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UNIVERSITY OF LOUISVILLE

- I. CIGARETTE RESISTANT FINISH
- II. GLUE APPLICATOR DESIGN
- III. PRELIMINARY STUDY OF
RUBBER-PHENOL CO-POLYMERS

A Thesis

Submitted to the Faculty
of the University of Louisville
in Partial Fulfillment
of the Requirements
for the Degree of

MASTER OF CHEMICAL ENGINEERING

Department of Chemical Engineering

Glenn T. ^{Johnson} Martin

1948

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- II. GLUE APPLICATOR DESIGN
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RUBBER-PHENOL CO-POLYMERS

Glenn T. Martin

Approved by the Examining Committee.

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December, 1948

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ABSTRACT

Results are presented for an investigation of materials to be used in a cigarette resistant finish for solid wood. No completely satisfactory material was found although it was shown that the most important property of a cigarette resistant assembly is an ability to dissipate heat by conduction.

Design plans for a glue gun applicator weighing less than 10 ounces are presented. This device was designed primarily for use in the application of glue to furniture drawer construction on a mass production basis. Air pressure is the actuating force.

Results of a preliminary study of phenol-isoprene co-polymer are presented. The object of this study was to determine the feasibility of using these basic materials as a base for synthetic resins which could be used in coating formulations to impart high abrasion resistance to the resulting films. No positive conclusion was reached; however, the possibility of preparing such synthetic resins was demonstrated.

I. CIGARETTE RESISTANT FINISH

INTRODUCTION

The objective of this research was the development of an easily applied finish that would render solid wood resistant to the disfiguring action of a burning cigarette. The significance of this work was that wood rendered inert to the burning action of cigarettes could be used for table tops, desk tops, and the like with the obvious advantage that accidentally misplaced burning cigarettes would not damage the surface to the point that refinishing would be necessary. In discussions with representatives of the sponsoring company (The Mengel Company, Louisville, Kentucky) certain prerequisites were established. Specifically the finish would be for solid wood and preferably be clear and unpigmented, although limited usefulness might be expected of a pigmented finish. It was further brought out that should this finish be somewhat costly, this characteristic need not be considered objectionable since the market value of furniture protected by a cigarette resistant finish could reasonably be expected to include a premium price. These requirements were later modified, however, to stipulate that the cost of the protection of solid furniture by this preparation should not exceed the cost of preparation of a plywood or laminate that was cigarette resistant.

Although there has been considerable work on the development of cigarette resistant finishes prior to the work of this project, no successful materials for this purpose were known or found to be reported in the literature. However, a

cigarette resistant plywood finish had previously been developed by the Mengel Company. This material employed a sheet of aluminum foil immediately beneath the surface ply of the laminate thereby introducing sufficient heat conduction into the assembly to prevent damaging temperatures at the surface. The actual finish consisted of a pressure cured polyester resin developed by the American Cyanamide Company.

The initial phases of the experimental work were conducted by J. V. D. Fear during the period May-December, 1947.

HISTORICAL

Although no specific reports of research on the problem of protection of solid wood from the damaging action of accidentally misplaced burning cigarettes were found in the literature, there is little doubt that this and allied projects have absorbed considerable expenditures in research and development in recent years.

The only such work to achieve even partial success is that which resulted in the cigarette proof plywood preparation now being produced by the Mengel Company. In this assembly a thin aluminum sheet is glued to the lower ply, of which the quality and thickness are of little importance. Over this metal sheet is glued a top ply which has been impregnated and mechanically compressed until the thickness is less than one-sixteenth inch. Over this is spread a polyester resin (No. 4201 Laminack, manufactured by American Cyanamide Company) incorporating a catalyst which is cured in ten minutes by mechanical application of a pressure of about ten pounds per square inch with a temperature of approximately 250° F. This resin is not thermosetting although its softening temperature is high. The finish is very hard, clear, and glossy. After a cigarette has burned on the finished surface, the residue may be removed by use of a solvent such as acetone.

A number of patents (1,2,3,4) have been issued in recent years concerning so-called fireproofing and fire retardant agents, but no novel departures from the technique of simply

reducing the ratio of combustible matter have become evident, with the possible exception of Albi-R. In general, these agents themselves are consumed or extensively damaged by a sustained flame; however, they will not support combustion after the flame is removed.

As far as paints are concerned fire- or flame-proofing is done in two ways, i.e. (1) pigmentation, and (2) introduction of inorganic constituents into organic materials. In the first category antimony oxide has received considerable attention, along with zinc oxide; however, almost any high melting, non-combustible pigment may be used. A number of silicates also have been proposed but antimony oxide appears to be the most versatile of the pigments thus far reported for this use (5).

In the second category halogenation appears as the most popular device for accomplishing this end. Organic phosphates are also used extensively.

These two approaches are often used together, as in the case of antimony oxide in chlorinated paraffine.

The development by Albi Chemical Company, Inc. of Albi-R paints (6) in recent months may be a departure from the usual type of fire-proofing although at this time the exact compounding agents for this coating have not become public knowledge. This material, at high temperatures and on exposure to flame, blackens and swells apparently forming a film of

bubbles on the surface of the wood which effectively insulates the wood from damage. The coating is ruined and the piece must be refinished.

There have been a number of impregnating agents employed in this work. Silicates, phosphates, borates, sulfates, and chlorides are reported to be useful (7). Also it is observed that cotton laminates treated with melamine formaldehyde resins exhibit flameproof properties without additional treatment (7).

THEORETICAL

In all probability the development of any unusual protective coating must ultimately reduce to a trial and error procedure in that those materials having the desirable properties must be prepared in the appropriate form, applied, and critically examined in tests simulating or identical to actual service conditions. Nevertheless, certain principles and theory must be employed in preparing the test finishes. Accordingly, certain fundamentals were examined so that finish components having properties consistent with the requirements of the desired coating could be secured for use in experiments.

The path of attack on the problem was complicated by the difficulty in producing quantitative calculations of the heat transfer phenomena occurring when a lighted cigarette was placed in contact with a finished surface. To this end a considerable number of assumptions and simplifications were necessary to analyze the transfer mathematically; however, some useful conclusions were derived from these considerations.

If a burning cigarette is placed on a varnished wood surface, the heat is transferred to the wood primarily by radiation and conduction. The heat must overcome an air film resistance and the resistance of the varnish film, and this total resistance is known from reported data to be considerable. The net radiation is dependent on the emissivities of the surfaces and the difference of the fourth power of the absolute temperatures of the surfaces. Under the circumstances, it

is postulated that the transfer by radiation is the mechanism of the transfer of the major portion of the energy. Evidently, the calculation of this transfer requires the use of empirical data, for the emissivities are not available in the literature, and inconvenient, if not impossible, to obtain experimentally. It was decided, therefore, to by-pass this phase of the calculations by experimentally determining the temperature attained on a wood surface subjected to contact with a burning cigarette. The value of this temperature, along with the value of the thermal diffusivity, can be used to calculate the thickness of film necessary to protect a wood surface under the attack of a burning cigarette. (See appendix). It is readily concluded that if a varnish film has the same properties as wood itself - a study of the critical properties of a few plastics tends to the conclusion that often these materials fall in the same property ranges as wood - a film of approximately 0.061 inches thickness will protect the wood surface beneath.

A study of oak wood panels in an oven indicates that the temperature, 350° F., used as the highest permissible temperature at the lower surface of the finish is almost surely conservative. Also, a temperature drop can be expected from the film surface to the wood. That such a gradient exists is demonstrated by sawing through a cigarette-damaged piece of wood and observing the extent of damage. In several such experiments with oak panels the extent of damage did not exceed

one thirty-second of an inch in a direction normal to the surface. Evidently, then, the primary problem is one centering around the attack by the cigarette on the finish itself.

The effect of varying the thermal diffusivity, the ratio of the thermal conductivity to the product of the specific heat and density, could be calculated from the expression for the heat transfer if the conditions prevailing were constant. A material having a high thermal conductivity conducts the heat away from the focus of the cigarette attack so rapidly that the combustion of the cigarette is actually slowed and the surface temperatures do not attain the levels otherwise expected.

With these considerations in mind the several possibilities of protecting the wood against the disfiguring action of the burning cigarette were examined.

The first possibility is the use of an insulating film which will protect the wood but remain unharmed by the burning cigarette. Some of the necessary properties are, (1) thermal conductivity approximating that of wood, (2) thermal resistance sufficient to withstand temperatures in the range of 500° F., (3) sufficient resistance to thermal shock to prevent checking at the temperatures attained, (4) sufficient chemical resistance to resist the action of tars, gums, etc., generated by the partial combustion of the cigarette, (5) a sufficiently dense molecular structure to prevent diffusion of the tars, gums, etc., into the solid phase of the film.

On the basis of a literature survey with these prerequisites in mind the following assumptions were made.

The conductivity in the same range with wood is readily attainable. Some commercial materials, notably silicone polymers (8) and melamine-formaldehyde resins (9) as well as the experimental allyl sucrose (10) and allyl starch and polymerized organic phosphates, are reported to withstand the temperature levels when properly cured. Since the extent to which a material embodies the properties dictated by the last three conditions could not readily be ascertained from available data, it was concluded that these materials should be investigated.

