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UNIVERSITY OF LOUISVILLE

ETHYLCELLULOSE LACQUER COATINGS FOR POLYSTYRENE PLASTICS
#

A Thesis

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

MASTER OF CHEMICAL ENGINEERING

Department of Chemical Engineering

Stuart V. Heil
///

December, 1946

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ETHYLCELLULOSE LACQUER COATINGS FOR POLYSTYRENE PLASTICS

Stuart V. Heil

Approved by the Examining Committee.

Director R. C. ErnstG. C. WilliamsW. R. Barnes

December, 1946

CONTENTS

	Page
List of Tables.	iv
List of Figures	iv
Acknowledgment.	v
Abstract.	vi
Introduction.	1
Historical.	3
Theoretical	8
Experimental.	23
Discussion.	67
Summary and Conclusions	70
Literature Cited.	72
Acknowledgment.	74
Vita.	75

LIST OF TABLES

	Page
I Formulations of Preliminary Solvent Mixtures	27
II Results of Resin Evaluation by Means of Trial Lacquers	30
III Evaluation of Resins by Means of Modified Lacquers	32
IV Hardness and Adhesion Tests on Films of Pure Resin	33
V Experimental Solids Compositions used in Plotting the Trilinear Diagram	35
VI Relative Evaporation Rates of Solvent Mixtures	40
VII Results on Lacquers Formulated by Means of Relative Evaporation Rates	41
VIII Effect of Additions of n-Butanol to Formulation A-38	43
IX Effect of Solvent Mixtures on Polystyrene.	46
X Results of Plasticizer Spot Tests.	50
XI Formulations of Experimental Lacquers.	51
XII Formulation of Thinners for Experimental Lacquers	56

LIST OF FIGURES

I Trilinear Diagram Showing Effect of Change in Composition on the Physical Properties of Lacquer.	37
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ABSTRACT

An ethylcellulose lacquer system for both decorative and protective purposes was developed for use on polystyrene plastics. It was found that a one-coat lacquer containing only alcohol solvents produced the most satisfactory finish.

Formulations were based on experimental work, conducted to determine the effect of the various lacquer components on the plastic. The results of a study of formulations on a two-coat system are presented.

INTRODUCTION

INTRODUCTION

During World War II volume production of styrene was begun because of its use in the manufacture of synthetic tires. Now that this outlet has been somewhat curtailed, other uses of styrene are desired. Styrene in polymerized form has been used for some time in the plastics field. Polystyrene combines a number of attractive properties, the most important being transparency, resistance to chemicals, excellent electrical properties, and high strength at low temperatures. It is available in a wide range of colors from crystal clear through all transparent shades to translucent and opaque.

It has been felt that the value of the plastic could be increased by the application of decorative coatings to the end products. This coating would not only increase the attractiveness of the products, but would also cover any slight molding imperfection which might be present.

The most desirable coating is one which may be applied by spraying, and which dries very rapidly. Therefore, it was thought that a lacquer would be most suitable.

It is known that polystyrene is soluble in almost all the organic solvents, with the exception of alcohols and petroleum derivatives. The active solvents are absorbed by the plastic in an unknown manner and result in a crazing effect which extends deeply into the material. The problem

of the solvents to be employed, therefore, is one of the more important ones. Because of the wide range of solubility of polystyrene, ethylcellulose was chosen as the cellulosic derivative. Thus, solvents with less rigorous action could be used. The regular requirements of a lacquer gloss, hardness, and durability must also be fulfilled.

The purpose of this investigation was to formulate a lacquer which met these specifications. The major portion of the work was of an experimental nature, and was divided into two parts: first, the formulation of a lacquer containing only alcohols as solvent and deriving the necessary adhesion from the resin; second, formulation of a lacquer which contained hydrocarbons and in which adhesion was obtained from solvent action or solvent bite. These two systems were explored, and the work was concluded when lacquers having hardness, adhesion, and gloss were obtained. Future work may reveal other systems which are equally satisfactory.

HISTORICAL

HISTORICAL

Ethylcellulose

Although cellulose has been known to exist for centuries, and the first practical uses of nitrocellulose were made in 1848 by Maynard (20) and Bigelow (4), ethylcellulose is a relatively recent discovery in the cellulosic derivatives. Suida (28) found that cotton fibre could be dyed more easily after a treatment of caustic and ethyl sulphate. This was the first idea of etherfication of cellulose, and took place in 1905. Following this, patents were obtained by Leuchs (14), Lilienfeld (15), Dreyfus (8), and a number of others. Of these, Lilienfeld's contribution is the most noteworthy. In 1912 he presented detailed studies of ethylcellulose and its properties and recognized its potential use in coatings, plastics, and rayon. Denham et al (6) showed that the ethers could be produced by the substitution of alkyl or aryl radicals in place of a hydroxyl hydrogen atom in the cellulose molecule. At this time, the preparation of the ether was definitely known, but the high cost of manufacture prevented the wide use which was indicated. During the next 25 years, were done large amounts of development work which is described only in the patent literature (29). During this period ethylcellulose was produced on a small scale in Germany. It was imported to this country for use in a few specialties where cost of raw mate-

rials was unimportant.

The industrial growth of ethylcellulose began in 1935, when American production methods and lower costs of raw materials combined to make it available in a price range at which its use was greatly stimulated. New uses developed rapidly, as domestic producers passed on the benefits of process improvements and increased volume production in the form of price reductions. Ethylcellulose is now a standard article of commerce whose range of utility is widening as formulators appreciate that its properties and versatility adapt it to the solution of a wide variety of protective coatings problems (18). The two main American producers of ethylcellulose are the Dow Chemical Company, Midland, Michigan, (7), and Hercules Powder Company, Wilmington, Delaware (11).

Polystyrene

Historically, polystyrene is not new. The styrene monomer was first isolated by the distillation of purified form of balsam known as storax, in 1831. In 1839, Simon (26), noted the thermo-polymerization of styrene in the presence of sunlight. Thirty years elapsed, during which many investigators made public their findings (9) in various journals. Then Berthelot (3), the French chemist, discovered the synthesis of styrene from ethylene and benzene by pyrolysis in a red-hot tube. Work of a theoretical nature continued until the first recorded patents disclosing the possible uses

of styrene were granted to F. E. Matthews (16, 17) of London in 1911. Dr. Matthews observed the excellent insulating properties of polymerized styrene and felt that it would be an improvement over the then known materials for electrical application (21).

Since then, 1911, the popularity of polystyrene for molding material has been increasing in Europe. Not until 1933 was American interest garnered, when domestic industry began a thorough investigation of the material (21). Only after several years of intensive work did it become possible, in 1927, for American companies to produce a material of high quality in commercial quantities at a price comparing favorably with that of other plastic materials. Today, polystyrene is produced in the United States by Catalin Corporation, New York, N.Y.; the Dow Chemical Company, Midland, Michigan; Bakelite Corporation, New York, N.Y.; and Monsanto Chemical Company, Springfield, Mass.

Lacquers

Attempts to prepare protective coatings are as old as man himself. The record of the oldest coating is found in the Book of Genesis. Archeological findings have shown that improvements in the art have followed very closely to the rise of the various civilized cultures. The first lacquer type of coating which appeared in China and Japan in the 13th Century B.C., consisted of tree saps and natural resins dissolved in simple solvents. This form was essentially unchanged,

until 1848 when Maynard (20) and Bigelow (4) used a solution of cellulose nitrate to form a coating. The term lacquer today denotes a coating which dries by evaporation rather than oxidation and further implies a coating which utilizes cellulosic derivatives for the film forming ingredient (19).

The greatest of the pioneers, Alexander Parkes (22), realized the advantages of nitrocellulose as a film forming material, but the available solvents proved to be a handicap to him. The evaporation rates of the known solvents were too great, and the films deposited were white, opaque, and of low tensile strength. Undaunted, Parkes continued his work, and in 1864 discovered the advantages offered by plasticization of the films. Nitrocellulose lacquers may be said to have originated in 1882 when Stevens (27) patented the use of amyl acetate as a solvent for nitrocellulose. This solvent, for the first time, permitted the deposition of a hard, lustrous, transparent film of cellulose with good durability. The high viscosity of the cellulose solution made it suitable only for specialties such as brass and silver lacquering and in the production of leather. The rise of this new industry created a vast demand for solvents with the result that new and vastly improved methods of fermenting grain were developed for their production. The developments proved it possible to produce enough amyl and butyl alcohol to satisfy the needs of the industry until the advent of synthesized butanol. The next advancement of significance

was the patenting of a process for reducing the viscosity of the nitrocellulose so that a practical amount of solids could be sprayed.

Varnishes were first replaced by lacquer in the automotive industry, when automobile finishers realized the advantages of cellulose coatings. Use of the lacquers enabled production schedules to be speeded up from two weeks for the old slow drying varnish to a few days. The lacquer finishes also had the added advantages of greater durability, ease of application, and resistance to gasoline and acids. Lacquers have contained this replacement of other types of finishes in many industries requiring protective coatings.

The use of cellulosic derivatives has been further developed by the discovery of many new plasticizers and synthetic resins, until it has become one of our major industries. It has established a permanent place for itself in the finishing industries.

Although, primarily, nitrocellulose has been used, new cellulose derivatives are being developed and are replacing this early derivative in various fields because of their more desirable properties. The most notable of these in the coatings work is ethylcellulose. Use and application is still in the experimental stage. The little information which is available may be found in the literature (1, 2), literature of the companies producing it (7, 11, 25, 5) and in experimental work published at various colleges (10, 12, 13, 23, 24, 30).

