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UNIVERSITY OF LOUISVILLE

I. ETHYLCELLULOSE REACTION
IN A VARNISH

II. ETHYLCELLULOSE TRAFFIC
PAINT FORMULATION

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

Virgil H. Hulette, Jr.

1941

I. ETHYLCELLULOSE REACTION
IN A VARNISH

II. ETHYLCELLULOSE TRAFFIC
PAINT FORMULATION

Virgil H. Hulette, Jr.

Approved by Examining Committee:

Director
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June 1, 1941

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ETHYLCELLULOSE REACTION IN A VARNISH

Solvents were chosen to give reaction temperatures over the entire range of the ethylcellulose varnish cook. They were di-ethyl benzene (B.P. 180 C.), tetralin (B.P. 208 C.), tri-isopropyl benzene (B.P. 235 C.), and alpha-diphenyl ethane (B.P. 270 C.). Stoichiometric proportions of ethylcellulose and stearic acid, based on esterification of the hydroxy groups of ethylcellulose, were refluxed in each solvent to a sensibly minimum viscosity of the solution.

Analysis of the recovered ethylcellulose showed negligible reaction at the hydroxy groups. The stearic acid was reacted at the oxygen bridge and ethoxy groups in amounts up to 30% of the total stearic acid added.

ETHYLCELLULOSE TRAFFIC PAINT FORMULATION

Ethylcellulose traffic paints were made using the California state specification as a standard. The formulations used 15, 20, and 25% ethylcellulose, based on total gum solids, and the viscosity types were 7 and 20 centipoise. The plasticizers were raw tung oil, raw castor oil, and raw soya bean oil. The paints were subjected to weatherometer, cold check, moisture resistance and street test.

The results showed that ethylcellulose modified traffic paints compare favorably with commercial traffic paints now in use.

PART I

ETHYLOCELLULOSE REACTION IN A VARNISH

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INTRODUCTION

One of the applications of ethylcellulose in recent years has been its incorporation into varnishes. Its presence in varnishes definitely improves the drying time and the film structure of the varnish.

Varnishes are prepared by cooking natural or synthetic resins into drying oils and thinning this product with solvent. In ethylcellulose modified varnishes, the ethylcellulose is added at about 450 F. after the resin and oil have been cooked the same as in an ordinary varnish. The varnish oils are glycerides of the fatty acids, and the resins have various functional groups attached and are highly polymerized. It is desirable to determine whether cooking ethylcellulose into a varnish results in a simple dispersion of the ethylcellulose or whether it reacts with the glycerides of the fatty acids.

In this investigation the reaction of ethylcellulose with stearic acid at various cooking temperatures has been studied. Further investigations will be made using other acids and their glycerides to determine completely what takes place during the varnish cooking procedure.

HISTORICAL

Ethylcellulose modified varnishes and drying oils have been used successfully in the paint and varnish industries in recent years.

The incorporation of ethylcellulose into oleo-resinous varnishes definitely improves the drying time and initial print resistance of the varnish film, and its presence in the deposited film provides better "through drying" and minimizes wrinkling in thick varnish films.

The incorporation of ethylcellulose into drying oils results in oils which are markedly less tacky and have shorter drying times. They show less penetration into porous surfaces and produce tougher dried films than the heat-bodied oils.

No previous work has been done on the reaction of ethylcellulose with stearic acid at high temperatures, i.e. above 150 C. Worden (13) and Hunter (7) have reported the esterification of ethylcellulose with stearic acid by a reaction of ethylcellulose with stearyl chloride in pyridine-benzene solutions. The product was ethylcellulose stearate, soluble in benzene and benzine. This was a gentle esterification affecting the available hydroxy group of ethylcellulose only. Hunter (7) and Teupel (10) both report that the ethylcellulose stearate thus obtained showed little viscosity change over the pure ethylcellulose.

THEORETICAL

Varnish oils are mixed triglycerides of the saturated and unsaturated fatty acids. The reaction of ethylcellulose with these mixed glycerides may form the fatty acid esters of ethylcellulose with the liberation of glycerine. The fatty acids may also react at the ethoxy groups of the ethylcellulose or at the point of cleavage of the ethylcellulose chain.

The nature of this reaction will be solved by reacting ethylcellulose at the varnish cooking temperatures with all the possible types of acids and glycerides that might be present in actual varnish cooking practice. The complete solution of this problem would then be the reaction of ethylcellulose with stearic, linoleic, and linolenic fatty acids, followed by reaction with the mono-, di-, and tri-glycerides of these same acids.

In this investigation a study has been made of the reaction of ethylcellulose with stearic acid. This reaction is the simplest that could take place during the varnish cook and the results will be the basis for future work on the problem.

The cooking curve for an ethylcellulose modified varnish is shown in Figure 1. The procedure is given below. (4)

(1) Resin and oil are heated in the usual manner to between 525 F. and 575 F. The varnish is then checked to prevent overbodying and consequent low solids content.

