NBS CIRCULAR *493*

Development of the National Bureau of Standards Casting Resin

UNITED STATES DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

PERIODICALS OF THE NATIONAL BUREAU OF STANDARDS

As the principal agency of the Federal Government for fundamental research in physics, chemistry, mathematics, and engineering, the National Bureau of Standards conducts projects in fifteen fields: electricity, optics, metrology, heat and power, atomic and radiation physics, chemistry, mechanics, organic and fibrous materials, metallurgy, mineral products, building technology, applied mathematics, commodity standards, electronics, and radio propagation. The Bureau has custody of the national standards of measurement and conducts research leading to the improvement of scientific and engineering standards and of techniques and methods of measurement. Testing methods and instruments are developed; physical constants and properties of materials are determined; and technical processes are investigated.

Journal of Research

Internationally known as a leading scientific periodical, the Journal presents research papers by authorities in the specialized fields of physics, mathematics, chemistry, and engineering. Complete details of the work are presented, including laboratory data, experimental procedures, and theoretical and mathematical analyses. Each of the monthly issues averages 85 two-column pages; illustrated. Annual subscription: domestic, $4.50; foreign, $5.50.

Technical News Bulletin

Summaries of current research at the National Bureau of Standards are published each month in the Technical News Bulletin. The articles are brief, with emphasis on the results of research, chosen on the basis of their scientific or technologic importance. Lists of all Bureau publications during the preceding month are given, including Research Papers, Handbooks, Applied Mathematics Series, Building Materials and Structures Reports, and Circulars. Each issue contains 12 or more two-column pages; illustrated. Annual subscription: domestic, $1.00; foreign $1.35.

Basic Radio Propagation Predictions

The Predictions provide the information necessary for calculating the best frequencies for communication between any two points in the world at any time during the given month. The data are important to all users of long-range radio communications and navigation, including broadcasting, air line, steamship, and wireless services, as well as to investigators of radio propagation and ionosphere. Each issue, covering a period of one month, is released three months in advance and contains 16 large pages, including pertinent charts, drawings, and tables. Annual subscription: domestic, $1.00; foreign, $1.25.

Development of the National Bureau of Standards Casting Resin

by Philip J. Franklin, David M. French, and Wilbur C. Nyberg

Contents

Development of the National Bureau of Standards Casting Resin

By Philip J. Franklin, David M. French, and Wilbur C. Nyberg

The NBS Casting Resin fills the need for a plastic suitable for the potting of certain types of electronic circuits. This Circular has been prepared to present a definitive summary of the development, uses, and properties of the resin as well as new data obtained in the past 2 years. Choices of ingredients, methods of preparation, and characteristics of the finished resin are discussed.

I. Introduction

The NBS Casting Resin is an outgrowth of a project at the National Bureau of Standards in the development of specialized electronic equipment. During the development of the circuit components, it was found that the usual methods of assembly were unsatisfactory. Although commercial components were available, the conventional method of mounting them on metal chassis required too much space. Using the wiring for support eliminated the chassis but made the equipment insufficiently rugged for its intended use. A method long used by the telephone company, consisting of inserting the components into holes in a wooden block and sealing them in place with wax, was tried, but performance was found inefficient at the frequencies used in the equipment. This method suggested that if the electronic circuitry could be cast or potted in a rigid block of plastic, the assembly could be made rugged enough to withstand the mechanical shocks it was expected to encounter, and at the same time not of excessive size, while providing the desired electrical characteristics.

II. Need for a Casting Resin With Special Properties

Many potting materials were in existence, ranging from simple tars, pitches, and waxes, used in batteries and transformers, to synthetic resins with electrical and mechanical characteristics suitable for many radio applications, but none of these seemed suitable for use in the particular equipment being developed by the Bureau. The physical properties of the electronic components limited the temperature and pressure that could be applied to the resin; as the resin had to flow into and fill restricted spaces, its viscosity could not be very high; its dielectric constant and power factor had to be low over a wide range of frequencies; the leakage resistance was also required to be high over a wide range of temperatures; and the curing time of the resin needed to be as short as possible to reduce the use of ovens and space in production. The Bureau prepared performance specifications and submitted them to manufacturers of materials that showed promise. Unfortunately, no commercially available resin met all the minimum requirements.

As no suitable potting materials were available, the Bureau adopted the expedient of dividing the assembly into two units. One portion of the circuit was potted in tung oil polymerized with ferric chloride; the second section was cemented to a low-loss phenolic block with polystyrene cement. Tung oil could not be used for potting the second section because it caused excessive losses at the frequencies used. The iron salts used as a polymerizing agent in the tung oil were believed to cause corrosion of components and connections. The electrical characteristics of the units had been gradually changing and, when opened after shelf-life tests, it was discovered that some of the electrical connections and other parts of the electronic components were badly corroded.

To determine the cause of corrosion, additional assemblies were dipped in microcrystalline wax and then potted in tung oil. After shelf-life tests these units were also found to be corroded, even though the circuitry was separated from the tung oil by a film of wax. A test of the products of

corrosion revealed the cause to be the rosin flux used with the solder in making the electrical connections.

After a series of experiments with many possible fluxing materials, a rosin dimer was substituted for the ordinary rosin soldering flux, and was found to be much less corrosive. Its oxygen absorption was only one-half as great, and a water extract showed only about one-twentieth the conductance of a water extract of ordinary rosin. The rosin dimer is a better wetting agent and makes a much better soldered joint. For example, half-and-half tin-lead solder with rosin dimer as flux is as effective as 63–37 solder with ordinary rosin.

Since the cementing method previously mentioned was wasteful of space, the Bureau continued to seek a compound that could be used for potting both portions of the circuit, and that would have approximately the same coefficient of expansion as the components to be imbedded in it, so that they would not be damaged nor disarranged during the potting process. A satisfactory material would also have to meet the requirements of mechanical strength, chemical stability, and low electrical losses.

More success was obtained in tests on an oil-soluble soap that would saponify in situ, becoming hard and stable. The soap was weakly alkaline, and, therefore, produced less corrosion of the particular components used than did the iron salts in the polymerized tung oil. The soap, nevertheless, was unsatisfactory because of its low mechanical strength and the tendency of the plasticizer to bleed and produce an oil film over the whole exposed surface of the block. The electrical properties of the oil-soluble soap were superior to those of tung oil but, because of the polar material present, still not suitable for use at the frequencies desired.