THEORETICAL

THEORETICAL

I Ethylcellulose

Chemically, ethylcellulose is an ether of cellulose and ethyl alcohol. It is manufactured from alpha cellulose, caustic soda, and ethyl chloride. Purified cellulose, whether from cotton linters or from wood pulp, is converted to alkali cellulose by treating it with concentrated caustic soda. The uniformity of treatment and the ratio of caustic soda and of water to cellulose are very closely controlled. Since these factors very largely determine the degree of ethylation and the uniformity of behavior of ethylcellulose in solvents. The alkali cellulose is reacted with ethyl chloride in autoclaves until the desired ethoxy content and solubility are obtained. The reaction mass is treated to recover unreacted ethyl chloride and solvent by-products. The ethylcellulose is precipitated with hot water as fine porous granules which are then washed free of salt and dried.

The reaction in the autoclave may be expressed by the type reaction

in which the cellulose radical is represented by R (11).

There is some doubt about the exact structure of the cellulose molecule. The most widely accepted theory of structure for the cellulose molecule is a chain of cellobiose units, each composed of two glucose residues, bound together

by oxygen linkages.

These long chains of oxygen linked cellobiose units have great strength which is passed on to its derivatives, such as ethylcellulose, nitrocellulose and cellulose acetate. The desirable properties of flexibility and toughness in these materials are directly attributable to this long chain structure.

From the formula given previously, it is seen that each glucose residue has three hydroxyl groups which are available, in toto or in part, or the reaction noted above. The triethyl compound possessing a substitution value of 3 or 54.88% ethoxyl content may be obtained from the complete substitution of all three replaceable hydroxyl groups. Diagrammatically this molecule may be given by

The completely substituted triethylcellulose has no commercial significance, however, because it lacks strength

and flexibility, is not thermoplastic, and shows extremely limited compatibility and solubility. The commercial product which exhibits the remarkable combination of useful properties, has a substitution value between 2.15 and 2.58 ethoxy groups per glucose unit, or 43.5% to 49.5% ethoxyl content.

The versatility of ethylcellulose in coatings, films, and plastics is increased because certain of its physical properties vary considerably with its ethoxy content. Ethylcelluloses having an ethoxy content of 47.5 to 50.0% are the ones principally used for general-purpose coating compositions because they have the greatest solubility in solvents and the widest compatibility with plasticizers, resins, waxes, and varnish oils.

Although ethylcellulose, as received from the manufacturer, appears as a white granular solid, the film of ethylcellulose deposited from a lacquer is practically colorless; therefore it is not affected by sunlight or ultraviolet light. Accurate color control can be obtained through the use of dyes and pigments.

Ethylcellulose has compatibility properties which compare very favorably with nitrocellulose. Ethylcellulose yields clear films with a wider variety of plasticizers and resins than other cellulose derivatives, including waxes and oils. This excellent compatibility of ethylcellulose is one of the prime factors in its suitability for use in lacquers.

The low density of ethylcellulose is important; con-

sequently ethylcellulose yields a greater volume of film forming solids per unit weight than any other commercial cellulose derivative. The coverage per unit weight amounts to 20% more area than cellulose acetate and about 45% more area than nitrocellulose, in coatings.

The ether does not discolor on exposure to strong sunlight nor does it promote the discoloration of resins or plasticizers. This characteristic makes it possible to prepare permanently white lacquers and plastic.

Ethylcellulose dissolves in a wider variety of solvents than any other cellulosic derivative. It is soluble in such low cost solvents as coal tar hydrocarbons, high aromatic content petroleum naphtha, and alcohols. Even the purely aliphatic naphthas are latent solvents, for higher ethoxy-content ethylcellulose, since it will dissolve in mixtures of these naphthas with relatively small proportions of alcohol.

The films prepared from ethylcellulose are highly flexible and retain their flexibility at temperatures well below freezing. Ethylcellulose imparts flexibility, toughness, and cold-check resistance to lacquer and varnish films. It is useful flexibilizing agent for nitrocellulose lacquers.

Ethylcellulose will melt when exposed to an open flame and when once ignited will support combustion. Because of its low flammability, ethylcellulose offers no greater fire hazard on storage or handling than does paper or cellulose

in the same physical form. The material may be rendered non-inflammable in coatings and plastics by the use of suitable plasticizers. It may be hot colloided and worked in a plastic condition without fear of spontaneous ignition or decomposition.

Other important physical properties of ethylcellulose are light stability; chemical resistance, which is superior to other cellulosic materials; water resistance; thermal stability; and toughness. All these properties combine to make ethylcellulose a raw material suitable for lacquer formulation.

Polystyrene

Chemically, styrene is prepared by the removal of hydrogen from ethyl benzene. The ethyl benzene is obtained, to some extent, from natural sources or from direct syntheses. A familiar process involves the use of ethyl chloride and benzene to form ethylbenzene, which is cracked to form styrene, as shown in the following reaction:

Styrene can then be polymerized through the action of heat, light or catalyst, or combinations of them. In general, the more rapid the rate of polymerization through the effect of heat or catalyst, the lower the molecular weight and viscosity of the resulting polymer. While all

investigators do not agree, it is felt that the polymerization of styrene is a chain reaction. There appears to be a small amount of cross linkage between chains, attributable to impurities. This is affected to some degree by the rate of polymerization. The rate of polymerization also affects the molecular distribution or the range of molecular weights within a given polymer. In general it has been found that molecular weights from 40,000 to 140,000 are more advantageous for injection molding while the lower molecular weights, that is, down to 35,000, appear more suitable for resin modifying and —coating applications.

Polystyrene is then, a long methylene chain substituted alternately by phenyl groups. This conception of the molecular structure is confirmed by measurements of light absorption and Ramn spectra of solutions which indicate an alkylbenzene structure for the polymer. The end valences may be satisfied by (1) migration of an H-atom from one end of the chain to the other, or from one chain to another:

(2) Combination with a catalyst A-B, or solvent molecules and impurities present:

or (3) cyclization, ring formation by the union of the two ends of the chain. The structure would then become a flattened ring or double chain:

The question of the nature of the end groups of the polystyrene chain is still undecided.

While polystyrene will accept plasticizers, there appears to be little gained through the use of these added agents at room temperature. Polystyrene can, however, be supplied in several ranges of flow. The various glow grades are not accomplished through plasticization but rather through a control of molecular weight and molecular distribution. These molecular weights can be controlled through polymerization as mentioned above and through controlled milling. The use of small amounts of lubricants to improve flow and to aid in ejecting molded pieces has been found advantageous for some complicated molding problems. Since polystyrene contains no plasticizer, there is no material to be removed on exposure; consequently the product exhibits dimensional stability.

Since polystyrene is a thermoplastic material, it is most conveniently and economically handled by the injection process. The maximum number of pieces from each pound of material may be obtained because polystyrene has the lowest specific gravity (1.07) of any of the commercial injection materials.

Polystyrene is a clear, crystal line thermoplastic with no odor or taste. Available colors range from crystal clear through all transparent shades to translucent and opaque.

The resistance of this material to water is phenomenal, the water absorption being so low as to be measurable only on the most sensitive equipment. Consequently, it is not affected by humid conditions or actual contact with water from the standpoint of moldability, color bleaching, or dimensional stability.

Polystyrene has a comparatively high modulus of elasticity and makes excellent rigid moldings. It has a high heat distortion point and exhibits practically no cold flow at room temperature, even under high loads. Electrically, polystyrene has the lowest power loss of any plastic material, in most forms being equivalent to fused quartz.

Chemically, polystyrene is generally unaffected by any inorganic solutions, such as salts, acids, or bases. It is insoluble in petroleum hydrocarbons, low aliphatic alcohols, glycol ethers, and some organic acid esters. It is sufficient-

ly soluble in coal tar hydrocarbons, chlorinated hydrocarbons, and the acetic esters of the lower aliphatic alcohols to make it of interest as a lacquer and coating modifying agent.

Some materials, whether active solvents or not, have a tendency to penetrate the plastic and cause crazing. This crazing, if deep enough, may cause the destruction of a molded piece.

Because of its attractive properties, polystyrene is used in radio insulators, electrical products, medicinal equipment, and novelties of many kinds.

Lacquers

Many types of coatings have appeared under the title of "Lacquer" (19), but the word today denotes a protective coating which contains a cellulosic derivative as the major film forming constituent. The other materials which are combined to make the finished lacquer are resin, pigment, plasticizer, solvent, and diluent. The first three of these, together with the cellulose, constitute the non-volatile portion of the lacquer. The solvent and diluent are known as the volatile ingredients. These components will be discussed in detail later. Lacquers are distinguished from oleoresinous finishes because they harden and form films primarily by the evaporation of the solvent present, rather than by polymerization and oxidation of the constituents. Lacquers present numerous advantages over the oleoresinous coatings for the following reasons: they dry by evaporation, a fast

process compared with the relatively slow process of oxidation which causes the air drying of oleoresinous finishes; more uniform products are obtained because of close chemical control; the manufacture and control are more of a chemical technical problem than the making of varnishes and paints; they have remarkable durability, water resistance, mar and abrasion resistance, hardness, color retention, chemical resistance, flexibility, and toughness. All these characteristics have combined to give lacquers the popularity they enjoy today.

Of the permanent, film-forming materials in the lacquer, the cellulose derivative actually gives the resultant film the properties most truly characteristic of a lacquer finish. By the addition of cellulosic materials the film is greatly improved with respect to rapid setting, resistance to heat, water, and chemical attack. Ethylcellulose will provide all these advantages, especially in regard to toughness and chemical resistance, as well as heat stability, flexibility, light stability and low flammability.