A second possibility presented by consideration of the heat transfer phenomena occurring between the cigarette and wood is that of a conducting finish, that is, a film having a thermal conductivity considerably higher than that of wood which would by virtue of its superior heat distributing qualities, decrease the temperature prevailing at the film surface, slow the combustion of the cigarette, and thereby hold the surface damage to a minimum. The difficulty, revealed by the literature survey, was met in finding a suitably transparent material with the proper film forming properties. No such material was found; however, in this field sodium silicate films were marked for study. It was believed that the use of powdered silica or fibrous glass as a pigment material, could result in increasing

the thermal conductivity of some film forming materials. Similarly ethyl silicate (11) films were believed capable of effecting an increase in thermal conductivity when used in conjunction with a top coat.

A third possibility arises from a consideration of the effect of variation of the properties of wood. In this respect two types of treatment may be employed. (1) Increase the heat resisting properties and (2) increase the ability of the wood to absorb heat. The first, of course, is relatively unimportant since the wood can be protected by relatively thin films. The second prospect offered some promise since this change in heat capacity could be effected by increasing the density of the wood which could be effected by application of an impregnating agent, organic or inorganic, as well as the application of mechanical pressure. This change in the wood also serves to increase its heat resistance. Zinc chloride was chosen as representative of the inorganic impregnating agents and phenol-formaldehyde and melamine-formaldehyde resins were chosen for use as organic impregnants.

Thus, a consideration of the heat transfer to a wood surface when exposed to the attack of a burning cigarette resulted in the isolation of three major fields of experimental endeavor, namely,

- (1) The study of insulating films.
- (2) The study of conducting films.

- (3) The study of variations in the properties of wood affected by impregnation and mechanical compression.

Basic Chemistry of the Film-forming Materials

Probably the most rigid requirement of the film-forming material is that it be thermally and chemically resistant to conditions produced by the burning cigarette. This requirement permits ready elimination of a large number of film-forming materials. Only two commercial materials were considered possibilities, i.e. (1) silicones and (2) melamines. The polyester type varnish, since The Mengel Company had obtained "cigarette-proof" finishes with it, was also retained as a possibility though actually little hope was held for this thermoplastic to offer the solution, since the properties were derived from the thermal conductivity of aluminum beneath a thin heavily-impregnated plywood sheet which received the finish.

Silicones (3)

The chemistry of the general class of compounds known as silicones is highly complex and incompletely understood. The silicone resins are prepared from silica, chlorine and organic materials. First the silica is electrothermally reduced and the resulting metallic silicon treated with elemental halide or an organic halide. In the first case the end product is silicon tetrahalide. This compound is easily reacted with various organic compounds to produce silicones; in fact, one of the marked differences between silicon and carbon chemistry is the rapidity with which the halides of the former may be hydrolyzed. The result of the reaction between silicon and the organic halide is a complex mixture consisting of silicon tetrahalide and mono-, di-, and tri-halo organosilane compounds. By further reaction all these materials can be converted into silicones. The silicone resins used for high temperature finishes are mixtures of various condensable compounds. In general the polymerization of silicones takes place by elimination of water (or of an alcohol) in a manner represented by the following equation,

The introduction of trifunctional compounds can result in cross linkages or a three dimensional structure; i.e.,

The proportions of the trifunctional and bifunctional materials as well as the type of substituent organic groups will affect the properties of the end product. Although the orthosilicic acid monomer has only a hypothetical existence tetrafunctional groups may be introduced into the polymer by use of a hydrolyzable silicon compound which can be partially hydrolyzed and polymerized, after which the hydrolysis can be completed.

When the resistance to rupture of silicon-oxygen bonds by temperature (this is evidenced by the large amount of energy required to reduce silica) is recalled along with the

chemical inertness of this bond, the conclusion is reached that the polymers as briefly described here are capable of withstanding the temperature levels produced by the combustion of the cigarettes and would not be expected to enter into a chemical reaction with the tars, gums, etc., extruded from the cigarette. By a proper choice of monomers the ratio of organic material to silicon may be held to a minimum, thus reducing the proportion of the most vulnerable unit - both thermally and chemically - in the polymer.

A disadvantage of these materials appears in the drastic conditions necessary to cure the resins - the required temperatures for curing uncatalyzed silicones seem higher than could be permitted on a wood surface. It is not altogether unreasonable to hope that catalysts to effect a cure at lower temperatures may be found. Lead, cobalt, and manganese naphthenates are possibilities in this field (8).

Chemistry of Melamines (12)

Melamine is prepared from limestone, coke, and nitrogen. First the limestone is reacted with the coke to form calcium carbide. Then nitrogen is reacted with this product to form calcium cyanamide which is treated with sulphuric acid to produce cyanamide. This compound is subjected to elevated temperatures and pressure, using anhydrous ammonia as a catalyst, to produce melamine. The structure of melamine is

This material has six replaceable hydrogens and combines with formaldehyde to form methylol compounds which polymerize by elimination of water between molecules.

Evidently with six functional groups in the basic molecule, cross-linkages to produce three dimension polymers can be readily obtained and the final product would be expected to be hard, brittle, and thermosetting. These properties can to some extent be modified by introduction of other film forming materials with which the melamine is compatible.

The primary type of resin used for this purpose is alkyd resins.

The melamine resin preparations are normally sold in the methylol stage. The solvent must include an alcohol - although the percentage necessary to render the melamine resin soluble in mineral spirits is comparatively low. Commercial resins may be obtained with varying ratios of melamine to formaldehyde and this permits a range of properties. Also, some commercial formulations include various alkyd modifiers which give the resin increased hardness, better heat stability and improved chemical resistance.

Chemistry of Polyallyl Compounds (10)

The materials of this type thought to show promise are allyl starch and allyl sucrose. They may be prepared by the action of an allyl halide on the sodium salt of the polyhydric compound. Thus the carbohydrate may be treated with sodium hydroxide, allyl halide added, and the mixture (which includes a solvent) fractionated under vacuum to obtain the allyl ether of the carbohydrate. The limit of the number of allyl groups so added is determined by the number of free hydroxyls in the molecule - in the case of sucrose this number is eight, and in the case of starch the number of allyl units that can be added is four times the number of glucose units in the molecule.

Polymerization is effected by the reaction of the allyl double bonds, that is,

With the eight functional groups of allyl sucrose one molecule can initiate eight different chains and each of these chains retains a double bond for every two allyl groups. Although these bonds would be expected to be inactivated by steric hinderance to a large extent, nevertheless, a secondary reaction is possible as long as the molecule retains sufficient

energy to meet the thermodynamic requirements for reaction. The reaction is exothermic. In the case of allyl starch, exposure to the oxygen of the air activates the functional group; allyl sucrose may be activated by heating alone. Polymerization of allyl starch is speeded by use of an organic peroxide as a catalyst; allyl sucrose is not particularly affected by such agents.

In each case an insoluble, infusible, hard but brittle polymer results. The polymer of allyl sucrose is clear; that of allyl starch has a slightly yellow tint.

Two chemical disadvantages of this type of material are evident from the structure, i.e.,

(1) The residual double bond. Although the polymer units may have reached the point that they can no longer react with similar units in a film, it is more than possible that the double bonds remaining may reach, at the heightened temperatures, the point of activation toward the smaller molecular units extruded by the burning cigarette. Further, the latter units probably contain groups possessing a high degree of reactivity under the prevailing conditions.

(2) The ether type linkages. The solvent properties of this chemical structure toward a great number of organic materials lend credence to the belief that even though these linkages are relatively immobilized they can exert their effect in forming a solid solution between the film and the tars, gums, etc., of the cigarette.

Whether or not these factors are significant in this problem depends on factors thus far undetermined. Therefore, experimental methods are necessary to establish the usefulness of these materials.

EXPERIMENTAL

Before the preparations of many experimental finishes were undertaken, several items of a basic nature were investigated briefly.

Originally, the entire problem of the cigarette resistant finish was considered to be primarily one of locating or developing a finish which by one device or another would protect the wood, preventing charring as well as remaining inert during the contact with the burning cigarette. Consistent with this concept, three Dow-Corning silicones were prepared, applied to wood samples, and tested with burning cigarettes:

1. 99.8% D.C. 804, 0.2% cobalt naphthenate
2. 50% D.C. 804, 49.8% glyceryl-phthalate varnish,
0.2% cobalt naphthenate
3. 30% D.C. 802, 69.8% D.C. 804, 0.2% cobalt
naphthenate

These three coatings were glossy, medium hard, and clear. However, although the coatings resisted the heat, the wood beneath apparently charred.

The results of this first experiment indicated some possibility for the use of fireproofing agents applied to the wood before the application of the final cigarette resistant top coat. Since most of these fire-proofing agents function by the evolution of gases upon the application of a flame or excessive temperatures, no great success was anticipated, and no difference in charring was detected between mono-ammonium

phosphate treated and untreated wood panels under the action of a burning cigarette. Nevertheless, mono-ammonium phosphate applied to wood acts as a flame retardant.

Several additional trials with silicones emphasized that the better heat resistant properties of the silicones were attained with materials more highly polymerized than could be attained on wood surfaces. This polymerization of the silicones to the necessary degree required temperatures that readily charred the wood.

Other preliminary tests were carried out using a duPont varnish, Dulux RK5704. The compositions investigated and the results of cigarette testing are summarized in Table I. Although these coatings failed in testing with burning cigarettes, several pertinent observations were made: (1) the apparent charring was confined to the surface coatings; (2) the wood apparently was unharmed; and (3) if the coating remained continuous during the testing, i.e. did not soften or crack, the wood was protected.