Several types of synthetic materials were tried, but all had disadvantages that precluded their use. For example, a mixture of styrene, divinylbenzene, and polyisobutylene catalyzed with tin tetrachloride was found to be extremely viscous in monomeric form, and the control of this material was too critical for mass production of enblocked assemblies—during processing one lot might polymerize very slowly and unevenly, while the next might char in a few seconds. The usual phenolic casting resins were tried, but the catalysts present were so corrosive that the metallic salts formed were sufficient to affect adversely the operation of the unit.

Many polyesters were investigated because of their high mechanical strength, low viscosity, short curing time, and low volumetric shrinkage during polymerization. For the Bureau's application, however, the loss figures of the polyester resins in the radio frequency range were still too high. Allyl resins were unsatisfactory for the same reason. The Bureau's requirements were stringent because of the nature of the circuits to be imbedded in the resin. For ordinary applications the polyesters and allyls would probably give satisfactory service.

From the Bureau's studies of existing materials, it was possible to analyze the way in which each fell short of requirements. One prime requisite was that the material have minimum shrinkage upon polymerization. The forces set up by shrinkage are of the order of several thousand pounds per square inch, and excessive shrinkage would easily crush the electronic components and tear the wiring loose. Conversely, if the potting material were made sufficiently resilient to avoid crushing action, it would have the disadvantage of allowing the components to pull through the plastic material and break the electrical connections under stress. Obviously the material should become hard, but should not shrink in doing so.

Of equal importance was the mechanical strength of the potting material. High tensile strength was required to prevent the casting from tearing loose from its support. High compressive strength was needed to protect the enblocked unit. High impact strength was also desired. The usual Charpy and Izod tests for impact were not particularly useful in determining the impact strength of casting resins. An adequate test of the impact strength of various resins was to subject the material to the impact of a falling ball, or to drop a casting made from the resin onto a concrete surface.

One undesirable characteristic of all common plastics is their large coefficient of thermal expansion. Special techniques were necessary to eliminate this effect. One technique was to coat some of the components with a resilient material to cushion them against the forces of contraction.

In solids, resistance to thermal shock depends upon the coefficient of expansion, the presence or absence of strains, the rigidity of the material, its strength, and the size and shape of the sample. The coefficient of expansion of NBS Casting Resin is intermediate for organic polymers, but is much higher than that of metals or glasses. In the absence of strains, small pieces of NBS Resin may be cooled quickly from $+50°$ C to $-70°$ C and heated back to $+50°$ C without damage except for a surface craze. However, if the resin is disturbed in the gelling stage of polymerization, strains will be set up that will cause cracks if the polymerized piece is cooled too quickly. Therefore the castings should never be moved during the hardening process, and for strain-free castings the rate of polymerization should be slow in order to minimize heat gradients and circulation of the liquid. For large castings this may be impossible.

As previously stated, the most important consideration was the electrical characteristics of the resin, because the lowest possible dielectric constant and power factor are always desirable for greatest efficiency. As far as is now known, these

characteristics are adequately displayed by the NBS Casting Resin.[1]

A short curing time was desirable in order to save manufacturing space and equipment and to

[1] NBS Casting Resin should not be considered as "better" than other casting resins. It has characteristics that make it more suitable for the specific application upon which the Bureau worked; but it is comparatively expensive and has other characteristics that make it less suitable for various other applications. It is simply a resin that was designed to do a certain job. There are many applications to which other casting resins are better adapted.

expedite production. The usual low loss resins, such as polystyrene, require elevated temperatures in order to minimize the curing time. The NBS Casting Resin polymerizes at atmospheric pressure and at a temperature of 50°C, thus eliminating the costly autoclaves required in the high-pressure processing used to save time with some other resins.

III. Basis for a Choice of Materials

Because of the need for a potting material with excellent electrical properties, and because of encouraging experiences with styrene and its modifications as molding materials, it was decided to investigate the possibilities of using styrenes as casting or potting materials.

The requirements of operation over a wide range of frequency and temperature and the desire to eliminate losses due to interfacial and dipole effects limited the choice of materials to symmetrical hydrocarbons. Several different ingredients were required in order to achieve an optimum balance of desirable properties. Styrene was not a suitable material because of its long curing time and high shrinkage on polymerization. Both ethylene and isobutylene required such stringent conditions for polymerization that they were not useful as a low-pressure casting resin. A modified styrene supplied the necessary toughness, and a substituted styrene raised the heat distortion point and minimized the cold flow of the composition. Both styrene monomer and 2,5-dichlorostyrene monomer were used: the styrene reduced the viscosity of the monomer-polymer mixture and improved the compatibility of the mixture; the dichlorostyrene monomer was used for its high polymerization rate. To reduce brittleness, a hydrogenated terphenyl was added. This material has the futher effect of reducing the viscosity for pouring. The polystyrene and poly-2,5-dichlorostyrene are added to the mixture to reduce the shrinkage on polymerization. Divinylbenzene is added to decrease the solubility of the polymerized resin and to improve the heat distortion point, as well as to

increase the polymerization rate. With the divinylbenzene addition, the resin at high temperature takes on a rubber-like character instead of flowing. This means that the resin is more usable in the upper range of temperatures.

The kind and amount of catalyst added to the resin control the curing time and affect the mechanical and electrical properties of the final polymer. Some catalysts, such as boron trifluoride or stannic chloride, provide extremely short curing times but produce a polymer of low molecular weight with a consequent decrease in mechanical strength. The necessarily high concentration of such catalysts results in a high dissipation factor. By employing a trace of metallic salt promoters with a hydroperoxide, a great increase in the rate of polymerization may be obtained without impairing the electrical properties.

A mixture of several peroxide catalysts affords better results than does one catalyst alone. An active catalyst is used to initiate the polymerization; a somewhat more stable catalyst to carry the polymerization to within a small percentage of completion; and a very stable catalyst to carry the reaction to completion over a long period of time or at an elevated temperature.

The most generally used catalyst of intermediate activity is benzoyl peroxide. Good electrical properties are obtained in the resin by using 0.1 percent of this catalyst and curing from 12 hours to 6 days at 50° C. Shorter curing times may be employed at higher temperatures. For many purposes, however, the internal temperature in the resin should not be allowed to exceed 60° C.

