane; formal-novolac ratio by weight 30:70.

manifests itself after a short time in a rapid increase in viscosity. This reaction is initiated by a protolytic attack of the acid on the cyclic formal resulting in the release of formaldehyde and other reactive splitting products, which combine almost immediately in a secondary reaction in the acid medium with the free *ortho* or *para* positions of the phenolic nucleus. The formal now acts as a hardening agent and after a certain time the whole mixture gels (B-stage) and finally sets to a hard, insoluble, infusible resite resin (C-stage).

The overall reaction is strongly exothermic, so it is necessary to control the resinification process in order to obtain satisfactory results. The velocity of the curing reaction depends upon several different factors, the most important of which are the following: (1) nature and concentration of the acid catalyst; (2) composition of the resin mixture; (3) temperature. We will now discuss the influence of the above mentioned factors successively.

1. Nature and Concentration of the Acid Catalyst. This influence was studied by measuring the gelation time by a stroke cure method of a certain resin mixture, as a suitable parameter for the reaction rate of the curing process.

It is evident that the specifications are determined under comparable conditions as regards composition and temperature. It is clear from Figure 3 that the gelation time is strongly dependent upon the H^+ concen-

tration. A very useful catalyst system consists of a mixture of *o*- and *p*-phenolsulfonic acids, which is easily made by mixing equal parts by weight of phenol and concentrated sulfuric acid. Gelation time of this catalyst mixture is plotted in Figure 3 in comparison with *p*-toluenesulfonic acid, while in Figure 4 that of the phenol-sulfonic acids is compared with sulfuric acid. In the latter case, a reactive dioxolane compound was chosen as hardener by which it was possible to measure in a reasonable way the gelation time at room temperature. At very high acid concentrations $>6\%$ the curing reaction is difficult to control as a consequence of a quick release of much heat, and the mixture often sets to a homogeneous porous mass in a very short time.

In this connection it is clear that heat exchange in the total mass has much influence on the gelation and curing time. A large mass of resin going out of hand can react dangerously and sometimes with explosive violence.

At concentrations below 0.5% the gelation time is very long, especially at room temperature, and precautions must be taken in the case of applying the active, volatile curing agents. Otherwise the hardener has time to evaporate before the setting process can proceed in the usual way.

The common organic acids have in general not much catalytic activity for the curing of the resins. The dissociation constants of acids which are suitable must be in the order of 10^{-1} – 10^{-2} at least.

Therefore inorganic acids or organic sulfonic acids are used almost exclusively. It is also possible to apply so-called latent catalysts, which are compounds releasing strong acids under certain conditions, i.e., acid chlorides, α -chloroethers, and esters of strong inorganic acids.

TABLE III
Gelation Time for Different Catalysts

Catalyst compounds (0.01 mole/ 100 g. resin mixture)	Gelation time, min.	
	In novolac-1,3-dioxolane (70/30 mixture) at 60°C.	In novolac-4-phenyl- 1,3-dioxane (60/40 mixture) at 100°C.
Phosphoric acid	4-5	3-4
Hydrochloric acid	2	2
Sulfuric acid	1	1
Phenolsulfonic acids (<i>o-p</i> mixture)	10	3-4
<i>p</i> -Toluenesulfonic acid (PTS)	12	6
<i>p</i> -Toluenesulphonyl chloride	120-180	30
Methyl ester of PTS	900	70
Ethyl ester of PTS	1020	100
Butyl ester of PTS	1980	120
Phenylester of PTS	No gelation in 7 days	No gelation
Monochloroacetic acid	No gelation in 7 days	No gelation
Dichloroacetic acid	No gelation in 7 days	No gelation
Trichloroacetic acid	3-4 days	40
Triethyl phosphate	No gelation	No gelation

In Table III the measurements of gelation time of some catalysts in two different formal mixtures are given.

It is obvious that the gelation time is a function of the hydrolytic stability of the esters of *p*-toluenesulfonic esters, which increases in the order given.

For technical applications a suitable catalyst must meet some practical requirements. Most important are good compatibility with the resin blend, ease and safety of handling, while in connection with a reasonable pot-life and short curing cycles a sharp dependence of the curing time upon temperatures is very desirable.