Resins are added to cellulose derivatives in an attempt to introduce some of the desirable properties of a varnish. They perform various functions, some of which are to increase adhesion, body, depth, gloss, luster, brilliance, durability, water resistance, and to increase the solids content of the lacquer without raising the cost or viscosity of the lacquer. The most suitable resins are those which are

soluble in the lacquer solvent mixtures and give a clear, transparent film, with a good, permanent gloss. Naturally, the resin must also be compatible with the cellulosic material. The resins are of three types; natural, semi-synthetic, and synthetic. The natural gums previously found the widest use because of their low cost. Typical of this class are damar and shellac. Of the semi-synthetic type, ester-gum, a glycerol ester of rosin acids, is probably the most widely used. The synthetic resins are the recently developed materials capable of producing lacquers that are far superior to those made from the natural gums. These new resins are chemical combinations of such compounds as glycerol, phthalic anhydride, and fatty acids; phenol and formaldehyde; urea and formaldehyde; and various other polymers.

Plasticizers serve to improve the lacquer film in numerous ways. Their main purpose is to improve the flexibility of the film thus increasing its durability under adverse conditions. The cellulose film without plasticizer has a decided tendency to shrink and pull away from the surface to which it is applied. A properly plasticized film will resist the severe variations of temperature when exposed to the elements, and will retain its elasticity indefinitely. To obtain certain desired results, however, it is necessary to gage properly the amount of plasticizer to be used when formulating a product since it is often advisable to limit the degree of elasticity. An increase in plasti-

cizer may cause a decrease in lacquer hardness and may even make the lacquer permanently tacky. Plasticizer may also be classified into three types: oils, true cellulose solvents (chemical plasticizers), and resins of liquid consistency. Castor oil is representative of the first class and, because of its nonoxidizing properties and low cost, is by far the most widely used. As the oils are generally considered to be dispersed throughout the film in minute globules, they are not so efficient in plasticizing effect as the chemical plasticizers. The second class consists of such compounds as di-butyl phthalate, tricresyl phosphate, and tri-phenyl phosphate. The chemical plasticizers have less tendency to sweat or spew out of the film under heat, have less odor, greater stability, and though usually more expensive than the oils, they are used in considerable volume. The third class has been developed recently and includes such compounds as methyl, ethyl, and benzyl abietate, some of the chlorinated diphenyls, toluol-sulphonamide-aldehyde resins, and many of the softer varieties of alkyd resins. Besides being practically non-volatile, plasticizers should be water-white in color, non-toxic, and free from residual odors. At the same time they should possess high solvent strength, low flammability, and chemical and light stability.

Pigments, or dyes, are incorporated in lacquers to give the desired color. Here is noticed a marked difference in the pigmentation of oleoresinous paints and enamels, and

lacquers. Whereas an average paint might contain six or eight pounds of pigments to a gallon, an attempt to use an equal amount in a lacquer formula would give a product of poor durability and no adhesion. The high volatile content of lacquers as compared with oleoresinous materials shows that there is less binder to hold the pigment particles together. Thus the pigments used in lacquers are somewhat different from those used in other types of finishing materials. In general, the pigments of greatest strength and hiding capacity and low oil absorption give the best results. Besides imparting color to lacquer pigments also serve to protect it for exterior use by preventing penetration of the actinic rays of sunlight, which cause rapid decomposition and disintegration of a clear film. Pigments of high opacity enable the production of automotive and other exterior lacquer enamels which surpass in durability the best exterior oleoresinous and synthetic paints and enamels.

Although none of the volatile portion of lacquer appears in the final film, it serves a very important function. The solvent-diluent portion of the lacquer puts the constituents in a workable liquid form so that it may be applied. The formulation of the solvent mixture is one of the most important parts of lacquer technology.

The true solvent portion of the volatile constituents must be divided into two parts: First, the cellulose solvent, and second, the resin solvent. In this work, only solvents

for ethylcellulose need be considered when dealing with the cellulose solvents. Because of its wide solubility, esters, ketones, ethers, aromatics and alcohols may be employed as ethylcellulose solvents. The best resin solvents and also those that can be used for practically any resin are the aromatics, namely benzol, xylol, and toluol. Most resins are rather widely soluble materials. The last portion of the volatile components are the diluents. In the main these materials are composed of petroleum naphthas, either in their natural state or after they have been hydrogenated. These diluents are added for economic reasons because of the high cost of the true solvents. The extent to which they can be used depends upon the tolerance of the cellulose derivative and resin solvents as well as the cellulose derivative and resin itself.

In general no one solvent possesses all the requirements necessary to make a satisfactory lacquer; a blend of several solvents is necessary. The ideal solvent should be a good solvent for both the cellulose and the resin in the lacquer. To secure a perfectly clear, homogeneous film and to minimize the tendency towards blushing, particularly in the faster-drying lacquer, the solvent should be preferably non-hygroscopic, and not miscible with water. The presence of higher boiling solvents, which evaporate more slowly from the film, will counteract the effect of such fast evaporating solvents which may of necessity be present in the formulation.

The odor of solvents or diluents is of importance because most lacquers are applied indoors, where the usual method of spray application may throw a large amount of vapor into the atmosphere in a short time. Solvents and diluents should be pale or water-white, particularly when used in clear lacquers, white, and delicate tint lacquer enamels. This color requirement is important not only in the original liquid state but also during storage in drums and metal containers. Any solvent which has a tendency to darken through oxidation or resinification during storage is deleterious to best results. Toxicity of solvents is another important consideration, particularly when the lacquer user may be exposed to considerable volume of the vapors.

EXPERIMENTAL

EXPERIMENTAL

Equipment

The equipment used throughout this work was of the type usually found in a paint laboratory. The units were all small. The major pieces used were the following:

- 1) Laboratory mixes - This piece consisted of three rollers mounted in a horizontal plane. The center roller was driven by a small electric motor, and the other rollers were driven by friction from the paint cans themselves. In use, a can of lacquer was placed on the equipment so that it was in contact with the center and one outside roller, imparting to the can a rotary motion which aided the solution of the lacquer components. By this means, the lacquers could be completely mixed in 10 hours.
- 2) Differential-speed Roller Mill - Here again three rolls were mounted in a horizontal plane. All three of the rolls were driven. The two outside rolls had an adjustment screw, by means of which the distance between these rolls and the center roll could be changed. Each roll was driven at a different speed, to increase the fluid shear between the rolls. The ratio of speeds was approximately 1:2.3:3. This device was used to incorporate pigment into the lacquer. The action of the mill was dispersive, and not one of size reduction. The use of this equipment made it possible to produce good gloss

in the finished product.

- 3) Spraying Equipment - The spraying equipment was of an ordinary type, made by the DeVilbiss Manufacturing Company.

PROCEDURE

Throughout this work, the formulation will be divided in two parts, 1) solids, constituents to be reported as percentage of total solids, and 2) solvents, constituents reported as percentage of total solvent. The amount of solvent mixture to be added to a given weight of solids will be reported. Thus, a typical formulation would appear as

Solids	Ethylcellulose	_____%
	Resin	_____%
	Plasticizer	_____%
		<hr/> 100%

Dissolve and cut to spraying viscosity (17% solids) with

Solvent	Solvent 1	_____%
	Solvent 2	_____%
	Solvent 3	_____%

The percentages in all formulations indicate percent by weight.

Before being tested all panels were aged by being air dried for 24 hours and by being heated for one hour in a convection oven at 70°C.

With the exception of several preliminary formulations, one solvent composition was used for both the lacquer and thinner. Two solvent formulations were used by previous lacquer investigators, one for lacquer makeup and one for spraying thinner. The use of two solvent mixtures leads to confusion as to the final solvent composition. When only one solvent formulation is used, the composition of the thinned lacquer is definitely known regardless of the dilution. Hence, the lacquer composition may be specified by giving the solids

composition and the solvent composition together with thinning instructions. Thinning instructions are completed by specification of either the final solids composition or the final viscosity.

Preliminary work on the problem, including literature studies, showed that alcohols, pure or in mixtures of other alcohols, had absolutely no effect on the polystyrene plastic. Other types of solvent materials, whether they actually dissolve the plastic or not, showed some tendency to craze the plastic surface. For this reason, the work was divided into two parts. The first of these was the development of a lacquer containing only alcohols. This type of lacquer must, by necessity, derive its adhesion from the adhesion of the resin present. The second part of the work was the formulation of a lacquer which contained any type of solvent. Here, the adhesion is obtained by solvent bite.

Part I: Alcohol Solvents

A solvent mixture was designed containing only alcohols. The materials for use in this formulation were those which gave low, medium, and high boiling components in the final mixture. As a result, ethyl alcohol, butyl alcohol, isopropyl alcohol, and Cellosolve were chosen to give the required boiling point range. In order to determine the best combination of these solvents, the proportion of the various components were varied and made into lacquers. The solids content of these lacquers was the same in all formulations

and was

Solids	Ethylcellulose Med. 10 cp	30%
	Super Beckacite 3000	60%
	Tricresyl phosphate	10%
		<hr/> 100%

This formulation was chosen on the basis of previous experience. Super Beckacite 3000 and Tricresyl phosphate were used because of their availability, and medium-ethoxy Ethylcellulose was used on the recommendation of the manufacturer. These solvent formulations appear in Table I.