IV. Formula for and Preparation of NBS Casting Resin

The first step in the preparation of NBS casting resin is the removal of the inhibitor from the 2,5-dichlorostyrene monomer. One method of accomplishing this is to extract the inhibitor with 10-percent sodium hydroxide solution. A separatory funnel is filled about one-third full of the dichlorostyrene monomer, and an equal volume of 10-percent sodium hydroxide solution is added. The mixture is shaken well and allowed to stand until the liquids separate. After separation, the

monomer is found as the bottom layer. This is drawn off, and the upper layer—the sodium hydroxide solution—is discarded. This operation is repeated with the sodium hydroxide solution and then three times with distilled water. The washed monomer is poured into a beaker containing a drying agent such as calcium chloride or calcium sulfate, stirred thoroughly, and allowed to stand for 15 minutes. It is then filtered through a fluted filter containing calcium sulfate. The

dichlorostyrene monomer is now ready for use in formulating the casting resin.

An alternate and more convenient method [1] [2] is to percolate the monomer through activated alumina (see fig. 1). A ball of glass wool is pushed down to the bottom of a glass column, which is 8 to 10 times higher than it is wide. The column is then filled with activated alumina. (The best results have been obtained with alumina of the F–20 chromatographic grade with sieve size minus 80 plus 200 mesh.) The 2,5-dichlorostyrene monomer is then poured in at the top of the glass column. Pressure at the top or vacuum at the bottom of the column will facilitate the operation. When a colored band in the alumina, representing the removed t-butylcatechol, reaches the bottom of the column, the adsorbing power of the alumina is exhausted. The alumina can be desorbed by washing with several portions of methanol to remove the t-butylcatechol, and then with distilled water to remove the methanol. The washed alumina is reactivated in a muffle furnace by heating a layer of not more than 2 inches to a temperature of 400° C for 4 hours. After activation, the hot alumina is poured into a container that is kept sealed until used. The alumina can be reactivated an indefinite number of times.

The second step in preparing the NBS Casting Resin is mixing the ingredients. The liquids are

FIGURE 2. *Roll-mill for mixing NBS Casting Resin.*
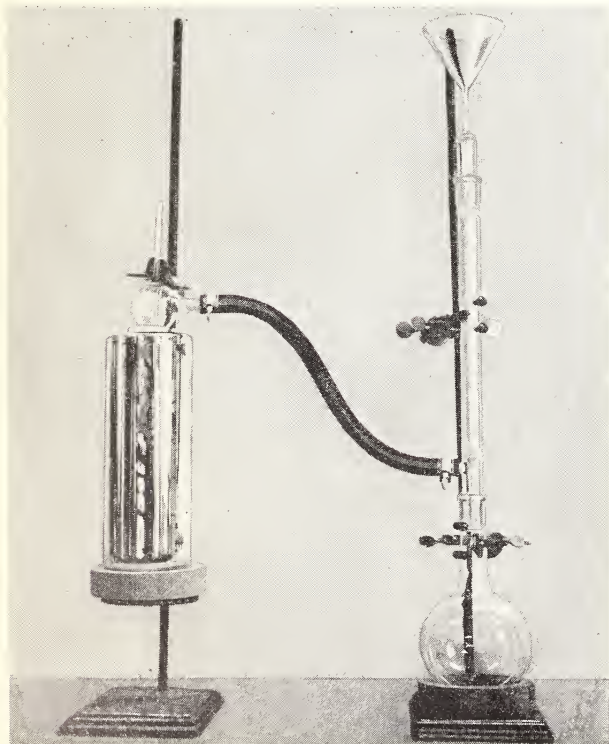

FIGURE 1. *Equipment for the removal of inhibitor from 2,5-dichlorostyrene.*
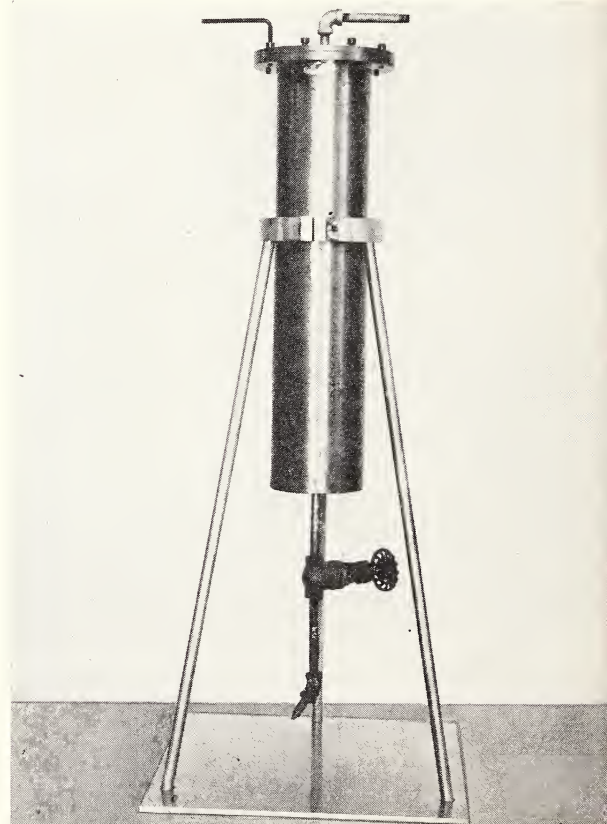
FIGURE 3. *Pressure filling unit for NBS Casting Resin.*

