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UNIVERSITY OF LOUISVILLE

- I. PLASTICIZING ETHYLCELLULOSE
- II. EFFECT OF ETHYLCELLULOSE IN
SPIRIT VARNISHES

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

Ira Walter Hutchison, Jr.

1940

I. PLASTICIZING ETHYLCELLULOSE

II. EFFECT OF ETHYLCELLULOSE IN
SPIRIT VARNISHES

Ira Walter Hutchison, Jr.

Approved by Examining Committee:

Director

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May 23, 1940

TABLE OF CONTENTS

	Page
Acknowledgement	iii
Abstract	iv
 PART I PLASTICIZING ETHYLCELLULOSE	
List of Tables	vi
Introduction	1
Historical	3
Theoretical	5
Raw Materials	8
Experimental	11
Block Test	13
Print Test	13
Tack Test	14
Data	15
Results	17
General	18
Effect of Orange Peeling on Tests	21
Miscellaneous Observations	22
Summary	24
Literature Cited	26
 PART II EFFECT OF ETHYLCELLULOSE IN SPIRIT VARNISHES	
Introduction	29
Historical	31

TABLE OF CONTENTS (CONCLUDED)

	Page
Theoretical	33
Raw Materials	35
Experimental	38
Abrasion Resistance	39
Hardness	41
Cold Check	42
Melting Point	42
Moisture Resistance	43
Procedure	44
Data	46
Results	48
Abrasion Resistance	49
Hardness	49
Cold Check	49
Melting Point	49
Moisture Resistance	49
Literature Cited	51
Appendix	53
Acknowledgements	56
Vita	57

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ABSTRACT

PLASTICIZING ETHYLCELLULOSE

Various percentages of several plasticizers were substituted for the ethylcellulose in ethylcellulose-solvent mixtures. Block, print, and "tack by feel" tests were run. These tests showed that large percentages of plasticizers could be used in many cases, but the final choice depends upon the application of the finished coating material. The application determines which of the three tests are the most significant.

Magazine covers are lacquered, and in transportation often stick together. The block tests provide comparison of the plasticizers under conditions similar to the treatment of the magazines. The print test would be most significant where there is cloth in contact with a lacquered surface. "Tack by feel" tests are least reliable in determining tackiness of a film.

EFFECT OF ETHYLCELLULOSE IN SPIRIT VARNISHES

Various percentages of ethylcellulose were substituted for resin in spirit varnishes. Spirit varnishes used were made with manila and pontianak resins. Abrasion resistance, hardness, cold check, moisture resistance, and melting point determinations were made in order to find the effect of the ethylcellulose. Experimental work indicated that the ethylcellulose improved the abrasion resistance, hardness, cold check resistance, and moisture resistance of the spirit varnishes, and increased their melting points.

PART I

PLASTICIZING ETHYLCELLULOSE

LIST OF TABLES

Table	Page
I Properties of plasticizers	9
II Properties of ethylcellulose	10
III Solvent combinations	12
IV Limits of plasticizer concentration standard ethoxy ethylcellulose . .	16
V Limits of plasticizer concentration medium ethoxy ethylcellulose	16
VI Limits of plasticizer concentration low ethoxy ethylcellulose	16
VII Special solvent combinations	22

INTRODUCTION

The purpose of this investigation was to determine the quantity of plasticizer that could be used in ethylcellulose-solvent mixtures without having the resulting films remain tacky or sticky after a reasonable drying time.

The use of fairly large amounts of plasticizers would provide a distinct price advantage because most of the plasticizers are less expensive than the cellulose derivative. Elongation of the film would be increased in some cases without materially reducing the yield point. A great many different types of plasticizers are on the market, consequently, the choice would not be limited.

The limits of concentrations of plasticizers that could be used without the resulting films remaining tacky over a certain period of time have been established. This was done by employing block, print, and "tack by feel" tests.

Results of the experimental work are given, and indicate possible use of large concentrations of plasticizers.

HISTORICAL

Plasticizers have always been used in order to increase the tensile strength and elongation of lacquer films. The use of the plasticizer as a major part of the film-forming materials, however, is of more recent date.