To further investigate the observations of the testing of the varnishes of Table I, additional experimental varnishes were prepared and examined. Also several commercial preparations were tested. These experimental varnishes and the results of cigarette testing are given in Table II. The commercial preparations were condensed steryl silicate containing admixed mica (Carbide and Carbon Chemicals Corporation), Skylac L-5882 and

TABLE I RESULTS OF TESTING MODIFIED DULUX RK 5704 VARNISH
WITH BURNING CIGARETTE

Sample No.	Composition	Results
1	3 coats of Dulux RK 5704 air dried and oven baked for 1-1/4 hrs. at 150° F.	Badly charred on the top coating, wood uncharred, coating did not soften or crack.
2	3 coats of Dulux RK 5704 air dried and infra-red baked for 10 min. at 150° F.	Same as sample 1.
3	3 coats of 80% Dulux RK 5704 and 20% 300 mesh powdered glass air dried and oven baked at 150° F. for 1-1/2 hrs.	Surface char only, wood uncharred.
4	3 coats of 60% Dulux RK 5704 and 40% 300 mesh powdered glass air dried and oven baked at 150° F. for 1-1/2 hrs.	Same as sample 3.
5	2 coats of 90% Dulux RK 5704 and 10% 300 mesh aluminum powder air dried and oven baked for 1-1/2 hrs. at 150° F.	Minor surface charring.
6	Same as sample 5 with one coat of 100% Dulux RK 5704 added before baking.	The Dulux top coat was badly charred. The aluminum under coat was unharmed.
7	1 coat of 90% Dulux RK 5704 and 10% 300 mesh aluminum powder air dried and oven baked for 1-1/2 hrs. at 150° F.	Same as sample 5.
8	Same as sample 7 with one coat of 100% Dulux RK 5704 added before baking.	Same as sample 6.
9	A wood sample was baked for 2 hrs. at 160° F. Two coats of Dulux RK 5704 were applied, air dried, and oven baked for 1-1/2 hrs. at 150° F.	Previously, bubbles had formed on some coatings when cured. This method of pre-baking eliminated the effect. Testing showed a slight wood char.

NOTE: All coatings were applied with a spray gun.

Thinner 6134 (Monsanto Chemical Company), Allyl Sucrose (U. S. Department of Agriculture), Phenoglaze P.H. - 3 (Phenoglaze Sales Corporation), Pliolite S-5 varnish (Goodyear Tire and Rubber Company), precured Dow-Corning Silicones 303 and 304, and silicones co-polymerized with tetrachlorophthalic anhydride and glycerol. In all of the varnishes, commercial as well as experimental, with the exception of Phenoglaze and allyl sucrose containing admixed mica, bad wood burns were produced with burning cigarettes. The Phenoglaze and the allyl sucrose containing the mica showed only surface discolorations more or less easily removable. However, the Phenoglaze was considered undesirable because of its green color.

The possible promise of the allyl sucrose containing the mica prompted a rather rough stability test of the finish. A metal panel was coated with this varnish, air dried, and heated to 450° F. for five minutes. A severe discoloration of the coating was observed, possibly indicating the need for greater polymerization or perhaps co-polymerization if this finish were to satisfactorily withstand the burning cigarette.

The results of these tests with the several commercial and experimental finishes clearly indicated the need for more basic knowledge of the mechanism of the damaging action of the burning cigarette. Accordingly, certain experiments were carried out to assist in determining the mechanism of this action. Using a fine wire thermocouple and potentiometer the effective temperature of the burning cigarette was measured and found to

TABLE II HEAT RESISTANT COATINGS

Sample No.	Vehicle Content	Solids Content	Air drying time in hours	Baking time hours	Adhesion	Remarks
1	Silicate of soda	---	24	---	Good	Raised encrustments formed
2	80% Dulux RK 5704	20% micronized mica	3	1	Poor	Bad burn--some wood burn, dull coating
3	90% Dulux RK 5704	10% micronized mica	3	1	Poor	Bad burn
4	90% Allyl sucrose	10% micronized mica	3	20	Good	Burn did not harm surface. Glossy. Mica improved coating
5	34% Tung oil, 40% VMP solvent	4% Penacolite B-1, 22% Cumar-W	4	20	Fair	Bad burn
6	17% Tung oil, 54% VMP solvent	5% Penacolite B-1, 24% Cumar-W	4	20	Good	Bad burn
7	90% Sample 5	10% Mica	4	20	Good	Bad burn
8	90% Sample 6	10% Mica	4	20	Good	Bad burn
9	34% Tung oil, 40% VMP solvent	40% Durez 210 Resin R-2 22% Cumar-W	4	20	Good	Bad burn

attain a maximum of 450° F. with an average value of about 380° F. Although much higher values have been reported elsewhere, a consideration of the heat transfer between a cigarette and the wood upon which it rests would indicate a maximum effective temperature of the wood no greater than 500° F. Therefore, it was felt that the measured values were in the proper range even though some variations were to be expected.

A consideration of the possibility of developing either an insulating or a conducting coating led to an inspection of thermal conductivity data in the literature. These data clearly indicated the advantages of inorganic materials for a conducting coating. However, any use of these data in calculations of theoretical coating thickness gave absurd results. Hence, one conclusion was that the protective coating on the wood did not have to withstand, other than momentarily, the effective temperatures of the burning cigarette in view of the fact that several relatively thin coatings, although certainly far from satisfactory, did offer protection to the wood.

The several tests outlined below were conducted in an attempt to clarify some of the apparent inconsistencies previously mentioned.

1. Burning Time of Cigarettes on Suspended Samples of Yellow Pine and Poplar.

Samples of yellow pine and poplar $6" \times 4" \times 3/4"$,

were suspended to permit free air circulation, and the following tests carried out.

(a) Cigarettes were lighted and placed on the samples and the time for complete burning of the cigarettes was recorded. Approximately thirty-five minutes was required, with normal air circulation in the room.

(b) A cigarette was placed on a panel for one minute, and then removed and the effects examined. The cigarette was smoked briefly and replaced on the same spot. This sequence was repeated at four intervals on each panel.

(c) Dry sand was thinly scattered on the surface, and four-one-minute intervals of burning were observed. The area and severity of burning were only slightly less than in (b).

2. Burning of Cigarettes on Wood Samples on a Cold Metal Surface.

Panels of poplar and yellow pine were placed on a cold metal surface and cigarettes burned on them for four one-minute intervals. No difference between these and the suspended samples was observed.

3. Burning of Cigarettes on Compressed Panels.

Panels of poplar and yellow pine, 6" x 4" x 3/4", were placed in a press and compressed at 300° F. and 1200 psi pressure to approximately 3/8" thickness. These panels were subjected to each test performed under Parts 1 and 2 and, in each test, the burning was less severe than with uncompressed panels.

4. Burning of Cigarettes on Enameled Panels.

Panels of poplar and yellow pine, 6" x 4" x 3/4" were given one coat of white enamel, and the tests of Parts 1 and 2 were again performed. The average time for the continuous burning test was only seven minutes, but the air circulation might have been less than in Part 1. In each test, the paint was blistered in the center and stained at the edges of the burn. The paper and ashes tended to adhere to the surface, and the finish was softened for a radius of 1/2" - 3/4", causing sand to adhere at that distance from the burn.

5. Tests of Wood with Water Glass as a Protective Coating.

All tests were continuous, the cigarette burning for 4 to 5 minutes.

(a) Water glass, as received, was allowed to soak into a panel for one hour. When exposed to the cigarette, this coating swelled and turned white, so that the finish was destroyed.

(b) A panel was soaked in a 50% solution of the water glass used in Part (a). There was no apparent protection afforded by this coating.

(c) A panel was soaked for one hour in a 25% solution of water glass. The burning was the same as on bare wood.

(d) A panel was soaked in water glass which had silica powder mixed into it. The coating swelled and charred.

6. Tests Using Varnish and Silica Powder.

Varying amounts of silica powder were mixed in varnish and applied to panels. It was found that, for the maximum amount of powder that could be used and still have the finish dry, there was protection offered to the wood, but the finish itself was destroyed.

7. Test to observe Gums Deposited by Burning Cigarettes.

A lighted cigarette was placed on a sheet of aluminum foil and allowed to burn completely. A deposit of brown and yellow gum was left on the foil the entire length of the cigarette.

8. Tests with Ethyl Silicate Prepared by the Two-Step Method.

(a) Panels were given several coats which were allowed to dry at room temperature. Silica was merely deposited and the finish was flaky. Little resistance to the burning cigarette was observed.

(b) Panels were prepared by applying coats of ethyl silicate and dried under an infra-red lamp at temperatures above 100° C. Ethyl silicate penetrated the wood, causing flaking on heating and offering no protection from the cigarette.

From these purely qualitative tests, the following conclusions were drawn:

1. The intermittent burning of a cigarette on wood was far less damaging than the continuous burning, in all

probability, because in the intermittent process, there was greater opportunity for the dissipation of the heat.

2. The air-film between the burning cigarette and the wood offered considerable resistance to the transfer of heat, and increasing the distance of the cigarette from the wood by as much as 0.04 in. (with 20 mesh sand scattered over the wood surface) did not materially alter the action of the charring.

3. The more dense the wood, the greater was the resistance to the burning of the cigarette, as evidenced by the greater resistance of the compressed wood samples.

4. Much of the discoloration from the burning cigarette was the result of gums and tars of the cigarette becoming liquid enough to flow onto the surface. This action was demonstrated by the cigarette burning on the white enameled panel and the aluminum foil.