[2] Figures in brackets indicate the literature references at the end of this paper.
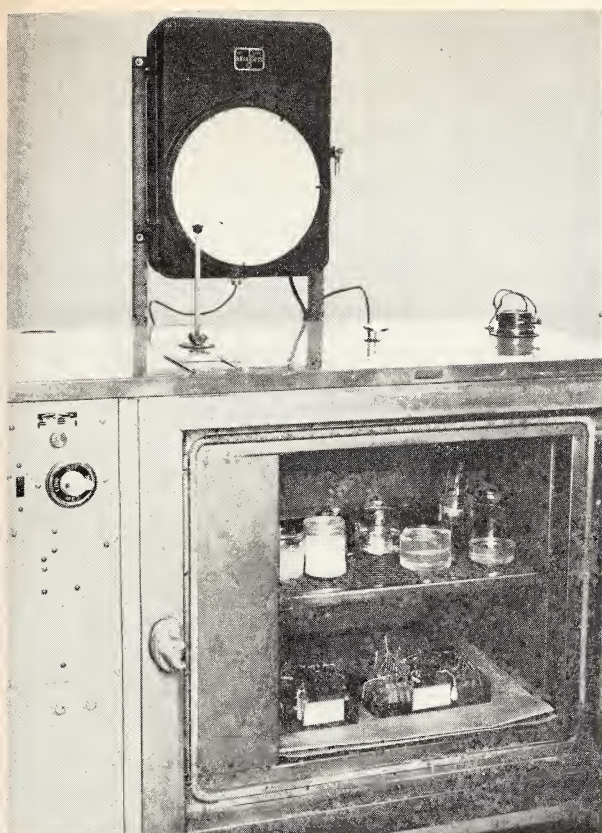
FIGURE 4. *Oven used for curing NBS Casting Resin.*

When the resin is thoroughly mixed and free from lumps, the catalyst—cumene hydroperoxide—is stirred in. If faster polymerization is desired, 0.05 percent of manganese naphthenate or manganese octoate solution containing 6.0 percent of manganese in the form of the naphthenate or octoate is added. This speeds the polymerization but colors the resin yellow.

The casting technique varies with the volume of casting resin required. The resin may be poured by using the apparatus shown in figure 3. For polymerizing small volumes, 0.1 to 0.5 percent of catalyst is used, and the mixture is allowed to stand at room temperature until gelled. For large volumes, from 0.05 to 0.1 percent of catalyst is used, with gelation at room temperature. After gelation, any exposed surface should be flooded with glycerol, to promote the formation of a hard surface. The gelled resin is then placed in an oven at 50° to 60° C and cured overnight, as shown in figure 4. If the resin becomes very hot and cracks during the polymerization, too much catalyst has probably been used, and the amount should be decreased. To stabilize the final casting, the resin should be cured for an additional period of 10 days at 50° to 60° C.

The material being potted in the resin will affect polymerization. Although adding traces of copper to the formulation increases the rate of polymerization, too much copper acts as an inhibitor. Bare copper wire may provide this excess when

weighed out first and placed in a wide-mouthed jar. Next, the solid polymers are weighed out and added slowly to the liquids, stirring constantly. The jar must be immediately sealed and vigorously shaken to prevent clumping of the solids. If this is not done, a much longer time is required to disperse the solids completely. The sealed jar should be placed on a roll mill, as shown in figure 2, and rolled until all the solids are dispersed. This requires about 16 hours. Quickest mixing is obtained by filling the container not more than two-thirds full.

The formula for NBS Casting Resin is as follows:

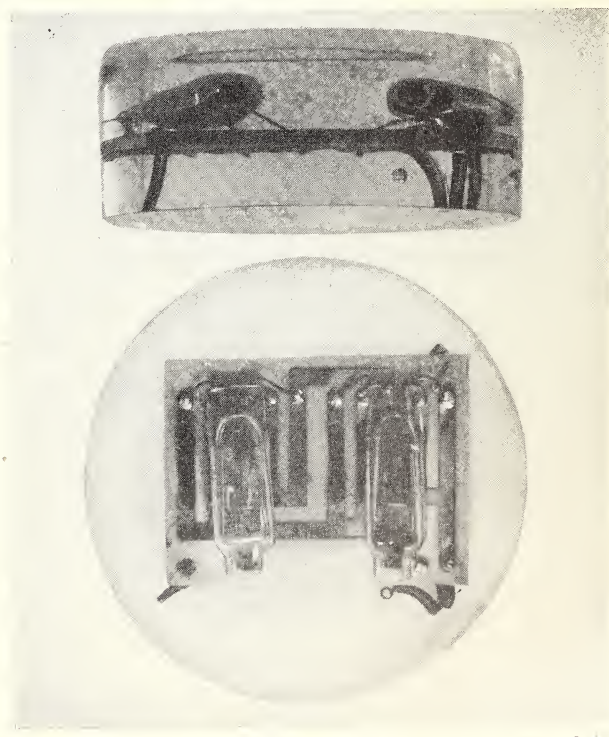| Compounds	Amount by weight
	Percent
2,5-dichlorostyrene _____	33
Styrene _____	21
Hydrogenated terphenyl [a] _____	13
40 percent Divinylbenzene solution [b] _____	0. 5
Poly-2,5-dichlorostyrene _____	21. 5
Polystyrene _____	11

[a] Monsanto HB-40.
[b] Dow Q302.4.

FIGURE 5. *Circuitry (two-stage audio amplifier) potted in NBS Casting Resin.*

electronic circuits are potted. Similarly, when rubber-insulated wiring is potted, the sulphur in the rubber inhibits polymerization.

Circuitry to be potted should be carefully designed (see fig. 5) not only so that the leads can be brought out in convenient positions, but also so that bare wiring is done with tinned wire, and that insulation is of Vinylite, glass, or some other material which will not affect the properties of the resin. Other component materials must also be of such nature that they will not inhibit polymerization.

V. Recent Developments

Recent work on NBS Casting Resin has been directed toward increasing the completeness, and decreasing the time, of polymerization. To this end, experiments have been conducted with various catalysts, accelerators, and modifying agents.

Although rapid curing times are desirable and obtainable with active catalysts, the necessary mechanical properties of the resin can be obtained only with relatively complete polymerization, and for this inactive catalysts must be added.

Examples of inactive catalysts that are commercially available are di-t-butyl peroxide, p-chlorobenzoyl peroxide, and di-t-butyl perphthalate. These are not usually used alone, because of their low activity. Very active peroxides used in NBS Casting Resin are cumene hydroperoxide, dichlorobenzoyl peroxide, and t-butyl hydroperoxide. These are generally used to initiate the polymerization either in conjunction with another peroxide or with metallic-salt promoting agents. The concentration of catalytic agents probably should not exceed 0.2 percent in order to retain the desirable electrical properties. Several ketone and aldehyde peroxides have shown little activity in NBS Casting Resin in contrast to their behavior in unsaturated polyester resins.