Bass and Kauppi (1,2) have shown by load-elongation curves that increasing the viscosity of ethylcellulose does not appreciably affect the yield point of films of the same plasticizer content. The increase in tensile strength and toughness becomes greater as larger percentages of plasticizers are used with higher viscosity material. Kraus (3) found by studying plasticizers in nitrocellulose lacquers, that plasticizers which impart favorable weathering properties are those that also prevent ultraviolet light from being detrimental to the physical properties of the films. He showed that the poorest weathering properties of plasticized films were observed when plasticizers containing long aliphatic carbon chains were used, while favorable properties were observed when aromatic groups were used. Van Heuckeroth (4) found that plasticizers are probably more important than resins in extending the durability of lacquers, although the favorable effect of the resins upon gloss and adhesion are significant.

THEORETICAL

A portion of a volatile solvent will remain in a film for a long time imparting to the film a certain amount of plasticity. After an indefinite period only a very small amount of the volatile solvent will be left and the film becomes brittle. To overcome or regulate this brittleness plasticizers or softeners are used. These materials, whether liquid or solid, are virtually non-volatile.

Non-volatility, then, is one of the most important properties of a plasticizer. Other desirable characteristics are resistance to moisture, atmospheric oxidation, light and moderate heat; miscibility and non-reactivity with cellulose derivatives, resins, and solvents; non-miscibility with water; neutrality, and lack of color and pronounced odor.

Plasticizers affect the "secondary flow" and consequently the gloss of the film.

Liquid plasticizers are considered more desirable than solid plasticizers. One explanation for this is that solid plasticizers might crystallize from the film when used under unfavorable conditions. Such is the case with triphenyl phosphate. The reason for this condition is that the temperature of the solution at the critical point is above the atmospheric temperature and the amount of softener is in excess of that which can be held in stable solution at that temperature. This condition may be remedied by using smaller amounts of plasticizers or adding another plasticizer, the critical solution temperature of which is well below the atmospheric temperature.

The action of a plasticizer in a film depends upon the concentration of the plasticizing material present. This was shown by previous investigation of Bass and Kauppi (1,2). The plasticizer at low concentrations seems to act as a flexible adhesive between the molecules of the cellulose chain. Increase of plasticizer concentration causes the molecules to become surrounded by the fluid and the plasticizer acts as a lubricant. The chains of ethylcellulose are thus separated and the film weakened with a consequent reduction of yield point. This reduction of yield point in some cases is considerable. Increase of complexity of the molecule of a plasticizer in a given series causes the yield point to become higher.

RAW MATERIALS

The raw materials used in this investigation included ten different plasticizers; ethylcellulose of standard, medium, and low ethoxy grade; toluene and ethyl alcohol.

The properties and source of the plasticizers used are given in the following table:

TABLE I

PROPERTIES OF PLASTICIZERS*

Plasticizer	Source	Boiling Range °C	Melting Point °C	Specific Gravity
Dow Plasticizer 6	Dow Chem. Co.	280	-	1.230
Trioresyl Phosphate	Monsanto Chem. Co.	235 to 265	18	1.18
Triphenyl Phosphate	Dow Chem. Co.	368	49.9	1.185
Dibutyl Phthalate	U. S. Ind. Chem., Inc.	195 to 200	-	1.043
Diphenyl Phthalate	Monsanto Chem. Co.	250 to 257	70	-
Castor Oil	No information available			
Cocoanut Oil	No information available			
Blown Linseed Oil (No. 100)	Archer-Daniels- Midland	-	-	0.997
Blown Castor Oil (Pale No. 16)	Baker Castor Oil Co.	-	-	1.030 to 1.040
Butyl Stearate	--	220 to 360	19.5	0.855 to 0.857

*See Gardner, "Physical & Chemical Examination of Paints, Varnishes, Lacquers and Colors", 9th Edition, pages 533, 575-578 for specific conditions.

The ethylcellulose was supplied by the Dow Chemical Company and had the following properties:

TABLE II
PROPERTIES OF ETHYLCELLULOSE

Ethoxy Type	Standard	Medium	Low
Ethoxy content	48.5% to 49.5%	45.0% to 46.5%	41.0% to 45.0%
Viscosity, centipoises	20	20	20
Softening point, °C	138 to 133	155 to 145	205 to 150
Melting point, °C	173 to 165	195 to 185	210 to 200

The ethyl alcohol had a specific gravity of 0.789 and a boiling point of 78.4°C.

The toluene had a specific gravity of 0.866 and a boiling point of 111°C.

The paper used in the block and tack tests was special high-gloss paper, and in the print tests was kimpac paper.