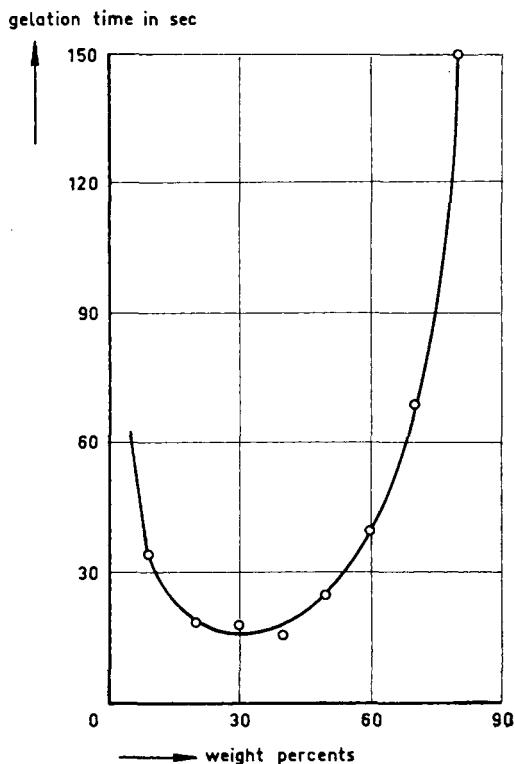


Fig. 5. Gelation time as a function of the formal concentration at 130°C. Resin system: phenol-novolac and 4-phenyl-1,3-dioxane; catalyst: 2% *p*-toluenesulfonic acid.

2. Gelation Time and Composition of the Resin Mixture. Both components, the novolac and the formal, as they are structurally incorporated in the final resite, have much influence on the rate of curing. In the acid curing reaction with the cyclic formals the phenolic novolacs exhibit the same kinetic features as already known from conventional phenolic resin chemistry. Thus, in reaction with the same formal, the gelation time varies with the degree of initial condensation with formaldehyde and the nature of the parent phenolic compound.

TABLE IV
Gelation Time of Different Formal–Novolac Mixtures at 65°C.

Cyclic formal	Gelation time, min.
1,3-Dioxolane	2-4
4-Methyl-1,3-dioxolane	6-8
4,5-Dimethyl-1,3-dioxolane	9-11
4-Chloromethyl-1,3-dioxolane	11-13
4-Phenyl-1,3-dioxolane	6-7
1,3-Dioxane	14-15
4-Vinyl-1,3-dioxane	24-25
4-Phenyl-1,3-dioxane	29-30
4-Ethylphenyl-1,3-dioxane	23-24
4,4-Methylphenyl-1,3-dioxane	18-19
2,4,8,10-Tetroxaspiro-(5,5)-hendecane (bis-formal of pentaerythritol)	90-92

Because of greater activity, resorcinol or *m*-cresol resins can thus be used to increase the rate of curing of the novolac mixtures.

The influence of the mixing ratio on the curing reaction is given in Figure 5, where the gelation time is given as a function of the formal concentration. For convenience, the system 4-phenyl-1,3-dioxane–phenol novolac was chosen. The formal concentration is plotted on the horizontal axis in weight per cent; the measurements were performed at 130°C. with 2% *p*-toluenesulfonic acid as a catalyst. At about 30% there is a definite minimum in gelation time. The normal increase in the reaction velocity of the resinification reaction with increasing the formal concentration is after this point counteracted by a decrease caused by the dilution effect of an excess in hardener concentration.

The minimum gives also the ratio in which both components should be mixed in order to get optimum curing relations and mechanical properties. The structure of the formal has much influence on the setting time. The protolytic stability of the ring structure is decisive in this connection, because the first reaction step is the scission of the formal ring.

We confirmed this by measuring the gelation time of a number of different novolac–formal combinations. In each case an equivalent novolac–formal ratio was used, while the other parameters are held constant. The catalyst was 1% phenolsulfonic acid. Results are summarized in Table IV.

A most important point is the much higher reactivity of the dioxolane compounds in comparison with the dioxanes. The activity of the former is in general higher by a factor of 5–6. This is in agreement with the data given by Leutner,⁴ who measured the speed of hydrolysis under acid conditions of some cyclic acetals. He found that the hydrolysis of the five-membered ring systems is 5–6 times more rapid than of the six-membered rings. He further found that the speed of hydrolysis is decreased by substituting a hydrogen atom by an alkyl radical in the alcohol (glycol) component. This effect is also shown in Table IV. The substituted formals have always a longer gelation time than the parent compound.