Traces of salts of manganese, iron, cobalt, and copper in the resin, varying from 0.0002 to 0.02 percent metal, have a great promoting effect on the activity of certain hydroperoxides. These metals impart color to the resin, which for some purposes is undesirable. The combination of t-butyl hydroperoxide 0.1 percent, copper mercaptobenzothiazole 0.003 percent, dibutylamine 0.03 percent (to dissolve the copper salt), and didodecyl disulfide 0.02 percent has been found to give rapid polymerization with a minimum of color. Other salts may be found to be superior in the future.
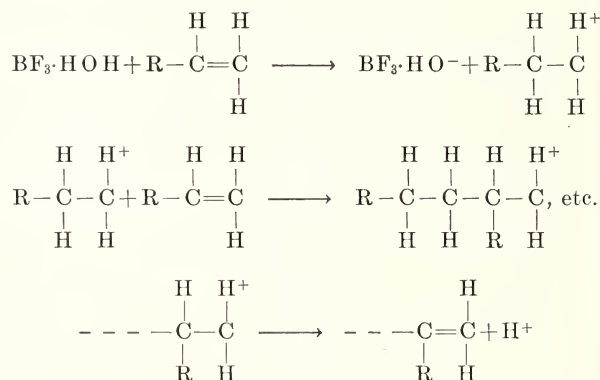
The use of reducing promoters, which are employed in the manufacture of "cold rubber" and in the curing of unsaturated polyester resins, has been found of little value in NBS Casting Resin, and no initiating agents other than peroxides and tertiary amines have been found at all satisfactory thus far.

Polymerization of olefins. The polymerization of olefins is commonly brought about either by means of "acid" (Friedel-Crafts) catalysts such as boron trifluoride or stannic chloride, or by means of free radicals produced by the decomposition of such substances as peroxides or diazo compounds or by the reaction of certain oxidizing agents with reducing agents.

Free-radical-producing compounds are those which decompose thermally to form fragments, each containing an odd number of electrons. The odd electron may or may not move about the radical, depending on its structure. The commonly accepted mechanisms of polymerization with the two types of catalysts are shown, somewhat abbreviated [2, 3, 4].
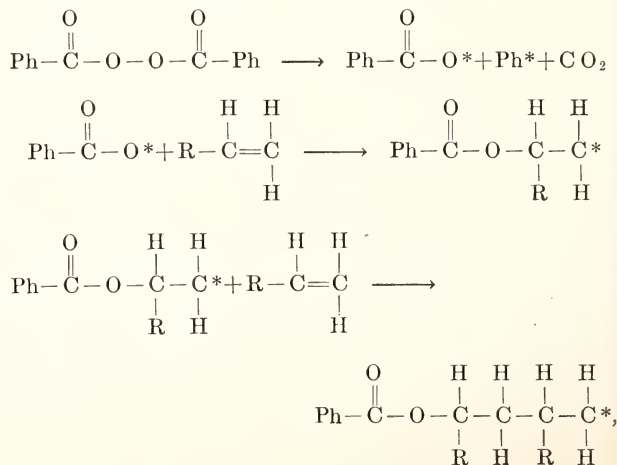
"Acid" catalysis:

$$BF_3 \cdot HOH + R - \overset{H}{\underset{H}{C}} = \overset{H}{\underset{H}{C}} \longrightarrow BF_3 \cdot HO^- + R - \overset{H}{\underset{H}{C}} - \overset{H^+}{\underset{H}{C}}$$

$$R - \overset{H}{\underset{H}{C}} - \overset{H^+}{\underset{H}{C}} + R - \overset{H}{\underset{H}{C}} = \overset{H}{\underset{H}{C}} \longrightarrow R - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{R}{C}} - \overset{H}{\underset{H}{C}} - \overset{H^+}{\underset{H}{C}}, \text{ etc.}$$

$$- - - - \overset{H}{\underset{R}{C}} - \overset{H^+}{\underset{H}{C}} \longrightarrow - - - \overset{H}{\underset{R}{C}} = \overset{H}{\underset{H}{C}} + H^+$$

where R is a negative radical.

A trace of a hydroxyl-containing compound is believed to be necessary as a cocatalyst in such systems [3, 5].

Free radical catalysis:

$$Ph - \overset{O}{\overset{\|}{C}} - O - O - \overset{O}{\overset{\|}{C}} - Ph \longrightarrow Ph - \overset{O}{\overset{\|}{C}} - O* + Ph* + CO_2$$

$$Ph - \overset{O}{\overset{\|}{C}} - O* + R - \overset{H}{\underset{}{C}} = \overset{H}{\underset{H}{C}} \longrightarrow Ph - \overset{O}{\overset{\|}{C}} - O - \overset{H}{\underset{R}{C}} - \overset{H}{\underset{H}{C}}*$$

$$Ph - \overset{O}{\overset{\|}{C}} - O - \overset{H}{\underset{R}{C}} - \overset{H}{\underset{H}{C}}* + R - \overset{H}{\underset{}{C}} = \overset{H}{\underset{H}{C}} \longrightarrow$$

$$Ph - \overset{O}{\overset{\|}{C}} - O - \overset{H}{\underset{R}{C}} - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{R}{C}} - \overset{H}{\underset{H}{C}}*,$$

where Ph is the phenyl group, and the star represents a free valence. Termination of the polymer chain is by collision with another free radical or by abstraction of a hydrogen atom from another chain or from some reducing agent. Peroxides are believed to function best in a basic medium. Hence the two types of catalysis are not generally regarded as occurring under the same conditions.

Effect of various peroxides. Numerous organic, oil-soluble peroxides are available commercially. They differ widely in their activity. If the odd electron that constitutes the free radical can occupy only one position in the molecule, it is likely that the activity of a peroxide would depend upon the extent to which it decomposes at a particular temperature to form its radicals.

The order of activity of these peroxides appears, however, to vary somewhat in different monomers. For example, the activity of peroxides relative to one another according to Rybolt and Swigert [6] in unsaturated polyester resins is not exactly the same as in NBS Casting Resin. Of approximately 25 to 30 organic peroxides available, 17 were chosen and added to NBS Resin so that the resin contained 0.010 g of active oxygen per 100 g of resin.