Fig. 1 COOKING CURVE OF AN ETHOCEL MODIFIED
10 GALLON PHENAC 615 N TUNG OIL VARNISH

(2) One per cent lead acetate, based on the weight of the oil, is added.

(3) Standard ethoxy ethylcellulose is added slowly with stirring, at a temperature between 450 F. and 525 F.

(4) The cook is held at 450 F. for 10 to 30 minutes to obtain the desired compatibility and viscosity.

(5) The varnish is thinned with 50:50 mineral spirits aromatic naphtha.

(6) Soluble manganese or cobalt driers are added as required.

The solvents used were di-ethyl benzene (B.P. 180C.), tetralin (B.P. 208 C.), tri-isopropyl benzene (B.P. 235 C.), and alpha-diphenyl ethane (B.P. 270 C.). These solvents were chosen to give reaction temperatures over the entire range of the ethylcellulose varnish cook. Stoichiometric proportions of ethylcellulose and stearic acid, based on esterification of the hydroxy groups of the ethylcellulose, were refluxed in each solvent to a sensibly minimum viscosity of the solution. The degraded ethylcellulose was then recovered from the solutions and analyzed.

Solutions of ethylcellulose in the same solvents, but containing no stearic acid, were given the same treatment to observe the effect of heat alone on the degradation of ethylcellulose.

THEORY OF CELLULOSE AND ETHYLCELLULOSE

Cellulose appears to have a chain structure composed of fundamental carbohydrate units called glucose residues. Each glucose residue contains three chemically active hydroxy groups which are capable of all the typical alcohol reactions. These glucose residues are joined to each other by an oxygen bridge to form a chain structure. Cellulose may be represented by the following formula:

The chain length of a particular cellulose is a function of the origin of the cellulose and its prior chemical treatment. W. Haworth (6) has claimed the chain length to be approximately 200 glucose units, molecular weight 25,000 to 30,000 for virgin cellulose.

Ethylcellulose, molecular weight 232 per glucose unit, is an ether of cellulose. It is prepared by reacting ethyl chloride and alkali cellulose. According to S. Uschakov and I. Schneer (11) the optimum conditions for formation of ethylcellulose require 6 mols of ethyl chloride to 1 mol of alkali cellulose heated to 120 - 130 C. for 18 hours, followed by mercerization with 50% sodium hydroxide solution. Ethyl-

cellulose is commercially available in ethoxy contents ranging from 41% to 49.5% ethoxy which corresponds to a mol ratio of 2.5 ethoxy groups per glucose residue. The structure of ethylcellulose is shown below:

It contains 1 hydroxy group for esterification per 2 glucose residues.

THEORETICAL REACTIONS

The four types of reaction possible between ethylcellulose and stearic acid are:

- (1) Esterification of the available hydroxy group.
- (2) Reaction at the ethoxy groups.
- (3) Cleavage and reaction at the oxygen bridge.
- (4) Cleavage at the oxygen bridge.

The esterification with stearic acid at the hydroxy groups should be a smooth reaction resulting in the evolution of an equivalent amount of water. Worden (13) describes the production of ethylcellulose stearate by reacting 1 part of ethylcellulose with 7 parts of stearic acid for 5 to 6 hours with stirring at 150 C. British Patent 270,347 describes ethylcellulose stearate and its production. Hunter (7) reports that the production of ethylcellulose stearate by reaction of

stearyl chloride and ethylcellulose in pyridine results in a product with very slight change in viscosity over the unmodified ethylcellulose. This retention of viscosity upon esterification is also reported by E. Teupel (10) in German Patent 510,424.

The reaction of stearic acid at the ethoxy group would split off ethyl alcohol and would be shown by a diminished ethoxy content. E. Berl and H. Schupp (1) report that diethylcellulose is broken down and ethyl groups split off by acetolysis. This type of reaction would also be shown by the saponification value of the degraded reaction product.

The cleavage accompanied by reaction at the oxygen bridge would not split off a compound. The reaction would produce an available hydroxy group on one glucose residue and an acid radical on the other glucose residue. This type of reaction would be indicated by diminished viscosity of the solution and the saponification number of the reaction product. E. Berl and H. Schupp (1) have indicated such a reaction in the following statements:

"There is a strong diminution in viscosity of solutions of ethylcellulose upon repeated alkylation, the degrading influence of the alkylating agent coupled with increase in alkyl content causes simultaneous progressive splitting of the cellulose complex. The inner friction of cellulose ethers from unchanged cellulose is extraordinarily greater than that of the ether prepared under the same conditions, but from a cellulose which has been primarily treated with acid. This is therefore a proof of the degradation of the highly complex cellulose aggregate by acid treating."