Table I
Formulations of Preliminary
Solvent Mixtures

Number	A-1	A-2	A-3	A-4	A-5
Cellosolve ($C_2H_5OC_2H_4OH$)	30	50	40	20	25
Isopropyl Alcohol	15	10	12	20	10
Ethyl Alcohol	50	30	40	60	55
Butyl Alcohol	5	10	8	--	10

The resultant lacquers were examined for spraying and drying characteristics. Of the five, mixture A-4 gave the best results from both spraying and drying viewpoints. This mixture was then used in the following work.

The next phase of the work was the evaluation of different types of resins. It was desired to determine the hardness, adhesion, and gloss of the resins on a relative basis. For this work, a formulation was designed which made it possible to put the resins in a form which would allow

comparison. The formulation, as designed, was not intended to be final but merely to see the relative merits of the resins. The formulation was:

Solids	Med. 10 cp Ethylcellulose	26%
	Resin	60%
	Tricresyl phosphate	14%
		<hr/> 100%

made into lacquer of 20% solids with

Solvent	Ethyl Alcohol	60%
	Cellosolve	20%
	Isopropyl Alcohol	20%
		<hr/> 100%

The composition used here was based upon general lacquer practice. Medium-ethoxy Ethylcellulose was used upon the recommendation of the manufacturer. The Tricresyl phosphate is widely used in the lacquer industry and was used here because of availability.

The resins which were used for the trials were

- Zein A - A corn protein product suggested as a substitute for shellac prepared by Corn Products Co., New York, New York
- Pontianak - A manila type natural resin distributed by The American Gum Importers Inc.
- Nevillac Soft - A condensation product of phenol and coumarone-indene type unsaturates. Notable for its solubility. Produced by the Neville Co., Pittsburg, Penna.
- Nevillac Hard - A resin similar to Nevillac Soft, but slightly higher melting point. Also made by the Neville Co.
- Nevillac RT - Similar to other Nevillac Resins, but has slight modification. Another Neville Co. product.
- Nevillac RP - Another modification of the basic Nevillac Soft resin. Made by the Neville Co.
- Estergum 241 - A glycerol ester of rosin acids. This type, 241, is specifically soluble in alcohols. Produced by the Paramet Chemical Corp., Long Island City, New York

Super Beckacite 3000 - A hard, pure phenolic resin made by Reichhold Chemicals Inc., Detroit, Michigan
 Durez 550 - A soft, pure phenolic resin. A product of Durez Plastics and Chemicals Inc., North Tonawanda, N.Y.
 Shellac - A natural resin with very good solubility in alcohol
 Staybellite 742 - Hydrogenated rosin, prepared by the Hercules Powder Co., Wilmington, Delaware
 Amberol 750 - Fortified Rosin
 Amberol 226 - Modified phenolic. Both Amberols are made by Resinous Products and Chemical Co., New York, N.Y.

The lacquers made from these resins were sprayed on small pieces of plastic, and the film was examined for hardness and adhesion. The results appear in Table II. The results in Table II showed that two of the resins, Zein A and Shellac, were unusable because of lack of solubility in the solvent mixture. Several other resins, including Pontianak, Nevillac RT, Nevillac RP, Super Beckacite 3000, and the Amberols, were shown to have very low adhesive properties. Estergum, Staybelite, and Nevillacs Hard and Soft displayed qualities which led to consideration of their use.

The adhesion of the lacquer was checked by the standard knife-blade test. In this test the lacquer film is cut, by means of a knife, in a criss-cross manner with the cuts being spaced about 1 mm. apart. The ease of removal of the small cut squares gives an index of the adhesion. At the same time, any brittleness will be shown.

The film hardness was measured by the use of standard pencils. A set of regular drafting pencils with a hardness

Table II
Results of Resin Evaluation by
Means of Trial Lacquers

No.	Resin	Results
A-6	Zein A (xy-19)	Resin insoluble in solvent mixture employed
A-7	Pontianak 1472	No adhesion, brittle, poor surface 5H hardness
A-8	Nevillac Soft	Adhesion satisfactory, poor surface 5H hardness
A-9	Nevillac Hard	Adhesion excellent, poor surface 7H hardness
A-10	Nevillac RT	Low adhesion, brittle, poor surface, 4H hardness
A-11	Nevillac RP	Poor adhesion, poor surface, 4H hardness
A-12	Estergum #241	Adhesion satisfactory, poor surface 5H hardness
A-13	Super Beckacite 3000	No adhesion, brittle, poor surface 7H hardness
A-14	Durez 550	Adhesion satisfactory, surface satisfactory, 2H hardness
A-41	Shellac	Resin insoluble in solvent mixture
A-42	Staybelite 742	Adhesion satisfactory, surface good less than 2H hardness
A-43	Amberol 750	No adhesion, surface good, 7H hardness
A-44	Amberol 226	No adhesion, 3H hardness, surface good

range of F to 8H was used for this work. Pencils of varying hardness are drawn with moderate pressure, across the film at an angle of 45°. The hardness of the pencil which cuts the surface of the film is given as the pencil hardness of the film.

The results obtained from first trial lacquers were used to make modifications for possible improvement of the film.

These modifications together with the results appear in Table III. The solvent was that employed previously. Nevillac RP and Nevillac RT, in the modified lacquer, showed a continued lack of adhesion which ruled out the possibility of their use. Modifications of the other resins resulted in very soft coatings, with one exception. Additions of plasticizer to the lacquer containing Super Beckacite 3000 still produced a brittle film. As a further check on the resins, ethyl alcohol solutions were made of the resins, and these solutions were spread on tin panels. These flow-outs were then cured in an oven at 70°C for 2 hours; then they were examined for adhesion and hardness. The results for this work are given in Table IV. All the resins in a pure state exhibited brittleness. The major difference was found in the hardness. The resins were not considered for use unless the hardness of the pure material was above 5H.

Those resins which showed a total lack of adhesion were eliminated immediately. The others were all dropped from

Table III

Evaluation of Resins by Means of Modified Lacquers

No.	Resin	%Ethyl- Cellulose	%Resin	%Tricresyl phosphate	Modification	Results
A-28	Nevillac RP	11	75	14	Decreased ethylcellu- lose and increased resin	Adhesion poor, brittle 5H hardness
A-29	Estergum	15	75	10	Decreased ethylcellu- lose & plasticizer & increased resin	Adhesion fair, 4H hardness
A-30	Nevillac Soft	10	80	10	Decrease in plastici- zer & ethylcellulose. Increase in resin	Adhesion poor, slight brittleness, 4H hardness
A-31	Pontianak	36	50	14	Decrease in resin & increase in ethyl- cellulose	Adhesion poor, decreased hardness, 3H
	*Pontianak				Addition of plasti- cizer	No adhesion, decreased hardness, brittle
	*Nevillac RT				Addition of plasti- cizer	No adhesion, decreased hardness brittle
	*Nevillac RP				Addition of plasti- cizer	No adhesion, decreased hardness
	*Super Beck- acite 3000				Addition of plasti- cizer	Brittle, fair adhesion, 6H hardness

*Additions of plasticizer to preliminary lacquer

Table IV

Adhesion and Hardness
Tests on Films of Pure Resin

Resin	Results
Nevillac Soft	4H hardness, slight brittleness
Durez 550	3H hardness
Nevillac RP	3H hardness, some brittleness
Nevillac RT	Greater than 4H hardness, very brittle
Estergum #741	4-5H hardness, brittle
Super Beckacite 3000	Very brittle, hardness indeterminant
Nevillac Hard	7H hardness, brittleness
Pontianak 1472	6H hardness, high brittleness
Shellac	5H hardness, very brittle
Staybelite 742	5H hardness, slight brittleness
Amberol 750	7H hardness
Amberol 226	4H hardness, slightly brittle

consideration because of brittleness, softness, or a combination of the two. Further work with some of these resins may uncover methods of using them advantageously.

After selection of the resin to be used, Nevillac Hard, it was necessary to determine the proper solids composition; therefore a trilinear diagram was used. Regular triangular coordinate paper was employed, and the system Nevillac Hard Resin - Ethylcellulose - Tricresyl phosphate was investigated. Solids compositions were selected and lacquers made for testing purposes. These lacquers were sprayed and tested for gloss, hardness, and brittleness. After tabulation of the results, areas were marked on the diagram to indicate areas of satisfactory properties. The compositions selected for this work are found in Table V and the resultant diagram appears as Fig. I. The adhesion of the sample lacquers is not given on the diagram since all points tested gave satisfactory results. Examination of the diagram showed the most acceptable solids composition to be

Nevillac Hard Resin	75%
10 cp. Med. Ethylcellulose	20%
Tricresyl phosphate	5%

This formulation gave 5H hardness, excellent adhesion, good gloss, and no brittleness. In the succeeding work, this was the composition used.

After the first trial lacquers were prepared, the solvent formulation was changed at will, in order to obtain films which were suitable for test purposes. After defining

Table V

Experimental Compositions Used
In plotting the Trilinear Diagram

No.	Ethyl- Cellulose	Nevillac Hard	Tricresyl Phosphate	Results
A-17	26	60	14	Adhesion excellent, gloss good, 5-6H hardness
A-18	10	70	20	Adhesion indeterminant, gloss excellent, hardness indeterminant
A-19	15	70	15	Adhesion indeterminant, gloss excellent, 2H hardness
A-20	20	75	5	Adhesion excellent, gloss excellent, 5H hardness
A-21	25	65	10	Adhesion excellent, gloss good, 5H hardness
A-22	35	55	10	Adhesion excellent, gloss poor, 6H hardness
A-23	35	45	20	Adhesion excellent, gloss fair, 5H hardness
A-24	40	45	15	Adhesion excellent, gloss poor, 5-6H hardness
A-25	40	55	5	Adhesion excellent, gloss poor, 5-6H hardness
A-26	55	30	15	Adhesion excellent, gloss bad. 6H hardness
A-27	65	25	10	Adhesion excellent, gloss bad, 3-4H hardness
A-32	19	80	1	Too brittle for adhesion determination, 5-6H hardness
A-33	20	77	3	Slightly brittle, adhesion excellent, 5H hardness, good gloss

Table V (Con't.)