5. It was further concluded that a continuous heat-conducting coating was necessary in view of the fact that a discontinuous silica coating from ethyl silicate was of little value, whereas a continuous coating from water glass, although destroyed, did protect the wood and dissipate the heat.

6. The top coat exposed to the burning of the cigarette must be of such a nature that the gums and tars from the cigarette cannot dissolve or penetrate the finish, thereby permitting easy burning and charring of finish and wood.

It was felt that the results with the experimental and commercial varnishes and the investigations into the mechanism of the damaging actions of the burning cigarette clearly indicated possibilities only in heat conductive protective coatings. Further studies of heat conducting coatings were made using admixtures of aluminum oxide in varnish. However, this device did not materially improve the behavior of the varnish.

Water glass (an aqueous solution of sodium silicates) was next used. This compound was tried in several ways. First, a commercial grade of water glass was diluted in various proportions with water and dried on wood in thin layers under an infra-red lamp. When too much water glass was applied, testing with a cigarette resulted in the formation of encrustments on the surface. Apparently only thin layers could be applied successfully. The degree to which a thin layer of silicate dissipated the heat was rather remarkable. Evidently, the sodium silicate did conduct away the heat quite well, and dissipate it over a wide area.

In thin layers, water glass alone was not sufficient to completely protect the wood. The next step, since thick layers of sodium silicate could not be used, was to cover a thin layer of water glass with a good varnish. Here, again, trouble was encountered in that most varnishes would not adhere to the glossy surface offered by the silicate. However, allyl

sucrose was found to adhere fairly well.

Since the oxides of silicon are good heat conductors, the possibilities of silicone varnishes were again considered. Previously, poor results were obtained with the silicones because of the inability to obtain sufficient polymerization without charring the wood in the process. In this case, the curing of the silicone was attempted using a hot blast of nitrogen. The same difficulty as before was experienced, i.e. although better cures were obtained, the polymerizations still were insufficient to give the desired protection (13).

Some of the earlier experiments had indicated that the desired finish must not only resist the imposed temperatures but also resist to a remarkable degree the solvent action of the gums and tars from the burning cigarette. One method of preparing such a finish was postulated, i.e., improving the conductivity of a base coat through the incorporation of materials of high conductivity and then applying a top coat of as low solubility as possible. For the attempted betterment of the conductivity, colloidal silica was employed and for the top coat allyl sucrose was used. The results of several of these two-coat systems are summarized in Table III.

Microscopic examinations of the burn areas showed considerable penetration of tars and gums with comparatively uniform distribution over the damaged area.

The obvious conclusion from these results was that either the conductivity of the base coat was not adequately

improved or the top coat was not sufficiently insoluble with respect to the tars and gums or a combination of the two.

In an effort to realize better properties a number of co-polymers were prepared and admixed with colloidal silica prior to the application to the wood as a base coat. These materials were cured, covered with an allyl sucrose top coat, and tested or tested without the top coat. Below is a list of the various mixtures and co-polymers used in this portion of the work.

M-1. A mixture of 90% DC 804 silicone and 10% allyl sucrose solutions was precured at 97° C. for 4.5 hours and the solvent removed by vacuum distillation to 135° C. Silica was added in varying amounts to samples of the polymer and this material applied to small wood panels.

M-2. A mixture of 80% DC 804 and 20% allyl sucrose was bodied for 5 hours at 97° C., after which time the material was of a jelly-like consistency. Acetone and turpentine were added to reduce the viscosity, silica added, and the coating applied to wood panels.

M-3. A mixture of 70% DC 804 and 30% allyl sucrose was bodied for 5.5 hours at 97° C. and the solvent removed by vacuum distillation to 125°. The polymer was taken up with acetone and silica added, after which the acetone was removed by heating at 97° C.

M-4. A mixture of 60% DC 804 and 40% allyl sucrose was bodied for 5 hours at 97° C. and the solvents removed by

TABLE III SUMMARY OF TWO-COAT FINISH TEST RESULTS

Base	Per Cent Silica	Top Coat	Curing Temp- erature °F.	Curing Time Hours	Character of Finish	Cigarette* Test Results
BK 5704	20	Allyl sucrose	240	15	Clear, hard	1, 2, 3
BK 5704	10	Allyl sucrose	240	15	Clear, hard	1, 2, 3
Phoresin (Victor Chem.Co.)	20	Allyl sucrose	240	4	Clear, hard	1, 2, 3
Phoresin	10	Allyl sucrose	240	4	Clear, hard	1, 2, 3
Allyl sucrose	20	-----	230	4	Clear, hard	1, 3
Allyl sucrose	20	Allyl sucrose	230	20	Clear, hard	1, 2, 3 (Checked)
Allyl sucrose 5% Bodied tung oil	20	Allyl sucrose	240	15	Clear, hard	3
Allyl sucrose 40% Bodied tung oil	20	Allyl sucrose	230	60	Clear, hard	3 (Checked)
Allyl sucrose 40% Phoresin	20	-----	230	1	Clear, hard (Checked)	1, 2, 3
DC 804 silicone 5% allyl sucrose	20	Allyl sucrose	230	48	Clear, hard (Checked)	1, 2, 3

- * 1 - Wood charred
 2 - Finish charred
 3 - Tar & gum penetration

vacuum distillation to 130° C. Silica was added and wood panels coated.

M-5. A mixture of 50% DC 804 and 50% allyl sucrose was bodied for 5 hours at 97° C. and the solvents removed by vacuum distillation to 135° C. Silica was added and wood panels coated.

M-6. A mixture of 10% allyl sucrose, 40% DC 804, and 50% Phoresin was bodied at 97° C. for 5 hours, the solvent removed by vacuum distillation to 130° C., silica and benzoyl peroxide (catalyst for Phoresin) added, and wood panels coated.

M-7. A mixture of 5% allyl sucrose, 20% DC 804 and 75% Phoresin was bodied 8 hours at 97° C., vacuum distilled to 135° C., silica added, and wood panels coated.

M-8. A mixture 90% DC 802 and 10% allyl sucrose was co-polymerized for 3 hours at 97° C., vacuum distilled at 97° C. for 20 minutes, and lead naphthenate added in the ratio of 5 drops to ten grams. Then the following modifications were used:

A - The M-8 resin was brought to 85° C. and applied hot to wood panels.

B - An equal amount of M-6 (25% silica) was added and the resulting coating applied to wood panels.

C - To the M-8 resin, 20% silica was added, and the mixture brought to 85° C. and applied hot to the wood panels.

M-9. Polyester resin (No. 4201 Laminack, made by American Cyanamide Company) with 2% catalyst, was thinned with alcohol, mixed with silica, and applied to wood.

In the following table the various coatings are itemized along with the tests and results. These results are indicated according to the following scheme:

- (A) 1 - wood char - damage by burning cigarette indicates severe damage, 2 - less severe, etc.
- (B) Finish resistance, damage by burning cigarette, charring of the finish itself. 1-indicates low resistance, 2-greater resistance, etc.
- (C) Penetration of tars and gums into the finish under the action of the burning cigarette. 1-easily penetrated, 2-less easily penetrated, etc.
- (D) Softening of the finish from the heat of the burning cigarette, 1-softened readily, 2-softened less readily, etc.

TABLE IV SUMMARY OF CO-POLYMER COATINGS AND TEST RESULTS

Basic Coat	% Silica	Base Coat Cure		Allyl Sucrose Cure		Cigarette Test Results			
		Temp. °F.	Time Hrs.	Temp. °F.	Time Hrs.	A	B	C	D
M-1	1	300	26	--	--	2	1	1	1
M-1	3	300	26	--	--	2	2	2	2
M-1	4	300	26	--	--	1	2	2	2
M-1	7	300	26	--	--	2	2	1	2
M-1	8	300	26	--	--	2	2	2	2
M-1	16	300	26	--	--	2	2	2	2
M-1	30	300	26	--	--	-	2	2	2
M-1	1	300	26	380	16	-	2	2	2
M-1	3	300	26	380	16	-	2	2	2
M-1	4	300	26	380	16	-	2	2	2
M-1	7	300	26	380	16	-	2	2	2
M-1	8	300	26	380	16	-	2	2	2
M-1	16	300	26	380	16	-	2	2	2
M-1	30	300	26	380	16	2	2	2	2
M-2	3	190	70	--	--	2	2	1	1
M-2	4	190	70	--	--	2	2	1	1
M-2	7	190	70	--	--	2	2	1	1
M-2	12	190	70	--	--	2	2	1	1
M-2	25	190	70	--	--	-	2	1	1
M-2	3	190	70	400	1.5	-	2	1	2
M-2	4	190	70	400	1.5	-	2	1	2
M-2	7	190	70	400	1.5	-	2	1	2
M-2	12	190	70	400	1.5	-	2	1	2
M-2	25	190	70	400	1.5	1	2	1	2
M-3	5	190	240	--	--	1	1	1	1
M-3	7	190	240	--	--	1	1	1	1
M-3	12	190	240	--	--	1	1	1	1
M-3	22	190	240	--	--	2	1	1	1
M-3	30	190	72	340	20	-	2	2	2
M-3	5	190	240	380	6	-	2	1	2
M-3	7	190	240	380	6	-	2	1	2
M-3	12	190	240	380	6	-	2	1	2
M-3	22	190	240	380	6	-	2	1	2
M-3	30	190	100	380	6	2	2	1	2
M-4	4	190	60	--	--	-	2	1	1
M-4	4	190	60	380	6	2	2	1	2

TABLE IV - (Continued)