The cleavage of ethylcellulose would be shown by a diminution of the viscosity of the solution. According to Doree (3) cellulose is not affected by heat up to a temperature of 140 C. even after heating for 4 hours. Above that temperature the reducing properties increase and the viscosity falls. Furthermore, Birtwell, Clibbens, and Geake (2) have shown that for celluloses reacted with acids over a wide range of conditions a definite relation exists between the loss of tensile strength and the loss of viscosity.

Richter (9) states that methylation of cellulose followed by hydrolysis of the product yields 2,3,6-trimethyl glucose. This product would be soluble in water and result in a low recovery of the reaction product.

EXPERIMENTAL

APPARATUS

The apparatus used for refluxing the ethylcellulose-stearic acid solutions is shown in Figure 2. It was a 2 liter, 3 necked, round bottom flask, fitted with a water cooled reflux condenser, thermometer holder, and viscosity pipette. The viscosity pipette was a 20 cc. glass bulb suspended on the inside of the flask. The trap connected to the bottom of the reflux condenser was designed to catch any water given off during the course of the reaction. All connections on the apparatus were of ground glass joints to assure no loss of solvent from the system. Heat was supplied to the system by an electric heater through the medium of molten Wood's metal.

MATERIALS

The materials used were ethylcellulose, stearic acid, di-ethyl benzene (B.P. 180 C.), tetralin (B.P. 208 C.), tri-isopropyl benzene (B.P. 235 C.), and alpha-diphenyl ethane (B.P. 270 C.).

The ethylcellulose was the standard ethoxy type with a viscosity of 145 cps., measured at 25 C. on a 5% solution in 80:20 toluene-ethyl alcohol. Its softening point

Fig. 2 Reaction Apparatus

was 138 to 133 C. and its melting point 173 to 165 C. (4)

The stearic acid was of technical grade. It had a melting point of 69 C. and a boiling point of 232 C.

The di-ethyl benzene, tetralin, tri-isopropyl benzene, and 1,1-diphenyl ethane were from commercial stocks.

EXPERIMENTAL PROCEDURE

The solvents used in all reactions were distilled to free them from water and other contaminating materials. Solutions containing stoichiometric proportions of ethyl-cellulose and stearic acid were made for each of the solvents. Similar solutions, but containing no stearic acid, were also made to determine the effect of heat alone on the degradation of ethylcellulose. The weight compositions of these solutions were:

TABLE I
COMPOSITION OF SOLUTIONS FOR REFLUXING

Sample No.	Solvent*	Grams Solvent	Grams Stearic Acid	Grams Ethocel
1	D.E.B.	600 g.	36 g.	60 g.
2	D.E.B.	600	--	60
3	Tetralin	600	36	60
4	Tetralin	600	--	60
5	S- I.P.B.	600	36	60
6	S- I.P.B.	600	--	60
7	alpha D.P.E.	600	36	60
8	alpha D.P.E.	600	--	60

The ethylcellulose and ethylcellulose-stearic acid solutions were dissolved by heating on a water bath until clear solutions were obtained. These solutions were refluxed at their respective reflux temperatures until a sensibly minimum viscosity was reached in each case. This final viscosity was measured with the viscosity pipette at 25 C., and indicated complete reaction of the ethylcellulose and stearic acid. The loss of viscosity of each solution as the reaction proceeded was obtained by viscosity measurements with the viscosity pipette during the reflux period. The pipette was held at the reflux temperature during this time by the vapors rising from the refluxing solution. All viscosities were measured as the time in seconds required for the solution to pass through the 20 cc. pipette.

The solutions were cooked under an atmosphere of carbon dioxide. The carbon dioxide was admitted to the flask through the viscosity pipette and made to bubble through the solution. The bubbling carbon dioxide provided agitation for the solution.

ANALYTICAL METHODS

To analyze the reaction product it was necessary to separate the product from the high boiling solvent. This was accomplished by steam distillation. The residue from the steam distillation was dissolved in acetone and precipitated

from the acetone solution by pouring it into an excess of water. The precipitate was recovered by filtering and was dried to constant weight in an atmospheric oven at 110 C. These samples were analyzed for ethoxy content.

The dark, charred character of the products presented a problem in the determination of the acid and saponification values. After some experimentation, the following method of Gardner (5) was found satisfactory for acid values:

"Dissolve a weighed amount of the material in 25 cc. benzene. Add 25 cc. carbon tetrachloride and 25 cc. neutral ethyl alcohol. To this add 1/2 teaspoon of C.P. sodium chloride and 10 to 20 cc. distilled water. Mix thoroughly. Titrate with .1 N sodium hydroxide to a faint pink top layer, using phenolphthalein as indicator. The pink layer should remain for at least 2 minutes."

For saponification values the method given above was modified slightly. The ethyl alcohol was added in the form of .5 N alcoholic sodium hydroxide (25 cc.) so that the solvent combination was not disturbed. The solutions were refluxed for 1 hour and the excess sodium hydroxide back-titrated with .5 N hydrochloric acid solution. The indicator used was thymol blue. The color change was from a blue-green to a yellow, and the end-point was distinct.