Experimental Compositions Used
In Plotting the Trilinear Diagram

No.	Ethyl- Cellulose	Nevillac Hard	Tricresyl Phosphate	Results
A-34	23	75	2	Brittle, adhesion excellent, 7H hardness, gloss good
A-35	28	70	2	Slightly brittle, adhesion excellent, 6H hardness, good gloss

Fig. 1

Trilinear Diagram Showing Effect of
Change in Composition on the Physical
Properties of Lacquer

the solids composition to be used, the proper solvent formulation was investigated. It had already been shown that the adhesion of the resin was satisfactory, and the solvent problem resolved itself into one of obtaining the desired spraying and drying characteristics. The majority of the solvent mixtures used this far had been very slow to aid the production of glossy films. During the tests made for the trilinear diagram, it was found that gloss improvement was to be obtained from proper solids formulation. This being the case, the drying rate of the lacquer could be increased without a decrease in gloss. The subsequent work was on this problem.

In the last stages of drying, the appearance of a separate solvent phase was observed. On the assumption that one of the solvents in the mixture was evaporating at a rate very much slower than the other components, tests were conducted to determine the miscibility of the components in all proportions. The solvents which had been used were n-Butanol, Ethanol, Isopropanol, Cellosolve, and Carbitol. These solvents were mixed in varying proportions, in which each material was allowed to predominate in the mixture. The mixtures were spread in a thin film on a porcelain plate, and a stream of air was blown over the surface. Observation of the samples was continued until completely evaporated. It was found that "puddles" similar to those previously noted were formed when Carbitol (Ethylene glycol monoethyl ether) and cellosolve (Diethylene glycol monoethyl ether) were present in excess;

therefore these two materials were eliminated from the solvent formulations. Ethanol, n-Butanol, and Isopropanol provided the range of evaporation rates necessary for producing a balanced solvent mixture, and hence, a solvent formulation was prepared from these materials. In order to eliminate the preparation of a large number of lacquers for testing solvent mixtures, the relative evaporation rates of several mixtures of solvents were determined. For this work, mixtures were prepared of the three components, ethanol, butanol, and isopropanol. Ten gram samples of these mixtures were then weighed into vessels of equal surface area (petrie dishes). The loss in weight, due to evaporation, was then recorded at intervals of 1 hour, 2 hours, 3 hours, and 5 hours. An integrated evaporation rate was then computed. After being graded in order of decreasing evaporation rate, the solvents were recorded as in Table VI and the results used for formulation. One trial lacquer was prepared and the drying characteristics observed. The solvent formulation was then changed, (faster, slower, etc.) as required by means of the relative evaporation rates. By this method, five lacquers were formulated as shown in Table VII. From these formulations, it was found that it was impossible to predict accurately the behavior of a lacquer by means of the relative evaporation rates of solvent mixtures. It appears that the evaporation of the solvent is influenced to a great extent by the presence of other lacquer constituents. Hence,

Table VI

Relative Evaporation Rates of Solvent Mixtures

No.	%Ethyl Alcohol	%Butyl Alcohol	%Isopropyl Alcohol	Overall Evaporation Rate GM/MIN
1	60	--	40	2.00
2	20	--	80	1.996
3	--	--	100	1.996
4	80	--	20	1.99
5	50	--	50	1.96
6	100	--	--	1.898
7	20	20	60	1.866
8	60	20	20	1.826
9	80	20	--	1.802
10	20	40	40	1.594
11	10	30	60	1.522
12	40	30	30	1.518
13	60	30	10	1.482
14	40	20	40	1.392
15	40	40	20	1.35
16	20	60	20	1.218
17	50	50	--	1.166
18	--	50	50	1.104
19	20	80	--	0.914
20	--	100	--	0.454

Table VII

Results on Lacquers Formulated by Means of
Relative Evaporation Rates

No.	%Ethyl Alcohol	%Butyl Alcohol	%Isopropyl Alcohol	Results
A-36	60	20	20	Pinholes
A-37	60	--	40	Pinholes
A-38	40	20	40	O.K., slight surface roughness
A-39	20	20	60	Gassy, pinholes
A-40	20	60	20	Slight pinholing

the work was continued by trial and error methods.

Lacquer A-38 showed very good characteristics in every respect with the exception of the final surface. Although the final surface was glossy, the surface itself contained minute irregularities. Trial and error methods showed that additions of Butanol corrected this condition considerably. Hence, trial lacquers were prepared, using the same solids formulation, but increasing the amount of Butanol. The results are recorded in Table VIII. It was noted that additions of Butanol above 40% did not have any effect on the condition of the surface. Formulation A-48 was then selected for further work. This lacquer was satisfactory from a coating point of view, but it was felt that it was not economical. At this point, the investigation was combined with the work on hydrocarbon solvents, Part 2, and reappears in Part 3.

Part 2: Hydrocarbon Solvents

It was known that polystyrene is soluble in all organic solvents with the exception of alcohols and petroleum derivatives. It was also known that many solvents, whether active solvents for polystyrene or not, crazed the plastic. For this reason, the preliminary work involved a survey of the solvent field to determine the effect of different types of solvent on the polystyrene surface. This examination was conducted with three points in mind. Solubility, crazing, and the condition of the surface of the

Table VIII

Effect of Additions of n-Butanol to Formulation A-38

No.	%Ethyl Alcohol	%Butyl Alcohol	%Isopropyl Alcohol	Results
A-45	37.5	25	37.5	Improved surface Better than A-38
A-46	35.0	30	35.0	Improved surface Better than A-45
A-47	32.5	35	32.5	Improved surface Better than A-46
A-48	30.0	40	30.0	Improved surface Acceptable. Better than A-47
A-49	27.5	45	27.5	No improvement

plastic were to be noted.

Crazing is a physical phenomenon which occurs in some plastic material as a result of interaction with solvent materials. The exact mechanism of this effect is unknown, but the results are well known. The effect is evidenced in several ways. The plastic surface is attacked in a manner which renders it opaque, because of the diffusion of light by the minute cracks in the surface of the plastic. A second effect is a decided roughening of the plastic surface. The third effect and probably the least desirable is the formation of deep cracks throughout the body of the plastic. This resembles the failure of "Safety Glass" in that the visible evidence is a network of cracks which gives a scintillating or opalescent appearance to the plastic shape. The physical appearance is not necessarily undesirable, but the condition indicates a weakening of the plastic. Under extreme conditions in fabricated forms, crazing may result in the spontaneous destruction of the item. The condition of the surface which was to be investigated was that due to solubility. Thus, when polystyrene is dissolved and the solvent allowed to evaporate, the re-deposited polystyrene does not possess the smooth finish of the original plastic. The solubility to be noted is in no need of explanation.

The solvent tests were carried out on small pieces of plastic which were cut from larger molded disks. These

small pieces were then spot tested. A small amount of solvent was evenly spread on the surface. Examination was then made for solvency and crazing. After observation of the immediate effects, the panels were allowed to stand until dry and were then re-examined. In no case was there any difference between the immediate and prolonged effects. Thus, if the solvent crazed the plastic at all, it did so immediately after application. When tests of mixtures were to be made, a drop of one solvent was placed on the panel. Small amounts of a second solvent were then added to the original drop until the solvent mixture was predominantly composed of the second solvent. At each addition, the solvents were thoroughly mixed. By means of this method, the effects of various solvent proportions could be observed. In recording the results, the general or overall effect was reported. During the tests, the comparative results were based upon rapidity of action, viscosity of resulting solution, and depth of solvent action. For the crazing effect, rapidity of action was again taken into consideration, as was the degree of opacity imparted. In Table IX the results are presented. In every case, the crazing effect is noted, while the solvency and surface effects are recorded only when they are different from those of the pure solvents.

A study was also made of the effect of plasticizers upon polystyrene plastic. The method originally used was the application of small amounts of plasticizer to the plastic

Table IX

Effect of Solvent Combinations for Plastic

Solvents	Acetone	Solvesso #1	Carbon Tetrachloride	Tolusol	Ethanol	Butanol
Acetone	sl. sol. high cr.	no cr. high sol. heavy S.E.	no cr. high sol. sl. S.E.	high cr.	no effect	sl. cr.
Solvesso #1	high sol. no cr. heavy S.E.	sl. sol. sl. cr.	no	no cr.	bad cr.	bad cr.
Carbon Tetrachloride	no cr. high sol. light S.E.	no cr.	sl. sol.	no cr.	sl. cr.	def. cr.
Tolusol	high cr.	no cr.	no cr.		no cr.	no cr.
Ethanol	no effect	bad cr.	sl. cr.	no cr.	no effect	no effect
Butanol	sl. cr.	bad cr.	def. cr.	no cr.	no effect	no effect
Mineral Spirits	high cr.	sl. cr.	sl. cr.	immisc.	no effect	sl. cr.
Shell TS-28	high cr.	no effect	no cr.	no cr.	no cr. high sol.	some cr.
Xylene	no cr. high sol.	no cr. sl. sol.	no cr.	no cr.	sl. cr.	some cr.
VM&P Naptha	high cr.	no cr.	some cr.	sl. cr.	no cr.	some cr.
Toluene	no cr. high S.E.	no cr.	no cr.	no cr.	sl. cr.	crazing
Troluoil	high cr.	no cr.	no cr.	no cr.	no cr.	crazing
Ethyl Acetate	much cr.	no cr.	no cr.	no cr. high S.E.	sl. cr.	crazing
Alkazene #13	no cr. no S.E. sl. sol.	no cr.	no cr.	no cr.	no cr.	no effect
Isopropyl Benzene	no cr. sl. S.E. sl. sol.	no cr.	no cr.	no cr.	no cr.	no effect
Tetralin	no cr. heavy S.E. high sol.	no cr.	no cr.	sl. cr.	sl. cr.	crazing

Table IX (Con't.)