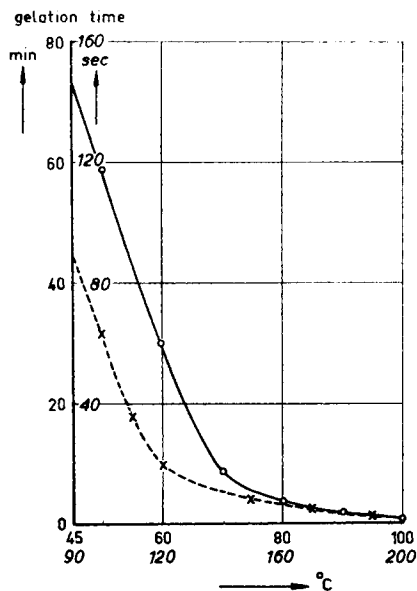


Fig. 6. Gelation time as a function of the temperature: (X) curve for temperatures above 100°C. (time in seconds); (O) curve for temperatures below 100°C. (time in minutes). Resin system: phenolic-novolac and 4-phenyl-1,3-dioxane, ratio by weight 50:50; catalyst: 1% phenolsulfonic acids.

The bis-formal of pentaerythritol is a very stable substance in this connection,⁵ as is confirmed by the peculiar long gelation time with phenolic novolac (90 min.).

Because at room-temperature the curing reaction of the bis-formal can practically be neglected, this compound is particularly well suited for the fabrication of molding powders with a long storage life.

3. Gelation Time and Temperature. Both the cleavage reaction of the formal and the secondary condensation of the phenolic resin with the scission products is strongly dependent upon temperature. In the case of the conventional acid-cured resole resins it is known that a rather rapid setting of those resins occurs at room temperature (cold-setting resins).

On the other hand it can again be shown that the gelation time for the phenolic formal resins is foremost defined by the nature of the formal. In Figure 6 the gelation time of a 4-phenyl-1,3-dioxane blend is plotted against temperature in two different curves, and it can be seen that at temperatures as high as 60°C. the gelation sets in only after 30 min., while in the case of 1,3-dioxolane the gelation time is in the order of 5 min. A conventional resole reacts in this range almost immediately. A practical consequence of these effects is that it is possible to compose resin mixtures of a rather long pot-life by suitable choice of the formals and catalyst concentration.

In connection with the low boiling points of some dioxolanes and their reactive character the maximum hardening temperatures recommended for

these systems must be about 10–20°C. below their respective boiling points, otherwise flaws and bubbles may occur in the end product, caused by the boiling of the hardener.

Below 10°C. the gelation time for most systems is too long to be measured. For the contact pressure application it is advisable not to work at temperatures much above 90°C. in connection with the formation of slight amount of water during the curing reactions.

Higher temperatures are always possible if the residues are already in a gelled B-stage or if the process is performed under low pressure in the range of 10–100 psi.

III. REACTION MECHANISM AND STRUCTURE OF THE CURED RESINS

It has already been indicated that the cyclic formal, in the gelling and curing reaction of the novolac resin, is more than a simple supplier of formaldehyde as a crosslinking agent. The chemical reactions actually occurring are without doubt very numerous and difficult to describe and lead to a highly complex structure of the final cured resin.

We have tried to get a better understanding of the reaction mechanism by estimating the amount of extractable matter of some cured novolac-formal resins as a function of the molar ratio. This was done by an extraction of pulverized resin samples in a Soxhlet apparatus with boiling acetone during 5 hr. In Figures 7 and 8 the results are given for the extraction of two different formals. The sol fraction is plotted against the molar ratio; the