DATA AND RESULTS

A summary of the data taken during the refluxing operation is given in Table II. This table includes the temperature of reflux, total hours of reflux, final viscosity of the solutions at room temperature, color of final solutions, and the amount of water given off during the reaction. All the solutions were refluxed to a sensibly minimum viscosity measured at 25 C. The reduction of viscosity at reflux temperature is shown in the curves of Figures 3 to 10 for all solutions. Incompatibility of solvent and ethylcellulose made it impossible to obtain a minimum viscosity in the case of the thermal reaction using tri-isopropyl benzene. No incompatibility was found for the same solution containing stearic acid.

TABLE II
SUMMARY OF REFLUXING OPERATION

Sample No.	Temp. Reflux	Hours Reflux	Final Vis. @ 25 C.	Solution Color	Water Trapped	Water of Ester.
1	180 C.	18 hr.	27 sec.	Straw	--	--
2	180	46	45	Straw	--	--
3	208	25	37	Dark straw	0.9 cc.	0.1 cc.
4	208	30	60	Straw	0.8	
5	235	9	29	Dark	0.7	0.2
6	235	12	--	Dark straw	0.5	
7	270	6	9	Very dark	0.25	0.25
8	270	8	35	Very dark	0

Fig. 3 VISCOSITY REDUCTION AT 160 C.
(Ethylcellulose, stearic acid, di-ethyl benzene solution)

Fig. 4 VISCOSITY REDUCTION AT 180 C.
(Ethylcellulose, di-ethyl benzene solution)

Fig. 5 VISCOSITY REDUCTION AT 208 C.
(Ethylcellulose, stearic acid, tetralin solution)

Fig. 6 VISCOSITY REDUCTION AT 208 C.
(Ethylcellulose, tetralin solution)

Fig. 7 VISCOSITY REDUCTION AT 235 C.
(Ethylcellulose, stearic acid, tri-isopropyl benzene)

Fig. 8 VISCOSITY REDUCTION AT 235 C.
(Ethylcellulose, tri-isopropyl benzene solution)

Fig. 9 VISCOSITY REDUCTION AT 270 C.
(Ethylcellulose, stearic acid, 1,1 diphenyl ethane solution)

Fig. 10 VISCOSITY REDUCTION AT 270 C.
(Ethylcellulose, 1,1 diphenyl ethane solution)

Table II shows that the time required to attain a sensibly minimum viscosity of the ethylcellulose solutions was an inverse function of the temperature at which the solution was refluxed. The increased darkening of the solutions at the high reflux temperatures indicated that carbonization of the ethylcellulose was appreciable. The charring action might produce solubility of some of the ethylcellulose present.

The amount of water trapped during the reflux period indicated that very little esterification of the available hydroxy group actually took place. The theoretical amount of water corresponding to complete esterification of the hydroxy group was 2.5 cc.

The rate of viscosity change of the solutions at the reflux temperature was shown in Figures 5 to 10. The presence of stearic acid definitely accelerated the breakdown to minimum viscosity.

Table III shows the properties of the ethylcellulose reaction product obtained from the stearic acid and thermal degradation reactions. The tabulation includes the per cent ethoxy of the degraded samples, calculated to the acid free basis, the free acid present, the saponification values, and the amounts of acid reacted at the hydroxy group and at the oxygen bridge and ethoxy groups. Saponification and acid values are given as grams sodium hydroxide per gram sample and grams stearic acid per gram samples respectively.

TABLE III

CHEMICAL PROPERTIES OF RECLAIMED ETHYLCELLULOSE

Sample No.	% Ethoxy	Free Acid (g. acid per g. sample)	Sap. Value (g. NaOH per g. sample)	Acid Re (Cleavage & ethoxy)	Acid Re (OH gr.)
1	42.1%	.306 g/g	.102 g/g	.082 g/g	--
2	46.3	.07 M.E.*	.068	--	--
3	39.5	.276 g/g	.104	.149	.017
4	44.9	.07 M.E.	.064	--	--
5	41.2	.313 g/g	.108	.133	.025
6	36.3	.119 M.E.	.065	--	--
7	41.5	.32 g/g	.116	.197	.072
8	42.8	.148 M.E.	.043	--	--

* Note- M.E. is milliequivalents of NaOH. The acid giving this value is unidentified. It is a decomposition product of the ethylcellulose.

Table III shows a definite loss of ethoxy groups during the refluxing periods both for the stearic acid solutions and those containing ethylcellulose only. The presence of stearic acid appears to give a slightly greater loss of ethoxy groups.