Basic Coat	X Silica	Base Coat Cure		Allyl Sacrose Cure		Cigarette Test Results			
		Temp. °F.	Time Hrs.	Temp. °F.	Time Hrs.	A	B	C	D
M-4	7	190	60	--	--	2	2	1	1
M-4	13	190	60	--	--	2	2	1	1
M-4	21	190	60	--	--	2	2	1	1
M-4	30	190	60	--	--	-	2	1	1
M-4	7	190	60	380	6	-	2	1	2
M-4	13	190	60	380	6	-	2	1	2
M-4	21	190	60	380	6	-	2	1	2
M-4	30	190	60	380	6	-	2	1	2
M-5	6	190	70	--	--	1	1	1	1
M-5	12	190	70	--	--	1	1	1	1
M-5	20	190	70	--	--	1	1	1	1
M-5	26	190	70	--	--	1	1	1	1
M-5	6	190	70	380	8	-	1	1	1
M-5	12	190	70	380	8	-	1	1	1
M-5	20	190	70	380	8	-	1	1	1
M-5	26	190	70	380	8	-	1	1	1
M-5	7	190	60	--	--	2	1	1	1
M-6	7	190	60	380	5	-	1	1	1
M-6	16	190	60	--	--	2	1	1	1
M-6	16	190	60	380	5	-	1	1	1
M-6	25	190	60	--	--	2	1	1	1
M-6	25	190	60	380	5	-	1	1	1
M-7	5	190	40	--	--	1	1	1	1
M-7	15	190	40	--	--	1	1	1	1
M-7	20	190	40	--	--	1	1	1	1
M-7	5	190	40	260	3	1	1	1	1
M-7	15	190	40	260	3	1	1	1	1
M-7	20	190	40	260	3	1	1	1	1
M-8-A	0	190	20	--	--	2	2	2	2
M-8-A	0	190	20	260	12	2	2	2	2
M-8-B	12.5	190	20	--	--	1	1	1	1
M-8-B	12.5	190	20	260	12	1	1	1	1
M-8-C	20	190	0.5	260	1.5	2	2	2	2
M-8-C	20	190	0.5	260	6	2	2	2	2
M-9	5	190	20	--	--	2	2	2	2
M-9	5	190	20	260	6	2	2	2	2
M-9	20	190	20	--	--	2	2	2	2
M-9	20	190	20	260	6	2	2	2	2

Although none of these co-polymer test finishes was entirely satisfactory, several significant trends were observed:

(1) No uncatalyzed allyl sucrose-silicone films can be satisfactorily cured under the conditions dictated by the physical limitations of wood.

(2) The use of lead naphthenate as a drier for silicone films decreases the curing temperature, decreases the curing time, and decreases the hardness of the film obtained.

(3) Phoresin mixtures lack the desired physical properties; increasing Phoresin content decreases film resistance.

(4) Allyl sucrose does not possess the properties desired for the insoluble film; application over films of high conductivity resulted in lessened resistance to a burning cigarette.

(5) Polyester films can be prepared that compare favorably in hardness to allyl sucrose films, but lack the brittleness of allyl sucrose films.

(6) Crazeing of high silica-content coatings can be controlled to a large degree by curing in a press.

(7) Penetration of gums, tars, etc., actually presents the most difficult problem; several coatings appeared to meet all other requirements.

Still another group of experimental varnishes was employed. In this portion of the work application techniques were of interest, although a variety of materials were used

including: MM-55 Uformite (Resinous Products and Chemical Company), a melamine-formaldehyde resin; Melmac Resin (American Cyanamide), a melamine resin; 3501-Super Beckamine (Reichold Chemicals), as well as allyl sucroses modified with polyvinyl chloride.

The various resins and resin combinations examined as cigarette resistant finishes are listed below.

TABLE V RESINS AND RESIN COMBINATIONS

<u>Number</u>	<u>Composition</u>
N1	90% DC-802, catalyzed (lead naphthenate) 10% MM-55
N2	80% DC-802, catalyzed, 20% MM-55
N3	70% DC-802, catalyzed, 30% MM-55
N4	60% DC-802, catalyzed, 40% MM-55
N5	50% DC-802, catalyzed, 50% MM-55
N6	40% DC-802, catalyzed, 60% MM-55
N11	90% Polyester, catalyzed 10% MM-55
N12	80% Polyester, catalyzed 20% MM-55
N13	70% Polyester, catalyzed 30% MM-55
N14	60% Polyester, catalyzed 40% MM-55
N15	50% Polyester, catalyzed 50% MM-55
N16	40% Polyester, catalyzed 60% MM-55
N20	3501 - Super Beckamine
N21	10% AD-81 Alkyd (Chas. R. Long), 90% MM-55
N22	20% AD-81 Alkyd, 80% MM-55
N23	30% AD-81 Alkyd, 70% MM-55
PN-I	90% MM-55, 10% Phenol (3 hrs. reflux)
PN-II	80% MM-55, 20% Phenol (3 hrs. reflux)
XI	33% DC-802, catalyzed, 33% allyl starch and 34% DG-804

These materials were used in several different applications to wood panels to produce the protective finish.

Mechanical mixtures with 0 to 10 per cent silica (higher silica percentages usually were not tolerated by the

resin mixtures) were prepared, applied to the wood panels, air dried, oven dried from 1/2 to 1 hour, and finally press cured at pressures ranging from 10 to 500 lb. per sq. in. and temperatures from 250 to 300° F. With the exception of N20, N21, N22, and N23 (the alkyd modified melamine and urea-melamine), cigarette tests indicated reasonably good wood protection and resistance to the temperature but low resistance to the penetration of tars, gums, etc., from the cigarette. The N20, N21, N22, and N23 samples offered poor temperature or tar penetration resistance and little wood protection.

Another technique was that of an impregnation character requiring the soaking of the panels first in alcohol, then in acetone and finally in a boiling bath of Melmac E43-8. Other panels were merely air dried and immediately immersed in the boiling bath. An oven cure for 2 hours followed the soaking in the boiling resin, and a final cure was obtained in the press at 500 lb. per sq. in. and 275° F. for 2 hours. The resulting panels were approximately 3/4 the original thickness, hard and dense. However, cigarette tests indicated no significant improvement with impregnation.

In another series of tests, glass fibers were incorporated in the finish. Glass fibers were placed on the wood surface (with and without previous impregnation) and then covered with melamine-silica mixtures, allyl sacrose, and polyesters. These samples, press cured at 200 lb. per sq. in. and 300° F., demonstrated considerably less checking tendencies than similar

samples containing no fibers, but otherwise no improvement in properties.

Although no completely cigarette resistant finish was observed, certain trends were noted:

1. Oven-cured silica containing films were vastly inferior to the corresponding press-cured films.
2. Those films of high melamine content were brittle to the extent that the control of checking was very difficult.
3. The alkyd modified melamine finishes decreased in cigarette resistance as the alkyd content increased.
4. The alkyd modified melamines with high melamine content were not clear, perhaps indicating incompatibility in these proportions.
5. Melamine impregnation did not improve the cigarette resistance.
6. All the melamine containing films cured on the wood appeared to have low resistance to the penetration of the tars, gums, etc., of the burning cigarette. However, commercially prepared melamines on a phenolic base offered high resistance to the penetration of the tars. In all probability this difference was the result of the higher curing temperatures and pressures in the case of the commercial materials.
7. Urea-melamine films apparently possessed very little temperature resistance under the action of the burning cigarette.

All of the finishes employed to this stage of the

work were considered possible solutions if their thermal conductivities were great enough to dissipate the heat of the burning cigarette sufficiently to prevent excessive temperatures. At the same time it was felt that a reduction in the maximum temperature attained by the finish would reduce the solubility of the cigarette tars and gums, thereby reducing the marring of the finish itself. Thus, if a finish were sufficiently resistant to the penetration of the tars and gums, its inherent thermal conductivity could be expected to be maintained at a level higher than in the case of the finish containing penetrated tars.

Another possibility of preventing the marring action of the burning cigarette was the use of an insoluble top coat over a wood the heat capacity of which had been greatly increased. To investigate the possibility of this method, phenolic impregnations followed by press curing were undertaken. The impregnated wood was given a base coat of ethyl silicate saturated with boric acid and a top coat of polyesters yielding a finish somewhat resistant to the burning cigarette.

In another test the impregnation of the wood with concentrated zinc chloride solution saturated with boric acid was attempted. Unfortunately, the zinc chloride severely darkened the wood. When dilute zinc chloride solutions saturated with boric acid were employed the wood was not darkened but no resistance to the burning cigarette was observed.

In another group of experiments, the heat capacity and thermal conductivity of wood panels were increased by cutting grooves in the underside of the wood to within approximately one-quarter of an inch of the top surface, filling these slots with a mixture of a resorcinol cement and aluminum powder in one case, and resorcinol cement with small strips of aluminum foil in another, and finally curing in a press with a top coat of polyesters. The resorcinol mixed with aluminum powder as the back filling material did not materially improve the cigarette resistance of the top finish. However, the aluminum foil held in the slots with the resorcinol cement did produce a panel having a top coat that was cigarette resistant.

These results clearly indicated the nature of the necessary conducting material, i.e. it must be continuous as in the case of the aluminum foil and not of a discontinuous nature as in the case of the aluminum powder.