EXPERIMENTAL

Various methods, such as block, print, and "tack by feel", have been used previously to determine whether or not a film is dry. Block tests are less universal than the other two, and consist in folding a paper on which the film has been cast so that the paint films are adjacent. In print tests, a rough cloth is placed over the film and a weight is applied. Probably the most widely used, and certainly the least reliable, in a quantitative sense, is the "tack by feel" method. The result in this case is complicated by many factors such as moisture on the hands, humidity, condition of surface. These three tests were employed in this investigation in the manner described below.

The solutions were made up to 20% solids by weight and allowed to mix thoroughly on a tumbling mill until they were homogeneous. The amount of plasticizer was calculated as percentage of total solids. After selection of a starting percentage, more or less plasticizer was used in the following solution depending upon whether the individual tests gave satisfactory or unsatisfactory results. Solvents used were in the following proportions by volume:

TABLE III
SOLVENT COMBINATIONS

	Percent Toluene	Percent Ethanol
Standard Ethoxy	80	20
Medium Ethoxy	70	30
Low Ethoxy	60	40

The individual tests were run in the following manner:

BLOCK TEST

The films were cast to obtain a final dry film of 0.004 inches thickness on high-grade glossy paper and allowed to dry for six hours. When the films were dry the paper was folded so that two lacquer films were in contact and a lacquer film was next to an uncoated surface of the paper. The test samples were then placed in an oven maintained at 125°F under a pressure of 1 pound per square inch. The samples were allowed to remain in the oven overnight and were examined the following morning for adhesion between the various surfaces after 17 hours testing. In all cases, of course, adhesion between lacquer and uncoated surfaces was less than between lacquer surfaces.

PRINT TEST

Films were cast on polished plate glass panels. The films were allowed to dry for six hours and had a thickness of 0.004 inches. When they were dry a piece of kimpac paper was placed on the surface under a pressure of 1 pound per square inch. This test was run at room temperature. The sample was allowed to remain overnight and examined the following morning after 17 hours testing. Observations were made to see whether the kimpac paper adhered to the film or whether it left a print.

TACK TEST

Films were cast on high grade glossy paper as before to obtain a final film thickness of 0.004 inches. After the films were cast they were set aside and allowed to dry for 24 hours; then the tackiness was noted by feeling.

Results of these three tests are given in the following tables and indicate the limits of plasticizers that can be used.

DATA

TABLE IV

LIMITS OF PLASTICIZER CONCENTRATION¹ -- STANDARD ETHOXY

Plasticizer	Block	Print	Tack
Dow Plasticizer 6	30	30	45
Tricresyl Phosphate	20	20	35
Triphenyl Phosphate	20	25	35
Dibutyl Phthalate	20	25	35
Diphenyl Phthalate	20	35	40
Castor Oil	15	25	35
Cocoanut Oil	20	40	60
Blown Linseed Oil	30	45	60
Blown Castor Oil	35	35	45*
Butyl Stearate	20	50	60

TABLE V

LIMITS OF PLASTICIZER CONCENTRATION¹ -- MEDIUM ETHOXY

Plasticizer	Block	Print	Tack
Dow Plasticizer 6	35	60	60
Tricresyl Phosphate	30	50	60*
Triphenyl Phosphate	25	45	50*
Dibutyl Phthalate	30	50	70*
Diphenyl Phthalate	45*	45*	45*
Castor Oil	30	45	60
Cocoanut Oil	30*	30*	30*
Blown Linseed Oil	40	40*	40*
Blown Castor Oil	50	50*	50*
Butyl Stearate	30*	30*	30*

TABLE VI

LIMITS OF PLASTICIZER CONCENTRATION¹ -- LOW ETHOXY

Plasticizer	Block	Print	Tack
Dow Plasticizer 6	40	50	50*
Tricresyl Phosphate	35	55	55*
Triphenyl Phosphate	35	50	50*
Dibutyl Phthalate	35	50	65*
Diphenyl Phthalate	35	35*	35*
Castor Oil	35	50	55*
Cocoanut Oil	40*	40*	40*
Blown Linseed Oil	40*	40*	40
Blown Castor Oil	55	55	55*
Butyl Stearate	35*	35*	35*

¹ Plasticizer content, percent of the film.

*Next 5% increment caused incompatibility, although individual test was satisfactory.