Approximately 70% of the acid added is present as free acid in the recovered samples. The amount of acid reacted at the ethoxy groups and oxygen bridge in each case was calculated by subtracting the free acid value and saponification value of the non-acid ethylcellulose from the total saponification value. All calculations were made in terms of milliequivalents of sodium hydroxide. The amount of acid reacted at the hydroxy groups was calculated from the amount of water given off during the reaction.

The production of an unidentified acid is shown by

the acid values of the ethylcellulose obtained from the solutions which contained no stearic acid. Table IV shows the properties of the reclaimed ethylcellulose in terms of total amounts of acid and ethylcellulose used in each reaction.

TABLE IV

SUMMARY OF REACTION PRODUCTS

Sample No.	Total Grams Recovered	Free Acid	Acid Ester.	Acid Re (Cleavage & ethoxy)	Total Acid Rec'd	Ethocel Lost
1	96 g.	29.4g	--	7.9 g.	37.3 g.	None
2	61.5	--	--	--	--	None
3	92	25.4	1.55	13.7	40.6	4 g.
4	60	--	--	--	--	None
5	80	25.0	3.1	10.7	38.7	16 g.
6	63	--	--	--	--	None
7	54	17.8	4.0	10.7	32.0	41.8 g.
8	47.5	--	--	--	--	12.5

Table IV shows that the total grams of product recovered in each case diminished as the temperature of reflux rose. Since all the stearic acid was accounted for, the lost product was ethylcellulose.

The amount of acid that reacted at the oxygen bridge and ethoxy groups increased as the temperature of reflux rose. The amount of acid which reacted at the hydroxy group was essentially negligible in all cases.

The loss of ethylcellulose experienced at 270 C. was appreciable and was more a function of the length of refluxing at this temperature than a function of the presence of stearic acid.

CONCLUSIONS

The following conclusions may be drawn from the experimental work:

REACTION WITH STEARIC ACID

(1) Stearic acid promotes the loss of viscosity of solutions of ethylcellulose subjected to reflux at high temperatures. E. Berl and H. Schupp (1) have shown this to be true in their work on diethylcellulose. Their conclusions have been summarized on page 7 of this thesis.

(2) A loss of ethoxy groups is indicated during the reaction of ethylcellulose and stearic acid at high temperatures. Reaction of the stearic acid at the ethoxy groups probably occurs with the formation of ethylcellulose stearate. This result has been supported by the work of E. Berl and H. Schupp (1). An addition of stearic acid at the cleavage point in the cellulose chain may also occur. The work of the present thesis shows that about 30% of the stearic acid was accounted for by these two reactions.

(3) The amount of acid reacted at the available hydroxy group was slight in all cases. This slight reaction is explained when it is observed that Worden (13) required 7 parts of stearic acid to 1 part ethylcellulose to obtain ethylcellulose stearate at 150 C. In this problem only 1 part

of stearic acid to 8 parts of ethylcellulose was used, representing stoichiometric proportions of the reactants. The necessary excess of stearic acid was lacking in this problem, and no appreciable reaction occurred.

(4) Stearic acid promotes the breakdown of ethylcellulose to soluble materials at high temperatures. Richter (9) has pointed this out for the acid hydrolysis of methyl cellulose at high temperatures.

THERMAL REACTION

(1) Pure ethylcellulose solutions are subject to degradation under the effect of prolonged heating at high temperatures. The viscosity curves already mentioned have indicated this.

(2) High temperatures cause excessive charring accompanied by conversion of some of the ethylcellulose to soluble products.

(3) There is a loss of ethoxy groups which increases as the temperature of reaction rises.

(4) The final degraded ethylcellulose has a definite acid value. This acid value increases as the temperature of reflux increases.

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PART II**ETHYLCELLULOSE TRAFFIC PAINT FORMULATION**

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INTRODUCTION

Spirit varnishes as traffic paints are in wide use in the United States today. The war has given rise to economic conditions which have resulted in a marked increase in the price of many of the imported natural resins widely employed in the production of spirit varnishes and pigmented traffic paints. Therefore, a traffic paint made from domestic resins was considered.

This experimental program was designed to test the properties of traffic paints made from domestic resins built up with ethylcellulose and to compare these domestic resin traffic paints with standard and commercial traffic paints now in use in this country. Samples were made using Zitro as the resin and varying the percentage of ethylcellulose added and the type of plasticizer used. These traffic paints were then tested for moisture resistance, accelerated weathering, pencil hardness, cold check, abrasion resistance, and street test.

HISTORICAL

Spirit varnishes have been widely used as traffic paints throughout the United States for many years. The California traffic paint specifications have been adopted by the majority of the other States, and this specification has therefore been used as a basis for the experimental work done on this problem. A complete discussion of the California specifications will be given in the Experimental section of this thesis.

The use of ethylcellulose to improve the properties of spirit varnishes was first demonstrated by R. C. Ernst and J. B. Tepe (3) using manila and pontianak gums. These investigators found that the improvement in the properties of the varnishes was in approximately direct proportion to the amount of ethylcellulose added in the range 0 to 25% ethylcellulose.