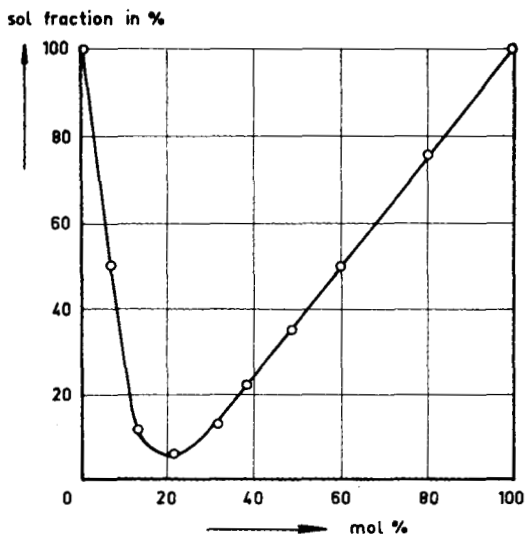


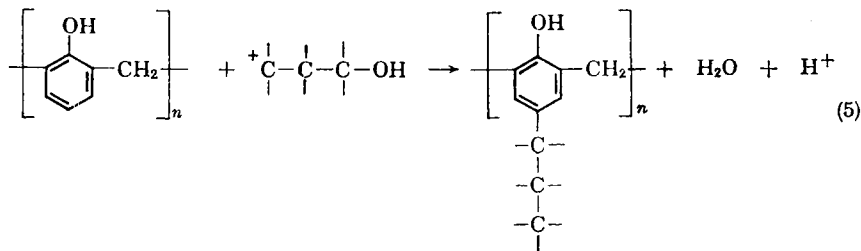
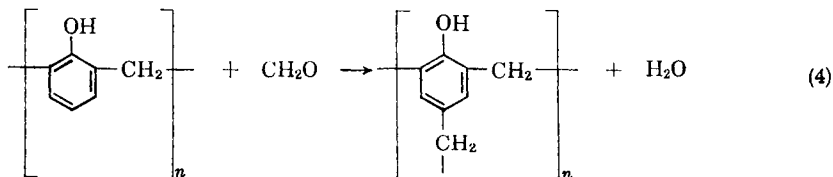
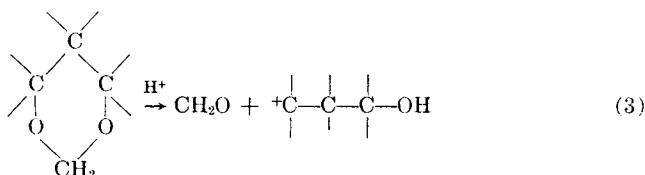
Fig. 7. Amount of extractable matter (sol fraction) as a function of resin composition. Phenol-novolac cured with 4-phenyl-1,3-dioxane.

two ordinates represent pure formal or polymerized products thereof and pure novolac resin, respectively.

The most interesting point of the curves is the presence of a rather sharp minimum at a definite molar ratio, which is characteristic of the formal in question.

The position of this minimum which represents the optimum degree of cure can also be calculated according to the following theoretical considerations. The resin system is typical of a two-stage resinification reaction. First a novolac is prepared from phenol and formaldehyde at a 1:0.9 molar ratio. If we assume that at maximum degree of cure all the reactive *ortho* and *para* positions of phenol are fully saturated, the molar ratio of phenol to the total amount of crosslinking agent must be 1:1.5. If the cyclic formal should only furnish formaldehyde as crosslinking component, about 0.6 mole formal or 37 mole-% is needed to saturate the residual active spots of the novolac resin. On the other hand, should each molecule cyclic formal deliver another active crosslinking component besides formaldehyde, this amount is reduced in the case of the normal cyclic formals to 0.3 mole or to a novolac-formal molar ratio of 1:0.3 or 23 mole-% (Fig. 7). This value can be still more reduced in the case of the bis-formal of pentaerythritol, where a theoretical optimum can be expected at a molar ratio 1:0.15 or 13 mole-% formal (Fig. 8).

Thus the experimental data confirm the assumption of two crosslinking components per molecule cyclic formal at the optimum ratio. In the case of 1,3-dioxane compounds we can formulate the reaction scheme shown in eqs. (3)–(5).