The order of activity of these peroxides in polymerizing NBS resin is roughly as shown in table 1

TABLE 1. *Order of activity of peroxides in polymerizing NBS resin*

Peroxide	Concentration, parts/100 as—		Percentage of polymer after 17 hr at 25° C plus—	
	Pure peroxide	Commercial product	2 hr at 50° C	24 hr at 50° C
Cumene hydroperoxide	0.12	0.17	75	98 to 100
"Uniperox 60", $C_7H_{13}OOH$	.13	.21	75	96
Dichlorobenzoyl peroxide	.24	.48	60	98 to 100
t-Butyl hydroperoxide	.06	.10	59	98 to 100
Benzoyl peroxide	.16	.16	20 to 30	98 to 100
t-Butyl perbenzoate	.16	.17	20 to 30	95
Acetyl benzoyl peroxide	.12	.13	<25	98
Caprylyl peroxide	.19	.21	<25	98 to 100
Lauroyl peroxide	.27	.31	<25	97
Hydroxyheptyl peroxide	.19	.20	--------	87
Methyl ethyl ketone peroxide	.06	.17	--------	80
1-Hydroxycyclohexyl hydroperoxide-1	.086	.095	--------	74
di-t-Butyl perphthalate	.11	.11	--------	70
Dibenzaldiperoxide	.08	.16	--------	61
t-Butyl peroxide	.09	.091	--------	<35
2,2-(t-butyl peroxy)butane	.08	.11	--------	24

The concentration of peroxide in the commercial products was determined in some cases from our own analyses and in others from the manufacturer's data. The amount of polymer was determined by density measurements that are not accurate above 95 percent conversion. The results were calculated on the basis of the percentage of monomers polymerizing. The order of activity of the peroxides in some cases is based on judgment. For instance, relatively rapid polymerization at the beginning of the reaction

may occur with a given peroxide and subsequently the rate may slow down. Thus "Uniperox 60" seems to give less polymer in 24 hours at 50° C than cumene hydroperoxide, although the rate of polymerization initially is about the same.

Rybolt and Swigert [6] have determined the order of activity of some peroxides in unsaturated polyester resins. At first glance there seem to be differences between the order of activity in the polyester resins and in NBS Casting Resin. However, if aldehyde and ketone peroxides and peroxides containing hydroxyl groups are considered apart from the other peroxides, it is found that within each classification the order of activity of peroxides in the two types of resins is nearly the same. A comparison of the activity of peroxides in order of decreasing activity is shown for NBS Casting Resin and unsaturated polyester resin, using the data of Rybolt and Swigert.

A. Aldehyde and ketone peroxides and those containing hydroxyl groups:

In NBS Casting Resin
Hydroxyheptyl peroxide. Methyl ethyl ketone peroxide. 1-Hydroxycyclohexyl hydroperoxide-1 Dibenzaldiperoxide.

In Polyester Resins
Hydroxyheptyl peroxide. Methyl ethyl ketone peroxide. 1-Hydroxycyclohexyl hydroperoxide-1. Dibenzaldiperoxide.

B. Other organic peroxides:

In NBS Casting Resin	In Polyester Resins
Dichlorobenzoyl peroxide.	Dichlorobenzoyl peroxide.
t-Butyl hydroperoxide.	t-Butyl hydroperoxide.
Benzoyl peroxide.	Lauroyl peroxide.
t-Butyl perbenzoate.	Benzoyl peroxide.
Lauroyl peroxide.	t-Butyl perbenzoate.
di-t-Butyl perphthalate.	di-t-Butyl perphthalate.

Among the peroxides not classified in type A above, the hydroperoxides are the most active, whereas dialkyl peroxides are the least active. Great bulk and polarity favor dissociation, as has been pointed out many times. In general the peroxides in type A show little activity in NBS Casting Resin, whereas many of them are very active in polyester resins. It has been suggested that chain termination may not be important in determining the rate of polymerization of unsaturated polyester resins, since the polymerization

reaction is primarily a cross-linking of existing polymer molecules by styrene. On the other hand, the rate of polymerization in NBS Casting Resin would be decreased by termination of chains or free radical transfer by reducing agents or compounds containing active hydrogen. Such considerations may account for the differences in activity of catalysts in various polymerizing systems. It would also seem that "reduction activation" would not greatly accelerate polymerization in single-phase systems where the rate of chain termination is important. This is borne out for NBS Resin by work shown below.

Effect of organic reducing agents. It has been reported on numerous occasions that reducing agents in the presence of peroxides or other oxidizing agents will accelerate free radical polymerization of olefins [4, 7, 8]. "Reduction activation" is most pronounced in unsaturated polyester resins, in emulsion polymerization systems, and in the polymerization of thin films in air. It presumably occurs because the reaction between oxidizing agent and a reducing agent may produce free radicals in greater concentration than are formed by the decomposition of the oxidizing agent alone, or may produce the free radicals even when the oxidizing agent forms no free radicals.

Various reducing agents were added to NBS Casting Resin with a peroxide also present in order to test their effect. The formulation was as follows:

        NBS Casting Resin_____ 100
        t-Butyl hydroperoxide (60%)_____   0. 10
        Reducing agent_____   . 05

The reducing agents were dodecyl mercaptan, α-furfuryl mercaptan, thioglycolic acid, thio-β-naphthol, ethyl *m*-toluidine, guaiacol, and mercaptothiazoline. No accelerating effect was observed with any of the above, except possibly at the very beginning of the reaction. If the radical formed by abstraction of a hydrogen atom, for example, from a mercaptan, cannot resonate within its molecule, then termination of a growing polymer chain by a mercaptan should produce a new free radical capable of beginning a new polymer chain. The rate of initiation of new chains in the above cases was either slower than the rate of chain growth, or else the catalytic systems were quickly destroyed in the presence of the reducing agents.

The monomer in a polymerization reaction is itself a reducing substrate and may accelerate the decomposition of peroxides [4]. Furthermore, a readily polymerizing monomer may, by increasing the number of free radicals, also enable a slowly polymerizing monomer to copolymerize more rapidly than it reacts alone. Acrylonitrile, for instance, has been used as an activator for polymerization [9]. Accordingly, tung oil, 0.5 percent, and acrylonitrile, 1.0 percent, were added to separate samples of NBS Casting Resin with

peroxide present. A decrease in the rate of polymerization was observed in both cases.