No previous work has been done on the use of domestic resins such as rosin, limed rosin, and Zitro with ethylcellulose in spirit varnishes as a direct substitute for imported natural gums.

THEORETICAL

There are two general classifications of varnishes--oil varnishes and spirit varnishes. The former contain either natural or synthetic resins, solvent, and varnish oils. To obtain these varnishes it is necessary to cook the oil and resins together at temperatures between 450 F. and 550 F. The resultant varnish provides coatings which find extensive use in the furniture and interior decoration industries where high grade finishes are necessary. Spirit varnishes are simple mixtures of solvent and natural resin, and are cold-cut. They are very cheap in comparison with oil varnishes and find application where an inexpensive coating is needed in large quantities.

Domestic resins such as rosin, limed rosin, and Zitro were available in abundance at prices lower than those being demanded for Manila, Pontianak, and other natural imported resins. However, these domestic resins could not be substituted directly for the imported natural resins because of their definitely inferior physical properties. The low cost of the domestic resins made it feasible to modify the accepted traffic paint formulas, employing the less expensive domestic resins and an addition agent, such as ethylcellulose. This modification would serve to make these products comparable in cost and properties with the traffic paints previously used.

RAW MATERIALS

The raw materials used in this investigation were ethylcellulose, Zitro, 1001 Super Beekacite, raw tung oil, raw soya bean oil, raw castor oil, Titanox B pigment, ethyl alcohol, toluene, and acetone.

The ethylcellulose was the standard ethoxy grade containing 46.5% to 49.5% ethoxy. The viscosities used were 7 and 20 centipoise as determined on a 5% by weight solution in 80:20 toluene-ethyl alcohol at 25 C. (1)

The resin used was Zitro, a derivative of wood rosin containing 4.8% combined metallic zinc. It had a specific gravity at 25 C. of 1.13 and a melting point at 130 to 135 C. Its acid value was 5 to 15, and it had a color rating "N". (2)

The resin used for water-proofing was 1001 Super Beekacite. This material was the commercial synthetic resin used extensively in the paint industry.

The raw tung oil, raw castor oil, and raw soya bean oil used as plasticizers were obtained from commercial lots and were representative of the raw oils used in the industry.

The pigment was Titanox B. It contained 70% barium sulfate and 30% titanium dioxide, and conformed to the A.S.T.M. standard, D 208-26.

The ethyl alcohol used for solvent was denatured 95% alcohol and 5% water. Its specific gravity was 0.78 and its boiling point was 78 C.

The toluene used as solvent had a specific gravity of 0.86 and a boiling point of 111 C.

The acetone used as solvent had a specific gravity of 0.78 and a boiling point of 56 C.

EXPERIMENTAL

The California specification has been generally accepted by the industry and has therefore been chosen as a basis for the proposed modification with domestic resins and ethylcellulose. It is as follows:

Pigment	45% by weight
Gum Vehicle	55% by weight

The gum vehicle is further broken down to

Gum solids	35% by weight
Solvent	65% by weight

The gum solid was East India D.B.B. Manila gum. The solvent had the following percentage composition by volume:

Raw Tung Oil	15%
Normal Butyl Alcohol	17%
Acetone	34%
Alcohol (180 proof)	34%

The pigment was titanium-barium which conformed to the requirements of the A.S.T.M. Standard Specifications, Serial designation D 208-26.

The specification demanded that all paints were sufficiently hard fifteen minutes after application to the street so that there was no pick-up under traffic and were thoroughly dry, free from any tackiness, within one hour after application at a temperature of 60 F.

In this investigation the California specification was modified by substituting 15, 20, and 25% ethylcellulose based on total gum solids. To obtain better moisture resistance 5% 1001 Super Beckacite was added to the total gum solids. The remainder of the gum solids was Zitro.

The introduction of ethylcellulose made it necessary to change the original solvent specification. This adjustment was made by producing unpigmented varnishes using the required amounts of Zitro and ethylcellulose and various solvent combinations. After some experimentation, the substitution of xylene for normal butyl alcohol was found satisfactory. The clear varnish made with the new solvent combination was within the specifications pertaining to drying time and tackiness of film.

Three different plasticizers and two types of ethylcellulose were used. The plasticizers were raw tung oil, raw soya bean oil, and raw castor oil. The viscosity types of ethylcellulose were 7 centipoise and 20 centipoise. Formulations of all samples are found in Table I.