RESULTS AND CONCLUSIONS

Of the several methods originally considered as possibilities for the preparation of cigarette resistant finishes only the use of a heat conducting material appears to have promise. As indicated by the use of the wood panel back - filled with aluminum foil and cement, the conductivity may be increased sufficiently so that surface temperatures are reduced, and a finish that otherwise cannot completely resist the solvent action of the tars and gums from the burning cigarette does offer adequate protection. However, it must be recognized that this technique of preparing a cigarette resistant finish is not the solution to the problem, since the operations required to prepare wood in this manner would be far more costly and time consuming than the preparation of cigarette resistant plywood.

Although no completely cigarette resistant finish was prepared that in all respects satisfied the requirements, a number of important facts were established, the most important of which is the fact that a heat conducting film is a necessity. Another point of extreme importance was the necessity for the finish to be resistant to the solution action of the cigarette tars and gums at the surface temperatures obtained.

In general it is felt that there are several finishes "almost satisfactory" since an occasional panel would behave as desired. However, those materials giving the desired results only with very special or unusual treatment can hardly be considered proper answers to the problem.

II. DESIGN OF A GLUE APPLICATOR

INTRODUCTION

In the present practice of furniture drawer construction in the Mengel Company plant, a factor of concern is the use of glue blocks to stabilize the drawer assembly. This application has been by hand heretofore, and hinders smooth operation of a mass production line. Accordingly, attention was directed to the problem of eliminating glue blocks. The proposed solution consisted of two parts, namely; (1) an improved glue mixture to be used without blocks and (2) an applicator (or glue gun, as it was termed) design.

Fear (13) conducted tests on various glue mixtures and proposed Amberlite PR-115 with P-117 catalyst admixed with asbestos fiber as the most suitable material tested. After this preliminary work for the selection of an appropriate glue the problem of designing a suitable applicator was undertaken.

OLUE GUN DESIGN

With the completion of the tests of the glue mixture indicating the workability of the technique for the elimination of the glue blocks, the design of the glue gun was undertaken. Certain general requirements for the gun had been established, namely (1) it should be light enough to be easily handled - no greater in effective weight than 10 ounces; (2) it should be supplied with glue from a central reservoir; (3) it should be easily operated so that the overall operation becomes more rapid than with the glue-block technique; and (4) there must be a minimum of stringing and smearing of the glue mixture.

Several preliminary sketches and designs of components were prepared and discussed. When the various components and mechanisms had been approved, an air actuated gun was designed and working drawings prepared. The drawings are shown in Figures 1, 2, 3, 4, and 5.

The several important features of the gun are itemized below:

(1) The air cylinder mechanism serves as the handle. The recommended materials of construction are aluminum for the case and stainless steel for the outside plates and working parts, thus permitting an approximate weight as designed of 9.8 oz.

(2) The operating speed of the gun will depend to a certain extent upon the glue and air pressures. It is assumed that these variables can be adjusted within limits so that the gun will be only slightly slower than the operator's reflexes.

Since the trigger is double acting, (i.e., delivery on compression, delivery on release, etc.) it is believed the required speed easily can be attained.

(3) The metering of the glue is accomplished by the glue closure and by the travel of the glue piston after the closure opens. Although movements were based on calculations for the use of a non-compressible glue, which, of course, cannot be completely realized, a positive pressure on the glue will permit proper metering.

(4) The glue inlet is closed except during discharge from the gun. Oozing is prevented by "overtravel" of the glue piston after the inlet closes, causing a sucking of the glue away from the delivery ports.

(5) The delivery tip will enter a 2-1/4" opening.

(6) Detachable plates at the bottom and rear of the glue cylinder permit ready entry to any part of the glue end of the gun. The air cylinder is detachable, as is the trigger mechanism in the top of the air cylinder.

(7) Glue must be delivered to the gun under pressure - about 1/4 to 1/2 the air pressure necessary for the operation of the gun.

With the completion of the glue gun design, more specific testing of the behavior of the glue mixture was possible. To learn something of the flow characteristics of the glue, a delivery port simulating that to be used in the

gun (i.e. 1/8" x 1/32" at the outside opening) was fabricated from copper. Amberlite glue with 20% asbestos was pushed through the port by air pressure. Although no quantitative study was made, it was found that the glue did not flow at 5 pounds per square inch gauge; however, at ten pounds pressure the flow was satisfactory. No unusual change in flow was observed up to 35 pounds pressure.

In other experiments of this type, glue containing 50% per cent fibrous talc (asbestine) appeared to have greater fluidity than that with 15 per cent asbestos.

Experimentation with glues containing asbestine as well as asbestos was carried out in the event that glues more fluid than those containing the asbestos would be desirable or necessary in the glue gun. Five different samples were prepared and examined in the right angle as well as the plywood shear tests.

To 100 parts of Amberlite PR-115 were added 15 parts of catalyst P-117. Then this catalyzed material was used in making the following mixtures:

1. 100-parts catalyzed glue plus 15 parts short fiber asbestos.
2. 100-parts catalyzed glue plus 25 parts short fiber asbestos.
3. 100-parts catalyzed glue plus 15 parts fibrous talc.

4. 100-parts catalyzed glue plus 25 parts fibrous talc.
5. 100-parts catalyzed glue plus 35 parts fibrous talc.

These mixtures were employed in the right angle shear test to give comparative strength data. The results are summarized in the table below along with an estimation of the per cent wood failure.

TABLE VI RIGHT ANGLE SHEAR TEST RESULTS

	<u>Glue Mixture</u>	<u>Breaking Range</u>	<u>Wood Failure-%</u>
1.	15 Pts. asbestos	300 - 400	80 - 90
2.	25 Pts. asbestos	300 - 375	80 - 90
3.	15 Pts. talc	200 - 250	0 - 20
4.	25 Pts. talc	200 - 230	0 - 10
5.	35 Pts. talc	190 - 210	0 - 10

These glue mixtures were also used in the A.S.F.M. plywood shear test with 1/16 in. birch veneer and 1/8 in. birch center stock. A glue spread of 35 lb. per 1000 ft. of glue line was used in the 3-ply panels. The curing pressure was 400 lb. per sq. in. at 300° F. for 13 minutes. The shear strength was obtained using a Richle tester. These data are summarized in the following table along with the estimated wood failure.

TABLE VII A.S.T.M. PLYWOOD SHEAR TEST RESULTS

<u>Glue Mixture</u>		<u>Breaking Range-Lb.</u>	<u>Wood Failure-%</u>
1.	15 Pts. asbestos	375 - 420	70 - 90
2.	25 Pts. asbestos	375 - 420	60 - 90
3.	15 Pts. talc	320 - 400	0 - 10
4.	25 Pts. talc	300 - 375	0 - 10
5.	35 Pts. talc	300 - 350	0 - 5

The results of both of these tests clearly indicated the advantages of the asbestos filled glue as far as relative strengths were concerned, even though the talc filled glue had considerable strength.

Figure 1 Glue Gun Design, Assembly View

Additional parts for glue gun design not shown on Figures 1, 2, 3, 4, and 5.

Screws

<u>Number</u>	<u>Length</u>	<u>Type</u>	<u>Specification</u>
8	3/8"	Flathead	3-48 NC-2
4	3/4"	"	"
5	1/8"	Allen	5-40 NC-2
5	1"	Roundhead Bolt	3-48 NC-2
4	1/4"	"	"
8	3/8"	"	"
4	1/2"	"	"

Pins - 1 - Air control valve pin 1/4" long, 0.125" diameter

1 - Trigger pin 1/2" long, close fit inside 1/8" hole.

Trigger Spring - To fit on 1/8" pin, 3/4" long in tension,
3/8" long in compression to be compressed by 2 to 3
pounds force.

III. PRELIMINARY STUDY OF RUBBER-PHENOL CO-POLYMERS

INTRODUCTION

In recent months the public press has acclaimed the advent of supersonic speeds by jet-propelled aircraft in the rarefied air of the stratosphere. It seems possible that speeds exceeding one thousand miles per hour may become a reality in the near future. If such is the case the efficiency of the new aircraft may be considerably increased by developments in the field of materials of construction. That the structural stresses and strains induced by the ultrasonic speeds may dictate new developments in the field of metal alloys is entirely feasible; also some means of eliminating completely the trouble caused by the high temperatures developed by jet type mechanism would be welcomed by designers.

Another problem, which has become evident even in the present type jet-propelled machines, is the unusually drastic erosion of the leading edges of the aircraft component parts. At heightened speeds every particle in the air is a potential abrasive; the impact of dust particles, drops of water, and other suspended matter results in a relatively rapid destruction of the aircraft coatings presently in use. The initial action is a wearing away of the coating at the leading edge, after which the rest of the film is simply stripped from the metal by the continued action of the abrasive medium. It is in this field of protective coatings that the research has been directed.

It was desired that the project actually have two aims: (1) the testing of coatings presently available to

determine their behavior in abrasive atmospheres and the establishment of the suitability of the materials for high speed aircraft coatings, and (2) by development research to attempt the production of new materials having the desired properties.

It was felt that the project could most efficiently be divided into two phases, the first concerned with the development of coating materials, and the second concerned with the mechanical problems surrounding the construction and operation of an adequate test unit.

The test stand design and construction is primarily the work of William B. Moore and his co-workers under the guidance of Dr. R. C. Ernst and will be reported at another time.

The initial work in the development of a coating material for aircraft moving through air at high speeds was an investigation of phenolic resin-modified elastomers. Some pertinent facts which prompted the study are as follows:

(1) Phenols are used extensively in resin manufacture. Many of these resins have excellent adhesive properties.

(2) Rubbers absorb phenol and this results in anti-oxidant properties for the rubber.