Effect of Solvent Combinations for Plastic

Solvents	Mineral Spirits	Shell TS-28	Xylene	V.M.&P. Naptha	Toluene	Troluoil
Acetone	high cr.	high cr.	no cr. high sol.	high cr.	no cr. heavy S.E.	high cr.
Solvesso #1	sl. cr.	no effect	no cr. sl. sol.	no cr.	no cr.	no cr.
Carbon Tetrachloride	sl. cr.	no cr.	no cr.	some cr.	no cr.	no cr.
Tolusol	immisc.	no cr.	no cr.	sl. cr.	no cr.	no cr.
Ethanol	no effect	no cr. high sol.	sl. cr.	no cr.	sl. cr.	no cr.
Butanol	sl. cr.	crazing	crazing	crazing	crazing	crazing
Mineral Spirits	no effect	crazing	no cr.	no cr.	no cr.	sl. cr.
Shell TS-28	crazing	sl. sol.	no cr.	bad cr.	no cr.	crazing
Xylene	no cr.	no cr.	good sol.	no cr.	no cr.	no cr.
VM&P Naptha	no cr.	bad cr.	no cr.	no sol. bad cr.	no cr.	crazing
Toluene	no cr.	no cr.	no cr.	no cr.	high sol.	crazing
Troluoil	sl. cr.	some cr.	no cr.	some cr.	crazing	sl. sol. high cr.
Ethyl Acetate	crazing	some cr.	no cr.	sl. cr.	no cr.	v.sl.cr.
Alkazene #13	no effect	no effect	no effect	no effect	v.sl.cr.	no cr.
Isopropyl	no effect	no effect	no effect	no cr.	no effect	no cr.
Tetralin	no cr.	no cr.	no cr.	no cr.	no cr.	no cr.
Decalin	no cr.	no effect	no effect	sl. cr.	no cr.	some cr.

Table IX (Con't.)

Effect of Solvent Combinations for Plastic

Solvents	Ethyl Acetate	Alkazene #13	Isopropyl Benzene	Tetralin	Decalin
Acetone	high cr.	no cr. no S.E. sl. sol.	no cr.	no cr.	high cr.
Solvesso #1	no cr.	no cr.	no cr.	no cr.	no cr.
Carbon Tetrachloride	no cr.	no cr.	no cr.	no cr.	no cr.
Tolusol	no cr. high S.E.	no cr.	no cr.	no cr.	no cr.
Ethanol	sl. cr.	no cr.	no cr.	sl. cr.	no cr.
Butanol	crazing	no effect	no effect	crazing	crazing
Mineral Spirits	crazing	no effect	no effect	no cr.	no cr.
Shell TS-28	some cr.	no effect	no effect	no cr.	no effect
Xylene	no cr.	no effect	no effect	no cr.	no effect
VM&P Naptha	sl. cr.	no effect	no effect	no cr.	sl. cr.
Toluene	no cr.	v.sl.cr.	no effect	no cr.	no cr.
Troluoil	v.sl.cr.	no cr.	no cr.	no cr.	some cr.
Ethyl Acetate		no cr.	no cr.	no cr.	no cr.
Alkazene #13	no cr.	no effect	no effect	no effect	no effect
Isopropyl Benzene	no cr.	no effect	high sol.	no effect	no effect
Tetralin	no cr.	no effect	no effect	sl. sol.	no effect
Decalin	no cr.	no effect	no effect	no effect	v.sl.sol.

Note: sl., slight; immisc., immiscible; def., definite; cr., crazing; sol., solvency; S.E., surface effect.
 Ratings in order of increasing effect: 1), definite; 2), very slight; 3) slight; 4) some; 5) much; 6) high; 7) bad.

surface and then observation of the results. It was found that the nature of the plasticizing materials obscured any effects present. To eliminate this difficulty, solutions of the various plasticizers were made, using n-Butanol. These solutions were then used for spot tests as before. After the tests, during which the immediate results were observed, the residual material was wiped from the panel, and the surface beneath was examined. For a representative group of plasticizers the results showed that the materials have no effect upon the panel. Pertinent data about these tests appear in Table X.

Formulation was then begun. The method applied to this work was largely trial and error. A formulation was prepared, and then changes were made as necessary. In several cases it was found necessary to back-track since some of the results were misinterpreted. During the course of investigation various ideas presented themselves, and these were investigated until their value was proved or disproved. All the formulations prepared for this part of the work appear in Table XI. Those formulations which appear in the table, but which are not discussed in the body of the thesis, were required to complete the data, but did not add enough to the investigation to warrant discussion.

As a starting point, a lacquer formulation was selected for application in order to observe the exact behavior of the panel when coated. The formulation contained

Table X

Plasticizer Spot Tests

<u>Plasticizer</u>	<u>Application and Results</u>
Dow P-6	Solution ineffective; no effect
Butyl Sterate	Solution not necessary; no effect
Tricresyl phosphate	Solution not necessary; no effect
Chlorinated Diphenyl	Cut in butanol; no effect
Castor oil	Used alcohol solution; no effect
Aroplas 930	Used butanol solution; no effect

Table XI
Formulation of Experimental Lacquers

Number	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9
Cellulose									
10cp Std. Ethylcellulose	26	26	26	30	30	30	26	30	30
10cp Med. Ethylcellulose	--	--	--	--	--	--	--	--	--
Plasticizer									
Tricresyl Phosphate	14	14	14	14	10	10	14	6	--
Resin									
Super Beckacite 3000	--	--	--	--	--	--	--	--	--
Super Beckacite 2100	--	--	--	--	--	--	--	--	--
Durez 550	--	--	--	--	60	60	60	--	70
Durez 570	--	60	60	60	--	--	--	--	--
Nevillac Hard	--	--	--	--	--	--	--	--	--
Bakelite RP 254	60	--	--	--	--	--	--	--	--
Teglac 152	--	--	--	--	--	--	--	64	--
Lewisol 305	--	--	--	--	--	--	--	--	--
Solvents									
Ethyl alcohol	--	--	60	70	--	--	--	60	60
n-Butyl alcohol	12	12	--	--	--	--	--	--	--
Mineral Spirits	56	56	35	--	--	--	35	35	35
VM&P Naptha	--	--	--	30	50	50	--	--	--
Toluene	--	--	5	--	--	--	65	5	5
Xylene	--	--	--	--	50	--	--	--	--
1-Nitropropane	--	--	--	--	--	--	--	--	--
Shell TS-28	32	32	--	--	--	50	--	--	--

Table XI (Con't.)

Formulation of Experimental Lacquers

Number	S-10	S-11	S-12	S-13	S-14	S-15	S-16	S-17	S-18
Cellulose									
10cp. Std. Ethylcellulose	30	30	30	30	--	--	--	--	--
10cp. Med. Ethylcellulose	--	--	--	--	30	30	30	--	26
Plasticizer									
Tricresyl Phosphate	--	6	6	6	6	14	14	--	14
Resin									
Super Beckacite 3000	70	--	--	--	64	54	54	--	60
Super Beckacite 2100	--	--	--	64	--	--	--	--	--
Durez 550	--	--	--	--	--	--	--	--	--
Durez 570	--	--	--	--	--	--	--	--	--
Nevillac Hard	--	--	--	--	--	--	--	--	--
Bakelite BR 254	--	--	--	--	--	--	--	--	--
Teglac 152	--	--	--	--	--	--	--	--	--
Lewisol 305	--	64	64	--	--	--	--	--	--
Solvents									
Ethyl alcohol	60	60	60	50	46.8	46.8	46.8	--	40
n-Butyl alcohol	--	--	5	15	--	15	15	--	5
Mineral Spirits	35	35	30	28	23.2	18.2	8.2	--	40
VM&P Naptha	--	--	--	--	--	--	--	--	--
Toluene	5	5	5	5	15	20	30	--	15
Xylene	--	--	--	--	--	--	--	--	--
1-Nitropropane	--	--	--	--	--	--	--	--	--
Shell TS-28	--	--	--	--	--	--	--	--	--

Table XI (Con't.)

Formulation of Experimental Lacquers

Number	S-19	S-20	S-21	S-22	S-23	S-24	S-25	S-26
Cellulose								
10cp. Std. Ethylcellulose	--	--	--	--	--	--	--	--
10cp. Med. Ethylcellulose	26	26	26	20	20	16	24	26
Plasticizer								
Tricresyl Phosphate	14	14	14	20	24	24	20	14
Resin								
Super Beckacite 3000	30	15	9	60	56	60	56	60
Super Beckacite 2100	--	--	--	--	--	--	--	--
Durez 550	30	45	51	--	--	--	--	--
Durez 570	--	--	--	--	--	--	--	--
Nevillac Hard	--	--	--	--	--	--	--	--
Bakelite BR 254	--	--	--	--	--	--	--	--
Teglac 152	--	--	--	--	--	--	--	--
Lewisol 305	--	--	--	--	--	--	--	--
Solvents								
Ethyl alcohol	40	40	40	51.4	45	45	45	40
n-Butyl alcohol	5	5	5	12.8	16	16	16	10
Mineral Spirits	40	40	40	--	--	--	--	35
VM&P Naptha	--	--	--	--	--	--	--	--
Toluene	15	15	15	19	19	19	19	15
Xylene	--	--	--	--	--	--	--	--
1-Nitropropane	--	--	--	16.8	20	20	20	--
Shell TS-28	--	--	--	--	--	--	--	--

Table XI (Con't.)