A typical modified formulation for 15% ethylcellulose, tung oil, and 7 centipoise viscosity type was as follows:

Sample No. 1

Pigment (Titanox B)	45% by weight
Gum Vehicle	55% by weight

TABLE I
FORMULATION

— Gum Vehicle 55% —										Pigment 45%
— Gum Solids 35% —					— Solvent 65% —					
Sample No.	E/C Viscosity	E/C (%)	Zitro (%)	1001 (%)	Ethyl Alcohol	Acetone	Xylene	Plast-leizer	Pigment (Titanox B)	
1	7 cps.	15%	80%	5%	34%	34%	17%	15%	Tung	45%
2	7	20	75	5	34	34	17	15	Tung	45
3	7	25	70	5	34	34	17	15	Tung	45
4	20	15	80	5	34	34	17	15	Tung	45
5	20	20	75	5	34	34	17	15	Tung	45
6	20	25	70	5	34	34	17	15	Tung	45
7	7	15	80	5	34	34	17	15	Soya	45
8	7	20	75	5	34	34	17	15	Soya	45
9	7	25	70	5	34	34	17	15	Soya	45
10	7	15	80	5	34	34	17	15	Castor	45
11	7	20	75	5	34	34	17	15	Castor	45
12	7	25	70	5	34	34	17	15	Castor	45
13	20	15	80	5	34	34	17	15	Soya	45
14	20	20	75	5	34	34	17	15	Soya	45
15	20	25	70	5	34	34	17	15	Soya	45
16	20	15	80	5	34	34	17	15	Castor	45
17	20	20	75	5	34	34	17	15	Castor	45
18	20	25	70	5	34	34	17	15	Castor	45
Standard Paints										
		E/C%	Manila				n-Butanol			
Std. Manila		—	100%	—	34	34	17	15%	Tung	45
Control #1		3%	97	—	34	34	17	15	Tung	45
Control #2		6	94	—	34	34	17	15	Tung	45

The gum vehicle was

Gum solids	35% by weight
Solvent	65% by weight

Gum solids:

Ethylcellulose (7cps.)	15% by weight
Super Beekacite	5% by weight
Zitro	<u>80%</u> by weight
Total	100%

Solvent:

Raw Tung Oil	17% by volume
Ethyl alcohol	34% by volume
Acetone	34% by volume
Xylene	<u>15%</u> by volume
Total	100%

EXPERIMENTAL PROCEDURE

Quart samples of each test paint were made up according to the formulations shown in Table I. Each paint was ground for 24 hours in a pebble mill. The finished paints were spread on glass plates and examined under a microscope at 100 diameters magnification to check the complete dispersion of the pigment.

Each sample was cast on glass, steel, and tin panels with a film caster calibrated for a film thickness of .008

inches. The films on the glass panels were tested for pencil hardness, moisture resistance, and abrasion resistance. The films on the steel panels were tested for cold check failure and the films on the tin panels were subjected to the accelerated weathering test. Details of these tests will be given under the title of Testing Procedure.

TESTING PROCEDURE

The following tests were run on the finished traffic paints:

- (1) Accelerated weathering
- (2) Moisture resistance
- (3) Pencil hardness
- (4) Cold check
- (5) Abrasion resistance
- (6) Street test

In the accelerated weathering test, a National Carbon Company accelerated weathering machine was used. The films were cast on tin-dipped steel panels and allowed to dry for 24 hours before testing was started. The weathering cycle employed consisted of 4 hours of light and water, 4½ hours of light only, 4 hours of light and water, and 2 hours of water only. All panels were refrigerated for 1 hour at -20 C. before repeating the above cycle. Failure occurred by checking of the

film in all cases.

Moisture resistance was tested by maintaining a layer of water on the films for 24 hours. The films were cast on glass and the results were reported as failure or non-failure of the film.

Pencil hardness was run using Standard Venus pencils on films cast on glass panels. Hardness increases with the H number of the pencils. This test was run using ordinary writing pressure at an angle of approximately 45 degrees between panel and pencil. Hardness was determined as that pencil which, under the above conditions, definitely scratched the surface of the film.

The cold check test (1) was run in 2 hour cycles, using films cast on 20 gauge steel panels. The panels were held at 60 C. for 1 hour, then rapidly cooled to -20 C., and held an additional hour. Results were reported in number of complete cycles to effect failure of the films.

The abrasion test (4) depended on the resistance of a film to the abrasion of a falling column of sand. Dry Ottawa sand was allowed to fall from a height of 60 inches onto the panels supported at 45 degrees with the horizontal. The tube used had an inside diameter of 6 millimeters. Results were reported in pounds of sand necessary to wear through the film.

The street test consisted of painting stripes of each sample on the street and observing the effects of traffic wear. The stripes were laid down on April 30, 1941.

RESULTS OF TESTING

The results of testing on all samples are tabulated in Table II. Detailed explanation of the methods of testing and the expression of results were given in the Experimental section of this thesis.