Traces of metallic salts. Salts of metals that exist in two oxidation states with a low potential between them have long been known to accelerate oxidation-reduction reactions. They presumably act as electron carriers, alternately losing an electron to the oxidizing agent and gaining one from the reducing agent. Hence, metallic salts have been used as true catalysts to promote the decomposition of peroxides in the presence of the reducing monomer or other agent and to form more free radicals to initiate polymerization, as in the production of "cold rubber" [10 to 16]. High concentrations of metals are said to retard polymerization. Concentrations that accelerate may be as low as 0.00001 percent of copper [12 to 15].

In order to test this idea in NBS Casting Resin, 4.6 to 7.8×10^{-5} mole of metals per 100 g of resin were added to the resin in the form of a solution of metallic naphthenates and the amounts of polymer formed after 20 hours at 25° C and 2 hours at 50° C were determined by density measurements.

Formulation.

    Resin_____ 100. 0
    t-butyl hydroperoxide (60%)_____   0. 10
    Metallic "naphthenate solution"_____   . 05

Metallic naphthenate	Concentration of solution, percentage by weight of metal	Percentage of polymer
None_____	_____	54
Calcium_____	5	42
Chromium_____	5	25 to 35
Manganese_____	6	92
Iron_____	6	85
Cobalt_____	6	86
Nickel_____	6	48
Copper_____	8	91
Zinc_____	8	74
Mercury_____	25	58
Lead_____	24	72

The product was colored in most cases. Wide variation was found between different salts of the same elements in ability to promote polymerization, as shown in table 2. In all cases the resin contained 0.1 percent of *t*-butyl hydroperoxide (60%).

The least amount of color was imparted by copper mercaptobenzothiazole, but with cumene hydroperoxide this salt also gave a high degree of color. Erratic results were found with both copper mercaptobenzothiazole and iron carbonyl. The inconsistency in the case of the copper salt

TABLE 2. *Effect of metallic salts on polymerization*

Salt	Parts per 100	Percentage of polymer after 20 hr at 25° C and 2 hr at 50° C
Copper mercaptobenzothiazole	0.003	90
Cuprous chloride	.003	76
Cupric chromate	.003	75
Copper diethyl dithiocarbamate	.001	55
Iron carbonyl	.05	95
Ferric dimethyl dithiocarbamate	.01	76
Ferric pyrophosphate (insoluble)	.001	63
Potassium ferricyanide (insoluble)	.05	32
Ferrous dodecyl mercaptide (insoluble)	.05	<30

was traced to the desirability of oxidizing the anion. Iron carbonyl yielded a brown product full of bubbles. Gelation occurred in 2 hours at room temperature. Amines are said to accelerate the decomposition of iron carbonyl, and iron carbonyl itself has been suggested as a polymerization agent. Hence the following formulations were made up and tested.

NBS Casting Resin	100	100	100	100	100
t-Butyl hydroperoxide (60%)	0.1	0.1	0.1	----	-----
Iron carbonyl	----	.05	.05	0.05	0.05
Dibutylamine	----	----	.05	----	.05
Percentage of polymer after 20 hr at 25° C and 2 hr at 50° C	58	95	95	<30	<30

The source of the catalytic activity of iron carbonyl is not known. It is possible that removal of inhibiting molecular oxygen may play a part in the activity of iron carbonyl. The desirability of examining other less highly colored metallic carbonyls is indicated. Resins promoted by metallic salts generally have a much less tacky air surface. Indeed, molecular oxygen itself may react with the monomer or compounding ingredients, and form accelerating peroxides under the influence of metallic salts [17].

Copper mercaptobenzothiazole was used with cumene hydroperoxide and a definite acceleration occurred, but no promoting action was found when benzoyl peroxide was the catalyst.

Various organic reducing agents were also used with the copper salt and t-butyl hydroperoxide; no further acceleration was found.

Diazo compounds and miscellaneous oxidizing agents. Other compounds have been added to NBS Casting Resin as possible initiators of polymerization. These include diazoaminobenzene, azodiisobutyronitrile, tetrachloroquinone, trinitro-toluene, and magnesium perchlorate. They proved of no value either alone or with promoters or peroxides.

Effect of acids and amines. The emulsion polymerization of butadiene-styrene mixture is said to occur most rapidly at about a pH of 8.5 [18], falling off at higher and lower pH values. Amines in general act as accelerators of any free-radical-induced reactions such as the vulcanization and oxidation of rubber. Hence it is reasonable to suppose that the degree of acidity of NBS Casting Resin would influence the rate of polymerization. Although no systematic work has been done, it appears that mono and disubstituted amines have a retarding action in NBS Resin, whereas trisubstituted amines, lacking hydrogen that could act as a chain breaker, have an accelerating effect, and acids cause only a slight, if any, decrease in the rate of reaction when t-butyl hydroperoxide is used as the catalyst. The strong acids, such as phosphoric acid, boron trifluoride, etc., would themselves act as "acid" catalysts.

Acid catalysts. "Acid" catalysts such as boron trifluoride and tin tetrachloride have been found to cause rapid polymerization of NBS Casting Resin, but the electrical properties of the resulting resin are poor. Low concentrations of boron trifluoride or tin tetrachloride alone give too slow polymerization. Addition of small quantities of these catalysts to resin containing 0.1 percent of t-butyl hydroperoxide (60%) has been found in some cases to have a definite promoting effect as shown below:

NBS Casting Resin	100	100	100	100
t-Butyl hydroperoxide (60%)	0.1	0.1	0.1	0.1
Boron trifluoride etherate	----	.01	----	-----
Stannic chloride	----	----	.02	-----
Aluminum chloride	----	----	----	.02
Percentage of polymer after 20 hr at 25° C and 2 hr at 50° C	54	73	<30	68

Aryl radical catalysts. Tetraphenyl tin is the only source of aryl radicals that has been used in NBS Casting Resin. At 50° C this compound is probably too stable to be of much value. When used alone, little polymerization occurred; when used with t-butyl hydroperoxide some promoting effect was observed.