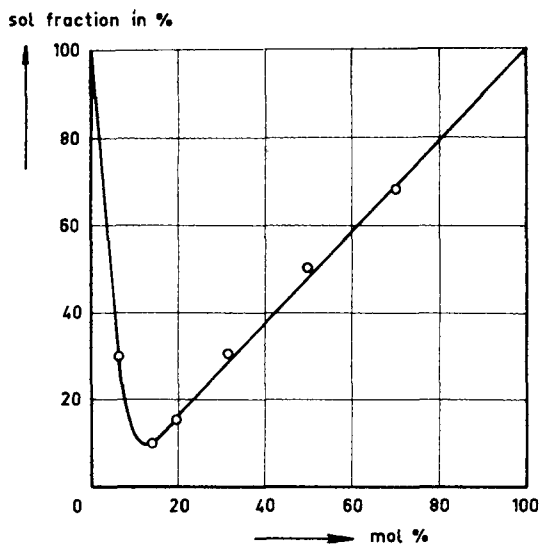
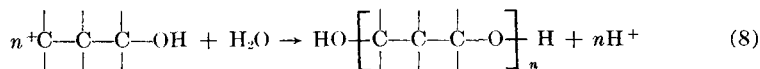
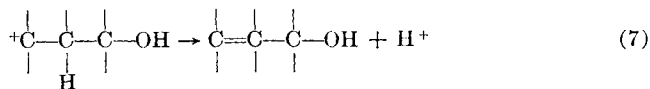
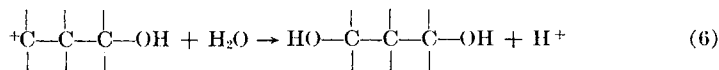


Fig. 8. Amount of extractable matter (sol fraction) as a function of resin composition. Phenol-novolac cured with the bis-formal of pentaerythritol.

In reaction (3) the cyclic formal is cleaved under the influence of protons in formaldehyde and hydroxyalkylcarbonium ion.⁶ Reactions (4) and (5) demonstrate the curing of the novolac by formaldehyde and the carbonium ion to a three-dimensional network, introducing both methylene and alkylene bridges in the resin, while each crosslink further delivers one molecule of water.

In the case of an excess of cyclic formal in relation to the novolac it is acceptable that the curing via reaction (4) is more pronounced, in agreement with the well-known rapid curing of phenol-resole resins in acid media.^{7,8} The now in a way superfluous hydroxyalkylcarbonium ion can stabilize itself in different ways:



(a) reaction with water to 1.3 glycols, eq. (6); (b) formation of an olefinic bond, eq. (7); (c) formation of polyoxyalkylene ethers, eq. (8). At a very large excess of cyclic formal, polymerization to linear formal resins is also possible. All the above mentioned end products of the scission reaction are easily extracted with acetone from the cured resin and represent the large sol fraction at high formal concentration. In this stage of our work

it is not yet possible to make a decision as regards the most probable course of the secondary reactions.

The formation of alkylene groups in the curing of novolac with formals finds a parallel in the well-known alkylating reactions of phenolic compounds with olefins or alcoholic compounds under the influence of strong acids.⁹⁻¹¹ In an additional investigation the actual presence of the alkylene groups in the final resin could be proved by a more direct method. This was done by curing the resin with a radioactive formal as a tracer and analyzing the sol and gel fractions after the extraction with acetone.

The results of this work will be published in a separate communication.

IV. NATURE AND PROPERTIES OF THE END PRODUCTS

In the final or resite stage the new resins resemble in outer appearance and physical properties the normal phenolic casting resins. They are mostly brown to orange in color and contain water in a highly dispersed colloidal phase. Depending upon the nature of the applied formal, the resins are translucent or opaque; this effect is probably also connected with the particle size of the water droplets.

At room temperature they are fairly resistant to the action of most chemical reagents except strongly alkaline solutions.

TABLE V
Chemical Resistance of Formal Resite Samples Immersed for 4 Weeks at Room Temperature

Reagent	Weight change, %			
	Novolac resite cured with 50% phenyl-1,3-dioxane	Novolac resite cured with 30% 4-methyl-1,3-dioxolane	Normal phenolic cast resin	Appearance of the formal-novolac resin
H ₂ O	+0.20	-0.53	+0.40	No change
H ₂ SO ₄ (10%)	+0.22	-0.12	+0.20	No change
H ₂ SO ₄ (50%)	+0.21	+0.10	+0.10	Slightly dark
H ₂ SO ₄ (conc.)	+1.91	-0.20	+1.8	Greatly darkened
NaOH (1%)	+0.22	+10.1	+6.4	Darkened
NaOH (10%)	+2.87	Disintegrated	Dissolved	Darkened
Alcohol (96%)	+5.46	+5.8	+0.10	Slightly swollen
Acetone	+5.49	+4.7	+0.60	Same
Toluene	-0.10	+0.12	-0.10	No change
Gasoline	-0.10	-0.10	-0.04	No change