RESULTS

The following conclusions can be drawn from the experimental work:

(1) All plasticizers tested could be used in fairly large amounts with satisfaction. As stated before, the yield point in some cases is so reduced that if an exceedingly tough film is desired the choice of a plasticizer in large concentration would be limited. It was also pointed out that viscosity does not materially affect the yield point; therefore, the use of a higher viscosity ethylcellulose than the relatively low 20 cps viscosity material used here would show increased toughness with virtually the same yield point.

(2) It was found that "tack by feel" tests are usually unreliable in determining tack, but that block tests are highly satisfactory, and produce a definite means of determining how dry a film is. The percentages reported as the maximum satisfactory were so reported whether films with an additional 5% of plasticizer were slightly or definitely sticky. For example, in the case of dibutyl phthalate and castor oil using medium ethoxy ethylcellulose, 30% of the plasticizer gave satisfactory block tests. Both gave unsatisfactory results at 35% of total solids, yet the dibutyl phthalate was recorded as having "much stickiness on block, while the castor oil had only a "slight amount".

(3) Incompatibility was encountered in several instances. This was especially true with medium ethoxy and low ethoxy, but was rarely evidenced when using standard ethoxy. The starred percentages listed in the tables are those in which the substitution of another 5% of plasticizer produced an incompatible film yet gave satisfactory tests. It was found that the phosphates could be incorporated,

generally, in much larger proportions than the oil type plasticizers without proving incompatible. Incompatibility was shown by blushing, greasiness, or crystallization of the film.

Several very interesting film failures were obtained. Most outstanding of the incompatible films was found in the case of butyl stearate and cocoanut oil. With 40% cocoanut oil in medium ethoxy and with 35% butyl stearate in medium, and 40% butyl stearate in low, a pronounced blushing resulted. The resulting films were opaque and resembled a white pigmented lacquer. In the case of butyl stearate there was a good gloss, while the cocoanut oil film had slightly less gloss. The film crystallized when using 55% triphenyl phosphate in medium ethoxy and 60% in low ethoxy. The film uniquely crystallized to a point in the center with 80% triphenyl phosphate in low ethoxy ethylcellulose.

(4) Magazine covers would require a lacquer coating free from stickiness because the magazines are bundled for transporting. The block tests would be most significant in this case, but it must be remembered that the tests were run at 125°F, a condition that would not be encountered in transporting magazines. In these cases slightly more plasticizer could be used. Results of block tests are much more definite quantitatively.

(5) Print tests are most important where the finished lacquer surface will be in contact with an unlike material. Furniture and toys are often lacquered and generally are in contact with cloth or some other fabric. There is possibility, too, that a pressure will be applied, and conditions will be met similar to those found in the experimental work.

Where adhesive tendencies are particularly desired, the following large percentages of plasticizers might be used with the ethoxy grade given:

Standard Ethoxy

1. 35% Dibutyl Phthalate, 65% Ethylcellulose
2. 45% Butyl Stearate, 55% Ethylcellulose

Medium Ethoxy

1. 65% Dibutyl Phthalate, 35% Ethylcellulose
2. 65% Triphenyl Phosphate, 35% Ethylcellulose (Incompatible)
3. 70% Dow Plasticizer 6, 30% Ethylcellulose (Incompatible)

Low Ethoxy

1. 80% Dibutyl Phthalate, 20% Ethylcellulose (Incompatible)
2. 80% Castor Oil, 20% Ethylcellulose

Extreme stickiness resulted in the block tests with these combinations. This condition was so marked that the folds of paper would not pull apart. Instead the lacquer films adhered so much that the folds of the paper pulled away in layers leaving a portion of the fold clinging to the other fold and film. Larger percentages, of course, would cause more pronounced stickiness, but in cases where incompatibility is indicated these combinations might be undesirable.