(3) Phenols combine with many compounds having double bonds.

In view of these facts the belief that phenols can be combined with elastomers having double bonds is justified.

Elasticity, chemical resistance, and good adhesive properties were predicted characteristics of the co-polymer. Accordingly, the investigation was initiated.

HISTORICAL

The aircraft industry, until very recently, met no unique painting problems and as might be expected materials used in this field were of various types (16).

Little attention was paid to relative merits of basic types until the advent of metal aircraft whereupon primary considerations shifted from decoration to protection of the metallic surfaces against corrosion.

Today a number of metals find use in aircraft, the most important being aluminum, steel, and magnesium. No protection is needed for aluminum unless exposed to other metals where galvanic corrosion may occur. The latter two metals do require protection under any except the most mild conditions; their low resistance to chemical attack is well known. A number of materials are used to this end. Zinc chromate primers have found almost universal acceptance as a primer coating. Use of phenolics, spar varnishes, oil based synthetic resin enamels, and alkyds as vehicles for the chromate and as a finish coat is widespread (16).

Use of aircraft for military operations has focused attention on the relative merits of coatings under the conditions of aircraft operations, particularly since the beginning of the last war. It is entirely possible that the efforts of the military will result in general advances in this field - that the narrow objective of simply keeping ahead of other powers in military development will lead to overall progress in the aviation industry.

THEORETICAL

In the search for a satisfactory coating it was necessary to establish certain criteria by which materials having little promise could be readily eliminated. Previous investigations had led to the conclusion that the most important properties of a satisfactory film were (17):

1. Resistance to abrasion.
2. Good adhesion to metal.
3. High flexibility.
4. Thermal expansion equal or approximately equal to that of the metal that is coated.

In addition, the film must meet certain minimum standards of hardness.

Resistance to abrasion and high flexibility are properties possessed by elastomeric substances.

The type of adhesion (18) is a function of both the surface and the coating material. In general, adhesion to metal is increased by incorporating polar groups in the resin, by roughing the metallic surface, and by proper choice of the type of surface; e.g., whether or not the surface has an oxide film. For instance, in the case of iron the oxide has little adhesion to the metal and this results in a point of weakness at the junction of an oxide film and the metal, while aluminum oxide clings tenaciously to the metal seal. Also, especially if polar groups are included in the film, the aluminum oxide film has greater adhesion to the paint film. This adhesion

improvement is due to orientation of the polar group, i.e., the oxide film has both positive and negative charges and these cause the polar groups of the coating to "orient" themselves near groups having the opposite electrical charges. This rearranging causes a decrease in potential energy of the charges and results in a stronger bond since separation of these charges can only be effected by supplying the energy equivalent to the previous decrease in potential energy.

In the case of aluminum the procedure for securing an oxide film is called anodizing. This surface oxidation can be accomplished both in an electrolytic bath and in a chemical bath. A fairly rapid and simple method for experimental work is to submerge cleaned panels in a bath consisting of a solution of sodium carbonate and potassium dichromate. The concentrations of these components may be varied over wide limits (19), but the weight of sodium carbonate theoretically should not be twenty times the weight of the potassium dichromate. However, a ratio of ten to one is recommended with a sodium carbonate concentration of 20 to 30 grams per liter.

For the improvement of adhesion or bringing that adhesion within desirable limits a primer often is used. Occasionally such a material is available having greater adhesion for both the metal surface and the paint film, than the paint film has for the metal surface. If the material can meet certain requirements as far as flexibility, thermal prop-

erties, and tensile strength are concerned, the adhesion problem can be solved through the application of the primer to the metal and the paint film to the primed surface.

Thermal expansion properties, if unsatisfactory, may in some cases be adjusted by use of pigments, plasticizers, or both.

In this particular problem certain other factors were important: The desired coating is one which could be brushed or sprayed onto the surface; coloration by pigmentation is desired, as well as good salt water resistance.

It was recognized at the beginning of the problem that a considerable number of materials might be selected for investigation. Those which were originally marked for study included: (a) Melamine-formaldehydes, (b) Melamine-urea, (c) Modified-urea formaldehydes, (d) Alkyds, (e) Dezrans, (f) Vinyls, (g) Polyurethanes.

Certain relevant data already were reported; the results of tests rotating arms at subsonic speeds (14,15). The major conclusion arising from this earlier work was that, in general, elastomeric materials possessed greater resistance to erosion under the test conditions than any material other than methyl methacrylate polymers. These data prompted the isolation of elastomeric type polymers as the field for intensive research.

The large number of available elastomeric materials

was increased by widespread research programs spurred by war-time shortages of natural rubber. In general, elastomers are materials having long chain polymers with a "linear" type structure permitting sufficient freedom of the molecular structure for the chains to be extended without rupturing valence bonds. In many cases a double bond is retained at intervals in the structure permitting linking between chains, giving a higher softening point, a decrease in elasticity, an increase in hardness, and decrease in solubility. Pigmentation in conjunction with cross-linking can result in a rather hard material, highly resistant to abrasion. In general, the soluble polymers or elastomers of this field result in solutions of very high viscosities.

The first phase of the problem was investigation of phenol-formaldehyde modified elastomers. The adsorption of phenol by rubber was known as well as the anti-oxidant properties of the resulting rubber (20). It was thought, therefore, that phenol could be combined with rubber and later reacted with formaldehyde to obtain a heat convertible resin. The projected reaction may be represented as follows:

Stage I

Stage II

Stage III

It was desired that the methylool compound be soluble in a suitable solvent in order that the coating be applied in this stage and carried into stage three by heating. Several factors were significant in this respect.

1. The ordinary phenolic resins, in general have low solubility in the best rubber solvents and rubbers have low solubility in the best phenolic solvents. Perhaps a mixed solvent will offer the answer to this problem.

2. Solubility of a polymer obtained from a particular monomer is an inverse function of molecular weight. For this reason a low molecular weight starting elastomer may prove advantageous.

3. A decrease in viscosity of a rubber solution should

result from the addition of phenol to rubber provided the solvent is a good solvent for phenol. A proper choice of solvent can, therefore, work advantageously in this respect.

4. Insolubility of the cross-linked polymer is a virtual certainty. This conclusion was based on the following reasoning.

- a. Before present day methods of purifying commercial styrene were developed, synthetic rubbers were prepared from butadiene and styrene which contained varying amounts of divinylbenzene. These polymers exhibited low solubility characteristics and investigation has shown that the primary factor contributing to this property was the presence of the divinylbenzene which provided means of obtaining a three dimensional structure. It has been reported that as little as 1% of the divinylbenzene in styrene results in complete insolubility in all the common solvents (21). It is further reported that vulcanization of rubber in most cases results in elimination of only a small percentage of the double bonds and the insolubility of vulcanates adds weight to the assumption that cross linking must be completely prevented if solubility is to be expected.

It is evident that the reaction which results in the

methylol compound is essentially the same as that which converts the methylol material into the thermosetting plastic. Some possible methods for controlling the reaction are available:

1. By a proper choice of catalyst for the formaldehyde reaction with the phenol-rubber material, the reaction may be arrested in the methylol stage. For this purpose it is probable that the milder basic catalysts are to be preferred over the somewhat more drastic acid catalysts.

2. Depress the conversion by preventing elimination of water from the reaction system. This means that the temperature should be kept low, and, if possible, water should be placed and retained in the reaction media to depress the premature reaction.

Both procedures present other problems. In the first case, the thermal energy of activation is probably higher with the milder catalyst. In the second case, it is evident that the water must ultimately be removed and the conditions for this removal will probably promote the condensation.

The solution to the problem may lie in the use of a condensation material other than formaldehyde. Use of hexamethylenetetramine in this respect is known and resins utilizing this material have been used to modify rubbers (22).

In the modifying process the contribution of the rubber to the physical properties of the protective coating was of primary importance, i.e., the most desirable property

of the film is abrasion resistance and this property is expected to be derived from the rubber. Actually, the object of the phenol modification was the incorporation of properties of a paint vehicle, i.e., solubility and low temperature curing. Therefore, if the initial investigation showed the feasibility of the rubber phenol combination to form a material condensable with formaldehyde to form a useable resin, the direction of the secondary investigation should be the determination of the lowest phenol-rubber ratio which would give the desired properties.

A solution to the problem was not assured even if phenolic-rubber resins were prepared. Therefore, other possibilities were considered.

One of the most promising materials with previous whirling arm tests was a pigmented resin of the butadiene-styrene type (Pliolite S-4, Goodyear Rubber Company) (23). For adhesion purposes a vinyl resin consisting primarily of vinyl chloride but with about 15% vinyl acetate (VACH, Bakelite Corporation) was added. One disadvantage of this material was the necessity of using a mixture of several solvents, some of which had boiling points in the range of 125-140° C., to dissolve the resins. The material was baked to remove the solvents. A low softening point (135° C.) added to the undesirability of this material (23). The properties of these materials led to the consideration that a three component co-polymer might overcome the undesirable features. Such a co-polymer would include

butadiene, vinyl-1, 1-dichloride, and vinylacetate. The butadiene would permit cross linking. The vinyl chloride would contribute toughness and adhesion and the vinyl acetate would permit the use of air drying solvents.

EXPERIMENTAL

The reaction of phenol and rubber may be represented as shown on page 76.

If phenol was present in sufficient quantities, of course, more than two phenol nuclei could be in the linking chain between the rubber molecules and up to three hydrogens of the phenol could be reacted.