Electrical properties of promoted casting resin. The electrical properties of NBS Casting Resin were determined, and it was found that the dielectric constant and dissipation factor of various samples cured 24 hours at 50° C were

NBS Casting Resin	100	100	100	100	100	100	100
Benzoyl peroxide	0.1	-------	-------	-------	-------	-------	-------
t-Butyl hydroperoxide (60%)	-------	0.1	0.1	0.1	0.1	0.1	0.1
6 Percent Manganese naphthenate	-------	-------	.025	.05	.1	-------	-------
Copper salt of mercaptobenzothiazole	-------	-------	-------	-------	-------	.003	0.006
Dibutylamine	-------	-------	-------	-------	-------	.03	.06
Dielectric constant at 1 kc	2.63	2.61	2.64	2.58	2.62	2.67	2.61
Dissipation factor at 1 kc	0.00073	0.00060	0.00067	0.00062	0.00049	0.00082	0.00099
Dielectric constant at 170 mc	2.50	2.50	2.50	2.51	2.42	2.49	2.50
Dissipation factor at 170 mc	0.00018	0.00011	0.00011	0.00011	0.00012	0.00015	0.00011

The values of dielectric constant and dissipation factor differ only slightly from one formulation to another, as shown in the preceding table. It appears that differences in degree of polymerization may be more important in determining the electrical properties than the addition of a trace of foreign material. Thus, less highly catalyzed resin may have slightly more unpolymerized monomer and hence somewhat poorer electrical properties. On curing the first sample (as shown in the table) for 6 days, the dissipation factor at 1 kilocycle was decreased to 0.00039.

*NBS casting resin as a coating material.* NBS Casting Resin has been used as a coating material where superior electrical properties and water resistance are required. The resin is catalyzed with 0.1-percent benzoyl peroxide, and the coated form is baked at 50° C for 12 to 20 hours. The monomers evaporate to some extent, leaving the cross-linked film with a higher proportion of plasticizer than the original resin. The film is flexible, somewhat soft, and adheres to metal.

If the resin is catalyzed with 0.1 percent *t*-butyl hydroperoxide and 0.05-percent manganese naphthenate or octoate solution containing 6.0 percent manganese, the resulting baked film is much harder but is more brittle and has poorer adhesion than when catalyzed with benzoyl peroxide.

VI. Properties of NBS Casting Resin

The following are some of the measured properties of NBS Casting Resin, cured at 50° C, employing 0.1 percent of benzoyl peroxide as the catalyst:

Tensile strength, lb/in.² _____ 4,000 to 4,500
Modulus of elasticity, lb/in.² _____ 440,000
Elongation at break, % _____ 0.9
Compressive strength lb/in.² _____ 17,100
Izod impact strength, ft-lb/in. of notch ___ 0.228
Rockwell hardness, M scale _____ M76
Rockwell hardness, L scale _____ L100
Coefficient of thermal expansion per ° C __ 11×10^{-5}
Water absorption, 24-hour immersion, % _ 0.01
Density of the monomer, 20°/4° C _____ 1.129
Density of the polymer, 20°/4° C _____ 1.220
Volumetric shrinkage on polymerization
  at 20° C, % _____ 7.5
Heat distortion temperature, ° C _____ 68 to 70
  NBS Casting Resin, on being heated 200 hours at 150° C, browned but was not degraded nor changed in shape.
Brittle point, 1 day cure, ° C _____ 54
Brittle point, 6 days' cure, ° C _____ 86
Index of refraction at 25° C, sodium D line_ 1.608
Dielectric strength (1/16-in. sample; volts/
  mil) _____ 610 to 660
Volumetric resistivity (megohm-cm) _____ 10^{17}
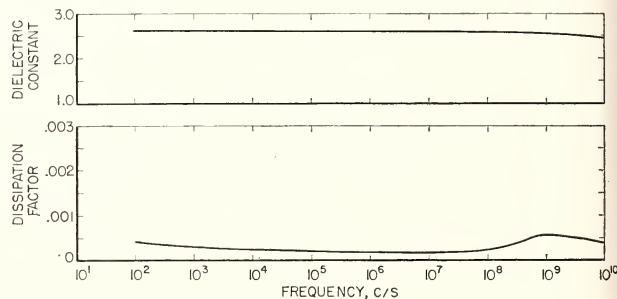
Electrical measurements at 1,000 and 3,000 Mc were conducted by Sheldon B. Akers and George Birnbaum of the Microwave Standards Section of the Radio Division. Electrical measurements at 100 kc were made by Arnold H. Scott of the Inductance and Capacitance Section of the Electricity and Optics Division. Mechanical properties were measured by the Organic Plastics Section of the Organic and Fibrous Materials Division. Other electrical measurements were made by Otto E. Spokas and Jessie E. Jones of the Ordnance Mechanics Section of the Electronics Division. Formulations were compounded by Emma Lee Hebb of the Ordnance Mechanics Section of the Electronics Division.

VII. References

[1] Mathieson Chemical Co., Inc., Technical Sales Bulletin No. 110.1.
[2] W. A. Waters, The chemistry of free radicals (Oxford University Press, 1948).
[3] F. S. Dainton and G. B. B. M. Sutherland, J. Polymer Sci. **4**, 37 (1949).
[4] W. P. Hohenstein and H. Mark, J. Polymer Sci. **1**, 549 (1946).
[5] D. C. Pepper, Trans. Faraday Soc. **45**, 397, 404 (1949).
[6] C. H. Rybolt and T. C. Swigert, Modern Plastics **26**, 101 (April 1949).
[7] R. G. R. Bacon, Trans. Faraday Soc. **42**, 140 (1946).
[8] J. H. Baxendale, M. G. Evans, and G. S. Park, Trans. Faraday Soc. **42**, 155 (1946).
[9] J. M. Willis, L. B. Wakefield, R. H. Poirier, and E. M. Glymph, Ind. Eng. Chem. **40**, 2210 (1948).
[10] W. D. Stewart, U. S. Patents 2,380,473; 2,380,710; 2,383,425.
[11] W. D. Stewart and M. B. G. Zwicker, U. S. Patents 2,380,617; 2,380,618.
[12] E. S. Pfau, U. S. Patent 2,397,201.
[13] M. A. Youker, U. S. Patents 2,365,035; 2,417,034.
[14] C. F. Fryling, U. S. Patents 2,379,431; 2,383,055.
[15] W. D. Stewart, U. S. Patent 2,451,180.
[16] F. T. Wall and T. J. Swoboda, J. Am. Chem. Soc. **71**, 919 (1949).
[17] W. Kern, Makromol. Chem. **2**, 48 (1948).
[18] P. H. Johnson and R. L. Bibb, J. Polymer Sci. **3**, 389 (1948).