EFFECT OF ORANGE PEELING ON TESTS

The films showed orange peeling in a great many of the medium ethoxy and low ethoxy solutions resulting no doubt from too rapid evaporation of the solvent. It was thought that this orange peeling might have some influence on the tests and cause unsatisfactory results on block and print when use of a higher boiling solvent combination would give satisfactory tests. The following six solutions were prepared in order to determine whether or not this was the case:

- I. 1. Standard Ethoxy, 25% Dibutyl Phthalate
2. Medium Ethoxy, 35% Tricresyl Phosphate
3. Low Ethoxy, 40% Castor Oil
- II. 1. Standard Ethoxy, 25% Diphenyl Phthalate
2. Medium Ethoxy, 40% Castor Oil
3. Low Ethoxy, 40% Triphenyl Phosphate

When made with the regular solvents solutions in Group I did not show orange peeling but gave unsatisfactory results on block or print tests. Solutions of Group II did show orange peeling with regular solvents and gave unsatisfactory results on block or print tests. It was felt that by choosing two such groups the tests would be made more general. The percentages were chosen at the turning point, that is, at the percentages which had just become unsatisfactory. To make the check complete, different types of plasticizers were chosen. Types selected were a phosphate, a phthalate, and an oil. Butanol with a boiling point of 117°C was the solvent selected to lessen the rate of evaporation. The following special solvent combinations by volume were used:

TABLE VII
SPECIAL SOLVENT COMBINATIONS

	Percent Toluene	Percent Butanol	Percent Ethanol
Standard Ethoxy	70	20	10
Medium Ethoxy	60	20	20
Low Ethoxy	50	30	20

The films were cast and found to be free of the objectionable orange peel. Tests on block and stickiness gave results identical to those on solutions with regular solvent combinations, and demonstrated that the orange peel did not have any influence in the tests used in this investigation.

MISCELLANEOUS OBSERVATIONS

Most interesting in the tabulated data is the fact that with medium and low ethoxy ethylcellulose almost all the tack tests were satisfactory. The materials became incompatible before the tack point was reached.

Another interesting point in the experimental work was the range over which the butyl stearate had to be taken when using standard ethoxy to reach the limits with which the tests were satisfactory. Here the range was 40%, while with medium ethoxy and low ethoxy there was no range. Tests were discontinued, though satisfactory, because the materials became incompatible at 35% plasticizer with medium ethoxy ethylcellulose and 40% plasticizer with low ethoxy ethylcellulose.

It was suggested that after only six hours of drying in air the films cast for block tests and print tests might still have retained some solvent. To check this suggestion two groups of films were prepared. One group was handled the same as described previously and the other group dried in the oven for 2 hours at 150°F and then dried for 4 hours in air. Both groups were put under test at the same time. Results were virtually identical, and indicated that there was very little solvent retention.

It was observed that when blushing might have been the result of high humidity, the films on paper still retained gloss; but when the solutions were incompatible, the films on paper had little or no gloss.

SUMMARY

Results of the investigation of various plasticizers in solution with ethylcellulose can be summarized as follows:

(1) All plasticizers tested can be used in fairly large amounts. Reduction of yield point and increasing softness as the percentage of plasticizer increases, however, would limit the choice.

(2) Block tests are usually most reliable in determining tackiness. Tack tests by feel on paper are unreliable.

(3) The choice of plasticizer is limited by compatibility characteristics in the case of medium ethoxy.

(4) The block test is most significant when the finished lacquer surface is to be placed next to a like surface, as in the case of magazine covers. In such instances almost any of the plasticizers would prove successful.

(5) The print test is most significant when the finished lacquer surface is to have contact with a different material. The choice of plasticizer here may vary with the percentage to be used.

(6) Unusual adhesive properties are shown in some instances by dibutyl phthalate, butyl stearate, and castor oil.

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PART II

EFFECT OF ETHYLCELLULOSE IN SPIRIT VARNISHES

INTRODUCTION

The object of this investigation was to determine the effect of substituting ethylcellulose for resin in spirit varnishes. The effect was observed by running abrasion, hardness, cold check, moisture resistance, and melting point determinations.

Ethylcellulose has found application in lacquers, in foils, in paper coatings, in plastics, in waxes, and in various other coatings when it was desired to impart some of the distinctive properties of ethylcellulose to the other materials. Among these properties are increased toughness, hardness, and moisture resistance.

HISTORICAL

Ethylcellulose has found application in various coatings, but it has not been employed commercially in spirit varnishes.

Its use in varnishes of any type, of course, is limited because of the relatively low price of varnishes as compared to the price of the cellulose derivative. There may be cases when a small amount of ethylcellulose can be employed and certain special properties given to the finished coating. A small differential on the price of the varnish, therefore, would be justified.