Means of reacting rubber and phenol were found after some preliminary study. Chopped rubber gum (or GR-S rubber gum) dissolved in boiling phenol and the solution time required was shortened by use of an acid catalyst. Sodium hydroxide did not assist the solution.

Proceeding on this basis various percentages of natural rubber gum and GR-S rubber gum were reacted with phenol. The two rubbers behaved in an analogous manner. The reaction was carried out in a three-neck flask equipped with a condenser, thermometer and mechanical stirrer. A gram molecular weight of phenol was used with varying percentages of rubber. Five grams of ninety-five per cent sulphuric acid were used as catalysts. The temperature of reaction was 160-170° C. One hundred milliliters of toluene were added and the rubber-phenol product dissolved easily and was cooled to room temperature. The pH of the solution was raised to about seven with 10% caustic soda solution and enough added to give three percent excess sodium hydroxide based on the phenol present. One and one quarter gram molecular weights of paraformaldehyde were added and the temperature brought to 65° C. A temperature of 60 to

70° was maintained until the temperature drop indicated that the formation of the methylol compound was essentially complete.

At this point the several experiments were varied in some respects. One procedure was to bring the reaction mixture to a boil and reflux for an hour. Another procedure was to permit the methylol material to stand, in the hope that separation of oil and water layers would result and the resinous material would be retained in the oil phase. A third treatment was dehydration of the material under vacuum. In every case the end result was the same; two phases appeared, both of which when diluted with the usual solvents precipitated the resinous material. Films cast from either of the two phases were rather brittle.

The use of butyl acetate instead of the toluene as described above led to similar results.

The question was raised as to whether the phenol and rubber actually reacted. A study of this phase of the reaction supported the conclusion that the velocity constant for the reaction was not great. The procedure was to use the rubber, phenol, and sulphuric acid in the manner described and recover the product by treating the reaction mixture with a dilute caustic soda solution. The precipitate was filtered out and washed with water. After drying in a desiccator the weight of recovered product was determined. In the case of mixtures receiving caustic treatment almost immediately on solution of the rubber in the phenol, very little increase in weight of

rubber was observed. When the reaction mixture was allowed to stand for several days with intermittent refluxing before the caustic soda treatment, a considerable weight increase was obtained, in some cases amounting to 100 per cent of the rubber weight. The reaction product was partially soluble in toluene and toluene solvent mixtures, but otherwise could not be dissolved in strong caustic soda solution nor in the usual resin solvents. Decomposition of the product occurred at temperatures somewhat in excess of 100° C. (This decomposition was expected to be a function of the extent to which the combination had proceeded).

A variation of the phenol-rubber combination was the use of maleic anhydride in place of the sulphuric acid. The results obtained by the aldehyde condensation were entirely analogous to the results obtained with the sulphuric acid reaction product.

Another method of carrying out the rubber phenol combination was the use of equi-molar quantities of these materials under the influence of the same molal quantity of anhydrous aluminum chloride in a toluene medium. The rubber and phenol were first dissolved in the toluene and the aluminum chloride added while the temperature was maintained at $20-25^{\circ}$ C. When the generation of hydrogen chloride had subsided the temperature was slowly raised (over a period of two or three hours) to the reflux temperature. When the lack of evolution of hydrogen chloride indicated the reaction was

essentially complete, the sides of the reaction vessel were coated with the product. Its insolubility prevented the continuation of the experiment with the aldehyde condensation.

Another way of accomplishing reactions resulting in phenol-rubber combination was that used by the author's co-worker(24). Rubber was reacted with bromine and this product was reacted with phenol to eliminate hydrogen bromide. The phenol nucleus was attached to the rubber molecule. The final reaction was carried out under the influence of anhydrous ferric chloride. The bromine was reacted with the rubber in a carbon tetrachloride medium at 5° C. The product recovered by precipitation with acetone was a "dibromo-rubber". This product was reacted with phenol in the presence of ferric chloride with evolution of hydrogen bromide. The resulting material after separation from the reaction mixture was soluble in caustic soda solution, toluene, and partially soluble in carbon tetrachloride.

Another phase of experimentation was the elasticizing of phenolics by cold-cutting with a rubber cement. Compatibility in the liquid phase was very difficult even for low concentrations in a complex solvent mixture. Even when solution was attained the films cast from such solutions were composed of two incompatible phases. This evidence supports the literature reports that ordinary phenol-formaldehyde resins cannot be externally elasticized (25). These sources also report that internal elastization can be effected by use of a sub-

stituted phenol as the material to be condensed with formaldehyde. Accordingly para-phenyl phenol was used as the basis for a formaldehyde condensation resin, but compatible films with rubber were not obtained, although liquid phase compatibility was more easily obtained than in the case of straight phenol resins.

The only report of a soluble rubber-phenol-formaldehyde product found in the literature utilized oxidizing conditions for the initial combination (26). Therefore, investigation of this experiment was undertaken. A gram of phenol, 20 grams rubber and 2.5 grams cobalt naphthenate was treated with a current of air at 150-160° C. until the rubber dissolved and this treatment was continued 10 hours more - until the material formed a cloudy solution in acetone. One mole of formaldehyde, as formalin, and 1 gram of oxalic acid were added. After five hours at 70-80° C. and 2 hours at 100° C. the condensation did not appear completed. Three grams oxalic acid were added and the reaction proceeded so rapidly that partial insolubility of the product in alcohol was almost immediately attained. The product was washed with water and parts of it extracted with 1, 4 dioxane. The leachings deposited a sticky film on solvent evaporation. Addition of hexamethylenetetramine in the cold caused a precipitate but the solution obtained by filtering deposited a brittle thermosetting film on drying. This would seem to indicate some promise for a soluble material if the rubber molecular weight is sufficiently reduced.

RESULTS AND CONCLUSIONS

The results of rubber-phenol combinations are consistent with the results expected from consideration of data reported in the literature. No unusual deviations from predicted behavior were encountered. The following premisses were substantiated:

1. Phenol-rubber combinations are possible.
2. "Cross linked" phenol-formaldehyde-rubber combinations are difficultly soluble in the usual solvents.
3. The action of phenol on rubber in the presence of a mutual solvent results in a solution having a lower viscosity than that exhibited by a rubber solution in the same solvent.

In addition, it was found that premature condensation of the methylool compound resulting from the action of formaldehyde on a phenol-rubber is very difficult - perhaps impossible - to prevent.

Further indications were that the use of a low molecular weight rubber may lead to soluble polymers.

Under these circumstances it is concluded that the resinous material sought as a solution to the problem of a high-speed aircraft finish probably does not lie in the combination of phenol with ordinary rubbers. With the reservation that low molecular weight rubbers may behave in such a manner as to result in increased solubility of the resin after the formaldehyde condensation, it is felt that this particular area of investigation can be profitably abandoned.

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APPENDIX

Calculation of Film Thickness for Protection of Wood

Surface temperature produced by a cigarette burning on wood = 380° F. (13)

This was determined by placing a fine wire thermocouple in a groove in a piece of wood so that the thermocouple was flush with the wood surface, and taking readings as a cigarette placed on the wood surface burned up to the thermocouple. It was estimated that the temperature attained an average high temperature of 380° F. over a period of 90 seconds.

Limit to which lower surface of finish film may be heated = 350° F.

Film properties: (26)

Thermal conductivity = $0.1 \frac{\text{BTU}}{(\text{hr.})(\text{sq.ft.})(^{\circ}\text{F/ft.})}$

Density = 50 lb./cu.ft.

Specific heat = $0.57 \frac{\text{BTU}}{(\text{lb.})(^{\circ}\text{F})}$

It is assumed that the transfer is approximated as unsteady state transfer from a plane to a semi-infinite solid. Transfer of energy from a plane will be approximated by the point at the center of the area of transfer and since damage to any point can be considered as beyond the limit of permissible phenomena, this may be used as a criterion for the film thickness.

The equations to be used are: (27)

$$Y = \frac{t' - t}{t' - t_0} = \frac{2}{\sqrt{\pi}} \int_0^z e^{-z^2} dz$$

$$z = \frac{x}{2\sqrt{\alpha\theta}}$$

$$Y = \frac{380 - 350}{380 - 70} = 0.0968$$

Referring to tables (28).

$$z = 0.086$$

$$x = (2)(12)(0.086) \sqrt{\frac{(0.1)(20)}{(3600)(50)(0.57)}}$$

$$= 0.061 \text{ inches}$$

NOMENCLATURE

α = ratio of thermal conductivity to the product of specific heat and density (sq.ft./hr.)

θ = time (hours)

x = distance of point from surface (ft.)

t' = surface temperature ($^{\circ}\text{F}$)

t_0 = initial temperature at distance x from surface ($^{\circ}\text{F}$)

t = instantaneous temperature at distance x from surface after time, ($^{\circ}\text{F}$)

Y and z = parameters

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Vita

Glenn Thompson Martin was born December 5, 1922 to James William and Viola (nee Thompson) Martin in McLain, Mississippi. He attended Mississippi Public Schools, graduating from McLain High School in 1940. For two years he attended Jones County Junior College in Ellisville, Mississippi, and after three years' service with the Army Air Force continued his education in 1945 at Mississippi State College, which institution granted him the Degree of Bachelor of Science in Chemical Engineering on January 12, 1948. Immediately thereafter he began graduate study at the University of Louisville. During his graduate study he received the assistance of a fellowship grant from the University of Louisville, Institute of Industrial Research. In December, 1948 he was granted the Degree of Master of Chemical Engineering.