A correlation of the results of testing found in Table II indicated the following:

- (1) The use of 7 cps. or 20 cps. ethylcellulose has no effect on the properties of the paints.
- (2) Castor oil as plasticizer was definitely inferior in cold check resistance and weatherometer test.
- (3) Soya bean oil as plasticizer gave extremely soft films in all cases.
- (4) The addition of 5% 1001 Super Beckacite did not improve the water resistance of the paints.
- (5) The ethylcellulose modified paints were inferior to the standards in abrasion resistance.
- (6) Cold check resistance was dependent on the plasticizer used. Both raw tung oil and raw soya bean oil were acceptable in cold check testing.
- (7) Paints which contained 25% ethylcellulose showed little improvement over those which contained 20% ethylcellulose.

TABLE II
RESULTS OF TESTING

Sample No.	Weatherometer (Cycles to failure)	Moisture Resistance	Pencil Hardness	Cold Check (Cycles to failure)	Abrasion (lbs. of sand to failure)
1	12	O.K.	7H	35	3# 11 oz.
2	3	O.K.	6H	35	3 8
3	3	O.K.	6H	14	3 13
4	3	O.K.	6H	32	3 3
5	12	O.K.	6H	35	3 8
6	12	O.K.	6H	35	3 8
7	10	O.K.	2H	35	6 8
8	6	O.K.	F	35	5 15
9	4	O.K.	F	35	4 3
10	3	O.K.	6H	6	2 14
11	3	O.K.	6H	15	3 4
12	4	O.K.	5H	15	3 5
13	8	O.K.	F	35	4 12
14	8	O.K.	F	35	10 3
15	12	O.K.	5H	35	5 8
16	4	O.K.	6H	14	4 8
17	3	O.K.	6H	14	5 6
18	10	O.K.	6H	23	4 12
Standard	12	O.K.	6H	35	5 15
Control 1	4	O.K.	7H	22	8 8
Control 2	12	O.K.	6H	35	5 15

CONCLUSIONS

The results of Table II have shown that raw tung oil was the best plasticizer for the traffic paints. Raw Castor oil was definitely inferior and the soya bean oil paints were extremely soft in pencil hardness.

Since there was no difference in properties as a function of the viscosity type used, it is recommended that 7 centipoise viscosity ethylcellulose be used to improve the brushing qualities of the paint.

From the Results of Testing it was concluded that a traffic paint of the formulation of Sample No. 5 was a good substitute for the standard manila gum traffic paints now in use. As has already been stated, it is recommended that 7 centipoise ethylcellulose be used in Sample No.5 and that the 5% 1001 Super Beckacite be replaced with Zitro.

A cost analysis on the ethylcellulose modified paint corresponding to Sample No. 5 revealed this paint to be comparable in price to the standard manila gum paint.

It was therefore concluded that ethylcellulose modified traffic paints are feasible and desirable paints comparable to standard formulations in both physical and economical aspects.

RECOMMENDATIONS

The traffic paint problem reported elsewhere in this thesis was the initial research on ethylcellulose modified traffic paints. The formulations followed the standard specifications closely so that the simplest modified formula was obtained. It is desirable to expand the scope of the problem to include other modifications. Further work is now in progress on additional modifications of the standard specifications.

The formulations of the work now in progress include:

RESINS

The resins now being used are Zitro and Zerex. Zerex is slightly more expensive than Zitro and differs from Zitro only in the amount of zinc added. Zerex contains 9.6% zinc while Zitro contains 4.8% zinc.

The ethylcellulose percentages being used are 10, 15, and 20%, based on total gum solids. The viscosity of the ethylcellulose is 8 centipoise.

PLASTICIZERS

The plasticizers being used are raw tung oil, raw oiticica oil, blown castor oil, and blown soya bean oil. The effect of increasing the plasticizer concentration is being

studied by using 15, 22.5, and 30% of the above mentioned plasticizers, based on total solvents present.

The variation of type of plasticizer, percentage plasticizer and ethylcellulose, and types of resins used has led to the formulation of 64 test paints.

The results of testing these paints along with the work already completed will complete the traffic paint problem.

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VITA

Virgil Hume Hulette, Jr., was born in Louisville, Kentucky, on February 20, 1919, the son of Virgil H. Hulette, Sr., and Elsie May Hulette. He received his primary and high school education in the public schools of Louisville. All his college work was carried on at the University of Louisville. He received a Bachelor of Chemical Engineering Degree in 1940, and a Master of Chemical Engineering Degree in June, 1941.

He was awarded the Dow Chemical Company Fellowship for the year 1940-1941, and upon completion of his academic work was employed by the Monsanto Chemical Company, St. Louis, Missouri.

Mr. Hulette is a member of Triangle Fraternity, national social engineering fraternity, Sigma Tau, national honorary engineering fraternity, and Theta Chi Delta, national honorary chemistry fraternity. He was President of the Louisville Chapter of Triangle Fraternity, President of Alpha Gamma Chapter of Theta Chi Delta, and secretary of Omicron Chapter of Sigma Tau. He was Co-Editor of the University of Louisville Annual, and a member of the "L" Club.