THEORETICAL

Varnishes are grouped into two general classifications--spirit varnishes and oleo-resinous varnishes. Spirit varnishes contain only solvent and natural resin, while oleo-resinous varnishes contain, besides the solvent, either natural or synthetic resins, and oils. Because of the nature of the raw materials, spirit varnishes are cheaper and find application when an inexpensive coating which can be supplied in large quantities is desired.

Many types of natural resins occur in large quantities. These resins are obtained either by tapping the trees or by gathering the exudations from them. The oleo-resinous varnishes, which are expensive, include the rubbing varnishes, furniture and floor varnishes. Among natural resins used in spirit varnishes are pontianak, manila, dammar, shellac, and congo. Pontianak and manila were chosen for this work as being representative of natural resins used industrially.

The resin cut of 3.0 pounds per gallon of solvent was chosen as being representative of the cut used in industry. The choice of cut depends upon the viscosity and solids content desired for the finished varnish.

RAW MATERIALS

The raw materials used were ethylcellulose, manila and pontianak resins, denatured ethyl alcohol, and toluene.

ETHYLCELLULOSE

This material, supplied by the Dow Chemical Company, was the standard ethoxy grade containing 48.5% to 49.5% ethoxy. It had a viscosity of 20 centipoises as determined on a 5% by weight solution in 80:20 toluene-ethyl alcohol solvent at 25°C. The softening point of the ethylcellulose was 138 to 133°C and the melting point was 173 to 165°C (1).

MANILA RESIN

Manila resins belong to the general class of Copal resins and are obtained from the *Agathis Alba* tree. The resin is obtained either by tapping the tree or by collecting the exudation resulting from accidental wounding. Further classification of the resin depends upon whether it is gathered from the wound after a few years or dug up after a long period underground. In the latter case the resin is graded according to color, size, and contamination. The small pale chips, the DBB grade of resin used in this investigation contained some bark and foreign matter. This resin had a specific gravity of 1.06 to 1.07, a softening point of 78 to 88°C, and a melting point of 120 to 129°C.

PONTIANAK RESIN

Pontianak is a semi-fossil copal belonging to the manila

group of resins. It is the exuded material gathered from the wound after a few years. After the resin is gathered it is graded according to color, size, and contamination.

The chip form used in this investigation had a specific gravity of 1.07 to 1.08, a softening point of 82 to 132°C, and a melting point of 136 to 156°C.

ETHYL ALCOHOL

The denatured ethyl alcohol had a specific gravity of 0.789 and a boiling point of 78.4°C.

TOLUENE

The toluene had a specific gravity of 0.866 and a boiling point of 111°C.

EXPERIMENTAL

Many methods of testing coatings including paints, varnishes, and lacquers have been devised to compare physical properties of their films. The effect of operating conditions and the varied equipment available make it impracticable to get more than a relative test of a series of paint compositions. In this research spirit varnishes containing varying percentages of ethylcellulose were compared. Varnishes were made using pontianak and manila resins and the following tests were run:

- (1) Abrasion Resistance
- (2) Hardness
- (3) Cold Check
- (4) Melting Point
- (5) Moisture Resistance

ABRASION RESISTANCE

The abrasion resistance or abrasion value of a film has been determined in several ways by other experimenters. The abrasion factor is influenced by several conditions. Schuh and Kern (5) have noted several contributing factors such as relative humidity and temperature, particle size of abrasive, rate of flow of particles, air pressure, the angle of inclination of panel. It must be remembered, though, that resistance to abrasion is not the same as resistance to wear, because the latter includes several factors besides resistance to abrasion. It is sometimes true that films having great abrasion resistance are often soft, and so there is no direct connection between abrasion resistance and hardness.

Several abrasives and methods were available for the tests. As outlined by Gardner (3) abrasives that can be used include carborundum particles, Ottawa sand, and more recently, artificial aluminum oxide. Methods of Koch (4) and others conclude in either measuring the amount of abrasive used to wear away the coating, or determining the loss in weight of the coating. The method of testing depends, in some cases, upon the use to which the final paint is to be subjected. Thus, in testing traffic paints, a solid rubber tire rotating at 2000 r. p. m. has been employed, while the modified Dorry apparatus used by the New York State Division of Highways for highway traffic paints utilizes a revolving abrasive material.

The use of carborundum has been advocated on the basis that it flows more freely than other materials and is not affected by moisture; however, it has a tendency to shatter. Sand in some cases does not give a rapid enough test, but was selected as the material to be employed here.