In Table V a list is given of the effects of various reagents on two types of formal-novolac resites, together with a normal phenolic cast resin as a comparison. The most important difference between the new and the conventional resin is the much higher degree of swelling in polar solvents of the former.

This effect is most probably a result of the presence of longer crosslinks as a consequence of the alkylation activity of the formals.

The mechanical properties of some phenol-formal resins are listed in Table VI. In order to get satisfactory results it is always highly important to choose the right curing conditions; otherwise over- or undercure will be the result. In this respect such factors as curing temperature, curing time, catalyst concentration, and proper formal content are particularly conclusive. In general, the highest strength figures are reached at the optimum novolac-formal ratio of 20–25 mole-% formal; a higher formal content results in an increasing plasticizing effect of the excess formal and scission products thereof.

TABLE VI
Mechanical Properties of Some Formal-Novolac Resins

Mechanical and electrical properties	Curing agent				ASTM test
	4-Phenyl-1,3-dioxane	Bis-formal of pentaerythritol	1,3-Dioxolane	Cast phenolic resin	
Specific gravity 25/25	1.2–1.3	1.2–1.3	1.1–1.2	1.3–1.7	D792
Flexural strength, kg./cm. ²	350–550	800–600	500–600	350–1000	D790-61
Tensile strength, kg./cm. ²	200–300	400–450	300–350	200–500	D638-61
Impact strength cm.-kg./cm. ²	0.8–1.1	1.2–1.3	1.0–1.3	1.0–3.0	D256-56
Elastic modulus $\times 10^3$, kg./cm. ²	25–45	38–47	27–30	28–42	
Hardness, Rockwell M	100–120	110–120	80–90	50–130	D785-61
Strain at fracture, %	0.5–1.0	0.7–1.5	1.2–4.5	0.5–2.0	
Shrinkage, vol.-%	0.8–2.0	0.8–2.0	1.0–2.0	1.0–2.0	
Volume resistance, ohm.-cm.	10^{11} – 10^{13}	10^{10}	10^{10}	10^{10}	D257
Surface resistance, ohm.-cm.	10^{13} – 10^{15}	10^{10}	10^{12}	10^{11}	
Heat distortion temp., °C.	110–130	120–160	100–140	60–160	D468

The figures in Table VI are not to be taken in too absolute a sense. They are only given for a rough classification of the new resins. Comparison with the normal cast resin figures shows very clearly that there is a good resemblance to that conventional type. The dielectrical properties of some phenol-formal resins were studied in a separate investigation, the results of which will be published in a later communication. A remarkable interaction effect between protons and the water droplets originating from the curing reaction could be demonstrated in the crosslinked resin.

The heat distortion temperature also depends greatly upon the curing conditions and the nature and concentration of the formal. In general, the same parameters as discussed above in connection with the gelation time

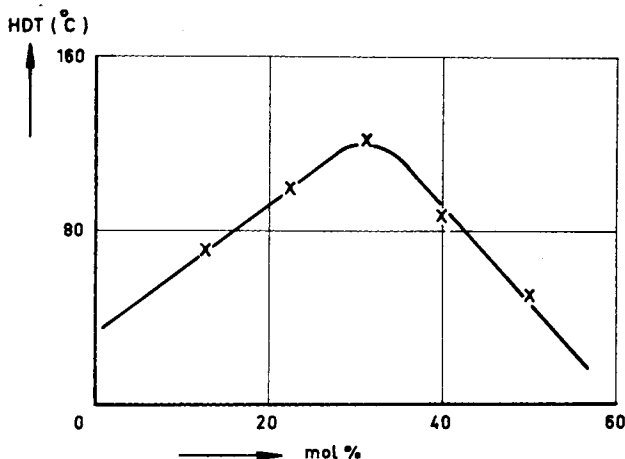


Fig. 9. Dependence of the heat distortion temperature (HDT) on the resin composition. Novolac resin cured with 4-phenyl-1,3-dioxane; catalyst: 1% phenolsulfonic acids.