Formulation of Experimental Lacquers

Number	S-27	S-28	S-29	S-30	S-31	S-32	S-33	S-34	S-35
Cellulose									
10cp. Med. Ethylcellulose	26	26	26	26	26	26	26	26	26
Plasticizer									
Tricresyl Phosphate	--	--	--	--	--	--	--	--	--
Diocetyl Phosphate	14	--	--	--	--	--	--	--	--
Chlorinated Diphenyl	--	14	--	--	--	--	--	--	--
Gum Elemi	--	--	14	--	--	--	--	--	--
Caster Oil	--	--	--	14	--	--	--	--	--
Butyl Stearate	--	--	--	--	14	--	--	--	--
Dibutyl Phthalate	--	--	--	--	--	14	--	--	--
Dow P-6	--	--	--	--	--	--	14	--	--
Methyl Cellosolve Stearate	--	--	--	--	--	--	--	14	--
Nevillac 100	--	--	--	--	--	--	--	--	14
Resin									
Super Beckacite 3000	60	60	60	60	60	60	60	60	60
Solvents									
Ethyl alcohol	40	40	40	40	40	40	40	40	40
n-Butyl alcohol	10	10	10	10	10	10	10	10	10
Mineral Spirits	35	35	35	35	35	35	35	35	35
Toluene	15	15	15	15	15	15	15	15	15
VM&P Naptha	--	--	--	--	--	--	--	--	--
Xylene	--	--	--	--	--	--	--	--	--
1-Nitropropane	--	--	--	--	--	--	--	--	--
Shell TS-28	--	--	--	--	--	--	--	--	--

Table XI (Con't.)

Formulation of Experimental Lacquers

Number	S-46	S-47	S-48
Cellulose			
10cp. Std. Ethylcellulose	--	--	--
10cp. Med. Ethylcellulose	20	20	20
Plasticizer			
Tricresyl Phosphate	5	5	5
Resin			
Super Beckacite 3000	--	--	--
Super Beckacite 2100	--	--	--
Durez 550	--	--	--
Durez 570	--	--	--
Nevillac Hard	75	75	75
Bakelite BR 254	--	--	--
Teglac 152	--	--	--
Lewisol 305	--	--	--
Solvents			
Ethyl alcohol	40	50	51.4
n-Butyl alcohol	10	20	12.8
Mineral Spirits	40	20	--
VM&P Naptha	--	--	--
Toluene	10	10	19
Xylene	--	--	--
1-Nitropropane	--	--	16.8
Shell TS-28	--	--	--

Table XII

Formulation of Thinners for Experimental Lacquer

Number	S-1	S-2	S-3	S-4	S-5--S-48
Ethyl alcohol	--	--	40	50	
Butyl alcohol	35	35	--	--	Thinner of
Mineral spirits	15	15	40	--	same composi-
Shell TS-28	50	50	--	--	tion as that used
VM&P Naptha	--	--	--	50	in preparing the
Toluene	--	--	20	--	lacquer

50% solids composed of

10 cp. Std. Ethylcellulose	26%
Resin	60%
Plasticizer	14%

These solids were then used in a completed formulation which contained the following:

Solids	10 cp. Std. Ethylcellulose	26%
	Resin	60%
	Plasticizer	14%

and solvent to make 50% solids

n-Butanol	12%
Mineral spirits	56%
Shell TS-28	32%

In the first formulations, S-1, the resin used was Bakelite BR-254, and the plasticizer was Tricresyl phosphate. After a short mixing period, an incompatibility was noted. A second lacquer, S-2, was prepared using Durez 550 resin and Tricresyl phosphate plasticizer. The proportion and other ingredients were unchanged. When S-2 was completely mixed, it was so very viscous that an additional amount of solvent was added. This addition consisted of 50 gm. of solvent, containing the same material and proportions that were used in making up the original lacquer. Thus the final lacquer contained 33 1/3% solids. For application purposes the lacquer was cut 1:1 with

n-Butanol	35%
Shell TS-28	50%
Mineral spirits	15%

The finished panel was unsatisfactory because of bad crazing, but showed the lines along which the investigation was to

continue. A new lacquer, S-3, was formulated using ethanol, mineral spirits, and toluene. The toluene was to serve the double purposes of giving bite and of making the ethanol and mineral spirits mutually soluble. The new solvent line-up was then

Ethanol	60%
Mineral spirits	35%
Toluene	5%

When this solvent was incorporated in the complete formulation, the results were

Solids	10 cp. Std. Ethylcellulose	26%
	Resin	60%
	Plasticizer	14%
		<u>100%</u>

prepared with 50% solids

Solvent	Ethanol	60%
	Mineral spirits	35%
	Toluene	5%
		<u>100%</u>

For the resin and plasticizer, Durez 550 and Tricresyl phosphate were used again, respectively. The resulting lacquer, in itself, had the proper appearance. This was then cut 2:1 with solvent prepared by mixing

Ethanol	40%
Mineral spirits	40%
Toluene	20%

When the thinned lacquer was sprayed, the panel crazed immediately. In order to determine the effect of the thinner some of S-3 was cut with pure ethanol. The crazing showed definite improvement, but air bubbles were trapped in the lacquer surface because of the rapidity of evaporation. The

surface appearance of this lacquer was good.

A review of the work, and further examination of the panels prepared this far, showed several points for consideration. The crazing which had been caused by the effect of mixing ethanol and toluene, could easily be eliminated by reworking the solvent line-up. At the same time, examination showed that the films were very soft. Because of this softness, it was difficult to obtain any index of the adhesion. At best, adhesion was only fair. At this time these facts would seem to call for a lower plasticizer content and a higher proportion of polystyrene solvent.

To include these points, a new formulation, S-4, was proposed. The solids were

10 cp. Std. Ethylcellulose	30%
Resin	60%
Plasticizer	10%

and the solvent consisted of

Ethanol	70%
VM&P Naptha	30%

producing a lacquer of 50% solids. In order to be able to relate this lacquer with those prepared previously, Durez 550 and Tricresyl phosphate were again employed. For spraying purposes, the lacquer was to be thinned 2:1 with

Ethanol	50%
VM&P Naptha	50%

When this thinner mixture was made, an immiscibility was found, which made it unsuitable for the work. This gave a hint of a difficulty which might be found in the lacquer

itself. In order to check this condition some of the lacquer, in its thick state, was spread on a piece of plastic. When it had dried, the surface was found to be good, but the film contained many bubbles. In addition, the film had no effect on the panel, was soft, and had no adhesion. Two of the difficulties noted in the formulation were eliminated by thinning the lacquer with VM&P Naptha alone, producing a lacquer with slower drying characteristics, and resulting in the prevention of the formation of bubbles in the film. With this formulation, suitable coatings could be prepared if the adhesion were improved. Because of its inertness with regard to the panel, it seemed to be suited for investigation of surface treatment of the panel before coating.

The idea behind this investigation was that the panel could be treated by a thin coating of some material which would attack the surface. This attack would roughen the surface slightly, whereupon a coating, inert with respect to the panel, might be applied. The slight roughness imparted by the first treatment would give the necessary adhesion to the final film. To carry out this surface treatment, small amounts of various solvents were sprayed on the panels by means of an atomizer. These treated panels were then coated and examined for adhesion. All the more common solvents were tried for this purpose, but none was satisfactory. The desired result could be achieved only with difficulty. This line of attack was abandoned because of the close control required

in the treatment made it commercially unfeasible.

Returning to systems of active polystyrene solvent in the lacquer, solvent mixtures with a minimum surface effect were investigated, by using aromatics in conjunction with naphthas, aromatic naphthas and some of the less well known solvents. The surface effects of the mixtures were tested by preparing the solvent mixture and spraying it, by means of a medicinal atomizer, on a small portion of plastic panel. When a suitable mixture appeared, it was incorporated in a lacquer and tested by application. As a starting point, toluene mixtures were selected for investigation. Toluene was used with various other materials, as pointed out above, but in every case the surface effect was very bad. The second investigation involved xylene with similar results. The surface effect was decreased somewhat, and the overall effect made the system seem suitable for formulation.

A lacquer was then prepared using this solvent. S-5 was made with xylene and VM&P Naptha. In order to keep the results on a comparative basis, Durez 550 and Tricresyl phosphate were again used in the solids. This gave a lacquer of the following composition

in	Solids 50%	10 cp. Std. Ethylcellulose	30%
		Durez 550	60%
		Tricresyl phosphate	10%
			<hr/> 100%
	Solvent	Xylene	50%
		VM&P Naptha	50%
			<hr/> 100%

This mixture was thinned as required with solvent of the same composition as the make-up. The coating resulting from this formulation was unsatisfactory. Other systems were tried, including Solvesso #1, Lacquer diluent, diethyl benzene, ethyl acetate and acetone. These materials were used in mixtures with various naphthas. By comparison with the action of xylene and VM&P Naptha, it was seen that none of these systems would be satisfactory. This work was then discontinued.