In this investigation abrasion resistance was determined by allowing dry Ottawa sand to fall freely through a 1 foot length of 8 mm. glass tubing onto a glass panel coated with the varnish to be tested. The average particle size of the sand was 1 mm. and the glass panel was inclined at an angle of 45° .

The weight of sand needed to wear just through the film was determined, and the thickness of film at the point of failure was measured. The abrasion value of the film was recorded as the weight in grams of sand needed to wear through a film of 0.0010 inches in thickness.

HARDNESS

As stated previously a film having great abrasive resistance might be soft. However, similar effects to those obtained in abrasion tests are noted in hardness tests when varying the relative humidity and temperature. Hardness tests are divided by Gardner (2) into three general procedures:

- (1) Scratch Hardness
- (2) Pendulum Hardness
- (3) Indentation Hardness

In scratch hardness points of various abrasive materials such as steel points, lead pencils, and steel knives are drawn over the coating and the result becomes the hardness of the abrasive necessary to cut through the film.

Pendulum hardness utilizes a swinging beam or two parallel rocking rings known as the Sward Rocker.

Indentation hardness tests include the Pfund, in which the load necessary to produce a certain indentation by a spherical tool is measured, and imprint tests which use a cloth material to form a print on the coating.

There is very little correlation between the various hardness tests.

The scratch hardness method was used here. In this test Venus drawing pencils were drawn over the films of equal thickness cast on plate glass. The hardness of the lead increases with increasing H number. The pencils were held at an angle of 45° and ordinary writing pressure used. Those films, which were harder

than the lead showed only a black mark on the surface. Films softer than the lead were scratched, and the material was torn away from the glass panel. Hardness was recorded as the number of that pencil needed to scratch the surface.

COLD CHECK

Steel panels on which the varnish films had been cast to equal thickness were alternated between an oven maintained at 120° to 125°F and a cold box maintained at 25° to 30°F. Panels were left in each chamber for periods of an hour and examined after each cycle. The cycle number on which definite checking of the film occurred was recorded as the point of failure. All panels were subjected to twelve complete cycles whether or not they had failed on an earlier cycle.

MELTING POINT

Virtually all methods used in determining the melting point of a resin employ a mercury layer over a resin plug in a tube. The resin upon melting rises to the surface of the mercury. The melting temperature is recorded as the temperature at which the resin appears on the top of the mercury layer. The familiar ball and ring method is still another way of determining melting point.

In this work the method was much simpler. The dry film was powdered and placed in a capillary tube in an oil bath. The oil was heated and the fusion range of the material recorded.

MOISTURE RESISTANCE

Varnish films of equal thickness were cast on plate glass panels and immersed in water for 24 hours. The panels were then removed and examined for effects of the water on the film. They were rated numerically in the order of their discoloration. After a period of drying in air the films were again examined to determine whether any had returned to the original state.

PROCEDURE

The procedure in each of the varnish series was as follows:

The resins were dissolved in alcohol and the ethylcellulose in toluene by tumbling on a roller mill. When thoroughly mixed, the two separate portions were combined and sufficient solvent was added to bring the cut to 3.0 pounds of resin per gallon of solvent. The mixture was made homogeneous by further tumbling and then filtered to remove the dirt and insoluble materials. The solvent consisted of 75% alcohol and 25% toluene by volume.

Films were prepared on glass for moisture resistance, abrasion resistance, hardness tests, and on steel panels for cold check tests. They were cast to equal thickness, and in the case of abrasion resistance the thickness was measured.

DATA

PONTIANAK VARNISHES

PERCENT ETHYLCELLULOSE

	0	5	10	15	20	25
ABRASION RESISTANCE						
Grams of sand required to penetrate film of 0.0010" thickness	24	40	1920	5280	8250	9800
HARDNESS						
Venus Pencil Number	2H	3H	4H	4H	4H	5H
COLD CHECK RESISTANCE						
Cold cycle on which definite failure occurred	2	3	4	5	11	12
MELTING RANGE						
Degrees Centigrade	143 to 153	146 to 156	149 to 159	151 to 161	153 to 163	155 to 165
MOISTURE RESISTANCE						
Order of Resistance	4th	3rd	2nd	1st	1st	1st