have also a great influence on the heat distortion temperature. As an example, the concentration of 4-phenyl-1,3-dioxane against the heat distortion temperature (HDT) is plotted in Figure 9. All test specimens were cured under the same conditions. A rather sharp optimum is formed at about 30 mole-% formal. This concentration point gives the most dense crosslinking of the cured resin. At higher formal content a strong plasticizing effect can be observed. Another interesting phenomenon is the influence of the formal structure on the heat distortion temperature. In Table VII is given the heat distortion temperature of some novolac resins cured with different formals. The test was performed according to ASTM D468.

From the data in Table VII it can be concluded that an increasing degree of substitution in the formal ring generally lowers the heat distortion temperature of the resins. In the case of the bis-formal of pentaerythritol

TABLE VII
Heat Distortion Temperature of Different Formal-Novolac Mixtures^a

Formal	Heat distortion temperature, °C.
1,3-Dioxolane	130-150
4-Methyl-1,3-dioxolane	90-110
2,4-Dimethyl-1,3-dioxolane	70-90
4-Chloromethyl-1,3-dioxolane	85-105
1,3-Dioxane	110-110
4-Phenyl-1,3-dioxane	110-125
Bis-formal of pentaerythritol	150-170

^a Catalyst concentration 1%, curing conditions 5 min. at 130°C.; molar ratio novolac-formal = 1:0.5.

it is evident that a very high degree of rigidity is achieved, in all probability as a consequence of the high functionality and short chain lengths of the crosslinks.

V. APPLICATIONS OF THE NEW RESINS

The major applications of the new novolac-cyclic formal resin system lie, broadly speaking, in the same fields already covered by the conventional phenolic resin types. Thus, through proper choice of the basic material it is possible to use them in the fields of molding, casting, laminating, adhesives, and additional minor applications.

A great advantage with regard to the normal phenolics lies in the fact that the curing with liquid formalins allows a low or contact pressure technique in molding operations.

The very versatile character of the new resins is clear when it is realized that the properties of both resoles and novolacs systems are, in a way, combined. The rather active dioxolanes are especially suitable for casting and laminating applications, while the more stable formal ring compounds, the dioxanes are well suited, in combination with acid-resistant fillers, to the production of molding powders. The viscosity or the degree of flow of the different resin systems can be easily adjusted to special needs by varying the formal concentration within certain limits.

However, an important drawback is without doubt the inevitable use of a rather strongly acid catalyst, which makes it impossible to compose good combinations with reinforcing fillers such as wood flour or cotton, which are attacked by the acid catalyst. Neither can fillers which contain alkaline material be used as a consequence of their neutralizing effect on the catalyst.

On the other hand, acid-resistant fillers can be applied without difficulty and permit the preparation of a broad range of molding materials whose strength characteristics compare favorably with the commercial phenolics.

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Résumé

Une nouvelle méthode pour durcir des résines phénol-novolaque à l'aide de formals cyclique sous l'influence catalytique des acides forts est décrite. Il pouvait être démontré que les formals réagissent avec les molécules de la résine novolaque ce qui conduit à une dense structure réticulée. En conséquence de ce nouveau procédé de durcissement il est possible d'appliquer les nouveaux types de résine dans le formage à basse pression ou à pression de contact. Les propriétés physiques des produits finals sont en général conformes à celles des résines coulées phénoliques conventionnelles.

Zusammenfassung

Es wird eine neue Methode zur Härtung von Phenol-Novolakharze mittels cyklischer Formale unter dem katalytischen Einfluss starker Säuren angegeben. Es konnte bewiesen werden, dass die Formale mit den Novolak-Molekülen reagieren unter Bildung einer stark vernetzten Resit-Struktur. Als eine praktische Folge dieses neuen Hartungsverfahrens ist es möglich geworden, die neuen Harztypen bei niedrigem Druck oder bei Kontaktdruck für formgebende Verarbeitung zu verwenden. Die physikalischen Eigenschaften der Endprodukte ähneln im grossen Ganzen den Standardtypen der Phenol-Giessharze.

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