Of the formulations which had been prepared so far, only one, S-3, had shown any real promise. This formulation gave a smooth film with minimum attack on the plastic base. This formulation was used for further study. The lacquer was thinned with mixtures of the make-up solvents in varying proportions. It was found that the thinning solvent could be changed within wide limits, as long as the amount of toluene did not become too high (less than 10% of the thinning solvent). Thus the drying and spraying characteristics of the lacquer could be varied to satisfy almost any condition. The finished coats produced by S-3 were smooth, but very soft and somewhat tacky. In order to eliminate these two difficulties, a change was indicated in both resin and plasticizer. For the change in plasticizer, S-3 was made in the original manner, but the plasticizer was omitted entirely in the solids formulation. For the change in resin, a hard phenolic, Super Beckacite 3000, was substituted for Durez 550 which is soft and tacky. These formulations were numbered S-9 and S-10 and appear in Table XI.

These formulations were thinned to spraying viscosity with a solvent mixture of the same composition as the make-up solvent. S-9 gave a coating which was harder than that of S-3, but the surface was still tacky. S-10 showed a considerable improvement over S-3, and was both hard and tack-free.

S-10 was then used as the starting point for another series of investigations. The finished coating, though having several desirable properties, needed some modifications for better spraying characteristics. It was also desired to substitute medium ethoxy ethylcellulose for the standard. The first modification was number S-14. In addition to the above modification, tricresyl phosphate was added to compensate for the loss in flexibility caused by the change in ethylcellulose. The S-14 formulation was

Solid	10 cp. Med. Ethylcellulose	30%
	Tricresyl phosphate	6%
	Super Beckacite 3000	64%
		<hr/> 100%

These solids were dissolved in the following solvent mixture until the desired viscosity was obtained.

Ethyl alcohol	46.8%
Mineral spirits	23.2%
Toluene	15 %
n-Butyl alcohol	15 %
	<hr/> 100 %

The finished lacquer sprayed easily and gave a smooth, hard coating, but the flexibility and adhesion were unsatisfactory. The solids content of this lacquer was modified as was the solvent contained. This work was done in formulation S-15-S-17.

There resulted formulation S-18

Med. 10 Cp. Ethylcellulose	26%
Durez 550	60%
Tricresyl phosphate	14%

and 50% solids in

Ethyl alcohol	40%
Mineral spirits	37%
Toluene	15%
Butyl alcohol	8%

After drying for 1 hour at 70°C, this lacquer had a hard, adhesive coating. The hardness was almost 5H. Slight crazing appeared during the drying period. Formulations S-19 - S-25 were prepared in an effort to eliminate this defect, but the results were unsuccessful. The mineral spirits content of S-18 was decreased. At the same time, adhesion was lost. Thus, it was seen that the adhesion in this formulation was derived from the action of the mineral spirits on the surface of the plastic. An attempt was made to substitute some material with less rigorous action for the mineral spirits. The best results were obtained using 1-nitropropane. Some improvement was noticed, but the results were still unsatisfactory.

In order to determine the effect of plasticizer on this formulation, lacquers S-26 - S-36 were prepared, and it was found that Tricresyl phosphate gave the most satisfactory results. At this point the experimental work was combined with the alcohol solvent work, Part 1, and reappears in Part 3.

Part 3: Combined Solvents

Up to this point, only one formulation, S-48, was considered as a solution to the problem. This formulation was satisfactory from a coating point of view, but it was felt that the composition was not economical; therefore, an investigation was carried out to find a solvent with which butanol might be replaced wholly or in part. Because of the presence of the butanol in the lacquer, no substitute was found for part of the butanol. The materials which would not craze the plastic, in combination with butanol, were more expensive than the butanol itself. Replacement of all the butanol by some other solvent was tried, but all the materials which would serve as a replacement crazed the plastic surface. Thus, the formulation A-48 was selected as the solution to the problem. The complete formulation is as follows

10 Cp. Med. Ethylcellulose	20%
Tricresyl phosphate	5%
Nevillac Hard Resin	75%

made into 50% solids solution with

n-Butanol	40%
Ethyl alcohol	30%
Isopropyl alcohol (99%)	30%

The lacquer was pigmented with TiO_2 , which was incorporated by means of the roller mill. Fifty parts of pigment were used for 100 parts of total lacquer solids. This gave the finished composition

Pigment	20%
10 Cp. Med. Ethylcellulose	8%
Tricresyl phosphate	2%
Nevillac Hard Resin	30%
n-Butyl alcohol	16%
Ethyl alcohol	12%
Isopropyl alcohol (99%)	12%
	<hr/> 100%

For spraying, this lacquer was thinned with 2 parts of solvent to 1 part of lacquer, using the same solvent composition as before. This lacquer was found to have 5H hardness, excellent adhesion, good gloss, freedom from sag, good leveling properties, and a drying time in an acceptable range.

DISCUSSION

DISCUSSION

Up to this point, the results of the work have been discussed in the experimental part of the thesis with respect to their influence upon the work. Several sideline investigations were presented as they were encountered, but the results and value of these investigations are in need of further discussion. Advantage will be taken of the opportunity to present this material here.

One of the systems considered was the activation of the plastic surface prior to the application of an inert lacquer coating. The activation of the surface was a treatment of the plastic with some polystyrene solvent which would open minute fissures in the surface. Upon application, the lacquer, inert with respect to the plastic, would flow into the cracks and thus adhere to the surface. The principle involved here is not new. In industrial practice, metals are given a surface treatment (Bonderizing, Parkerizing, etc.) before coating, to increase adhesion. A similar technique was investigated for polystyrene. The logical starting point was an examination of polystyrene solvents. These materials were unsatisfactory because they did not cause the formation of the necessary cracks in the plastic. Solvents which crazed the plastic were next tried, and although they produced the required cracks the action was too rigorous and the coated surface was not smooth. In an effort to retain the action, but decrease the vigorousness, these solvents were diluted

with other materials which had no effect on the plastic. The dilution served its purpose to a certain extent, but great care was required in the application of the solvent mixture to prevent excessive action. On a basis of the observations, this method offers a solution to the problem only as a last resort. The great amount of control necessary in the application of the activating material makes the procedure unattractive commercially. The fact that two operations would be required for each article makes the system more undesirable. Hence, investigations along this line were discontinued.

The solvent spot tests disclosed one of the unusual aspects of this problem. The pure solvents had varying effects on the plastic, but the effect of these solvents in combination with others might be totally different. This fact greatly limited the usable solvent combination. The only solvent mixtures which even approached a solution to the problem, and containing solvents other than alcohols, was formulation S-18. The solvent was a complex mixture of hydrocarbons and alcohols. The coatings produced by the use of S-18 were completely satisfactory with the exception of a very slight amount of crazing. For some uses the formulation would be acceptable. Attempts to modify S-18 slightly were unsuccessful. Solvent mixtures containing only alcohols offered no problem in attack of the surface but adhesion difficulties were encountered. The proper selection of a resin imparted the required adhesion, and gave an answer to the problem.

When formulating the lacquers containing only alcohols, a method was introduced which decreased the amount of trial and error investigation. The relative evaporation rates of solvent mixtures were determined and were plotted on a trilinear diagram. Lines of equal evaporation rate were then constructed. The data were found to be too incomplete to make a chart of this kind practical, and therefore the raw data were used as explained in the experimental part. The use of the rate data eliminated a large part of the guesswork involved in formulating an original lacquer. In the final analysis some trial and error formulations were required since the characteristics of evaporation of the solvent mixtures were changed somewhat by the addition of the other lacquer components.

SUMMARY AND CONCLUSIONS

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The investigation was carried out in two parts: first, the formulation of lacquers containing only alcohols for solvent; second, the formulation of lacquers employing only hydrocarbon solvents.

For part one, a number of resins were examined to evaluate their hardness, gloss, and adhesive properties. From these tests one resin was selected for use in the remainder of the investigation. A trilinear diagram was prepared for the system Ethylcellulose - Tricresyl phosphate - Nevillac Hard Resin as an aid in choosing the proper solids composition in the final lacquer. By means of experimentally determined evaporation rates a primary solvent formulation was prepared. This was modified to produce a solvent mixture with satisfactory properties. This solvent in combination produced the lacquer which was considered the solution to the problem in this part. This formulation was ultimately the answer to the problem.

The second part of work was carried out in a trial and error manner. Several experimental formulations were prepared with no concrete results. It was then felt that a surface activating treatment prior to the application of an inert coating might be a solution to the problem. A series of examinations along this line showed that the system would not be satisfactory. Experimental formulation was then continued on the basis of solvent spot tests conducted previously.

Each formulation was prepared as a modification of the preceding lacquer as was indicated by the results. After the preparation of a large number of lacquers, this work was abandoned in favor of the lacquer formulated in the work with alcohol solvents.

An attempt to modify the final alcohol solvent lacquer, by means of hydrocarbon solvents, was made in the interests of economy. Several lacquers were prepared with this idea in mind, but the results were not satisfactory. The alcohol-solvent lacquer was then selected, unchanged, as the final answer to the problem.

The lacquer was pigmented with TiO_2 , to produce the following composition

Pigment	20%
10 Cp. Med. Ethylcellulose	8%
Tricresyl phosphate	2%
Nevillac Hard Resin	30%
Ethyl alcohol	16%
n-Butyl alcohol	12%
Isopropyl alcohol (99%)	12%
	<hr/> 100%

Good gloss, hardness, adhesion, leveling, and freedom from sag were obtained, and the requirements of the problem were fulfilled.

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VITA

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Mr. Heil is a member of the American Chemical Society and Theta Chi Delta, National honorary chemical fraternity. During his undergraduate work, he was a member of the Student Chapter of the A.I.Ch.E. at the University.