MANILA VARNISHES

PERCENT ETHYLCELLULOSE

	0	5	10	15	20	25
ABRASION RESISTANCE						
Grams of sand required to penetrate film of 0.0010" thickness	60	68	4230	7320	11416	13410
HARDNESS						
Venus Pencil Number	2H	3H	3H	4H	4H	5H
COLD CHECK RESISTANCE						
Cold cycle on which definite failure occurred	3	4	10	11	>12	>12
MELTING RANGE						
Degrees Centigrade	120 to 130	123 to 133	128 to 138	132 to 142	136 to 146	140 to 150
MOISTURE RESISTANCE						
Order of Resistance	4th	3rd	2nd	1st	1st	1st

RESULTS

ABRASION RESISTANCE

A definite increase in abrasion resistance was obtained by substitution of ethylcellulose. This increase became very pronounced when at least 10% of ethylcellulose had been incorporated.

HARDNESS

Hardness of the films of varnishes containing ethylcellulose increased as more ethylcellulose was substituted. This is shown by increase in pencil number.

COLD CHECK

A gradual increase of resistance to cold check was noted upon substitution of ethylcellulose. Even after 12 cycles the manila varnishes containing 20% and 25% ethylcellulose had not failed.

MELTING POINT

As ethylcellulose was substituted the "melting range" rose. A "melting range" was obtained because with such materials it is impossible to get a definite fusion point.

MOISTURE RESISTANCE

The effect of moisture on the films was in all cases shown by a discoloration, which in the worst instances became a pronounced blushing. Adhesion to the glass panel was also materially reduced and in some cases, the film became completely detached from the panel. Films that contained no ethylcellulose showed marked

discoloration, while those containing 5% and 10% ethylcellulose were slightly discolored. Those containing 15% and more ethylcellulose were not discolored. After immersion the panels were dried in air and examined for permanent discoloration. Those varnishes that contained ethylcellulose regained their original appearance while those without ethylcellulose retained the discoloration.

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APPENDIX

The author has undertaken a study of the reaction involved when ethylcellulose is incorporated into a varnish. The object in this investigation is to determine whether there is merely a physical dispersion or actually a chemical reaction. The simple constituents of a varnish were selected as raw materials. These were oleic acid, linoleic acid, and soybean oil. Ethylcellulose to be used is of standard and medium ethoxy grade, of 7 and 145 centipoise viscosity types. The solvent to be employed is diethyl benzene. The following procedure for oleic acid is to be used in general for the other materials:

1. Heat together 30 parts ethylcellulose and 70 parts diethyl benzene to drive off all air and water.
2. Heat together 30 parts oleic acid and 70 parts diethyl benzene to drive off all air and water.
3. Mix equal parts of both of these mixtures and reflux. Run viscosity determinations every ten minutes, and discontinue heating when viscosity has reached a minimum.
4. Calculate the percentage of fatty acids reacted from the amount of water collected.
5. Determine acid number and saponification number of the mixture.
6. Steam distil off the solvent from some of the mixture. Saponify this residue with alcoholic caustic, add water, and boil off the alcohol. Filter and wash the precipitate. Determine the percentage ethoxy of the dry precipitate.

The procedure outlined will indicate the following:

1. Acids that have combined with the ethylcellulose will be determined by the difference between acid number and saponification number.

2. The amount of water collected and the difference between saponification and acid numbers will indicate whether there is more reaction of high viscosity than low viscosity ethylcellulose. If there is more reaction it will show that the addition takes place wherever the cellulose chain is broken.
3. Esterification of unethylated hydroxyl groups will be indicated by more reaction of medium ethoxy than standard ethoxy ethylcellulose.
4. Splitting off of ethoxy groups will be indicated by reduction of percentage ethoxy as compared with the original ethylcellulose.

This work is now in progress and is being carried on by Mr. Virgil H. Mulette, Jr., the Dow Chemical Company Fellow for 1940-41.

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VITA

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He was awarded the Dow Chemical Company Fellowship for the year 1939-1940, and upon completion of his academic work was employed by the Dow Chemical Company at the plant in Midland, Michigan.

Mr. Hutchison is a member of Sigma Tau, national honorary engineering fraternity, and Theta Chi Delta, national honorary chemistry fraternity. He was secretary of the student chapter of the American Institute of Chemical Engineers, and historian of the Omicron chapter of Sigma Tau.

He is co-author of the paper, "The Physical Properties of the Ternary System Butyl Alcohol-Ethyl Acetate-Toluene" which appeared in the March, 1940, issue of the Journal of Physical Chemistry.