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UNIVERSITY OF LOUISVILLE

PIGMENTATION OF ETHYLCELLULOSE
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

Alvin Walter Graef

1940

PIGMENTATION OF ETHYLCELLULOSE

VARNISHES

Alvin W. Greaf

Approved by Examining Committee:

Director
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May 23, 1940

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LIST OF SYMBOLS

The first initial (V) in the code formula number indicates that it represents a varnish. The first numeral denotes the type of oil which predominates in the varnish. The second and third numeral denotes the percentage of ethylcellulose in the varnish. The next letter signifies the type of gum in the varnish. If two letters are in the formula number, then there are two gums in the designated varnish; for example, "V-18-DE" is a wood oil varnish containing eight per cent ethylcellulose, Durez 210 and ester gum.

The following are the code symbols as used in this investigation:

First Numerals

- 1- China Wood Oil
- 2- Dehydrated Castor Oil
- 3- Bodied Perilla Oil
- 4- Ciccoil
- 5- Linseed

Last Initial

- D- Durez 210
- E- Ester Gum

The length is not designated for practical reasons, and the blank varnishes are represented in the percentage spaces by "00", e.g. V-100-D.

LIST OF FORMULAS

Formula No. 1	V-18-D, Eight Per Cent Ethylcellulose Wood Oil-Perilla Oil Varnish	35
Formula No. 2	V-210-D, Ten Per Cent Ethylcellulose Dehydrated Castor Oil Varnish	36
Formula No. 3	V-310-D, Ten Per Cent Ethylcellulose Perilla Oil Varnish	37
Formula No. 4	V-410-D, Ten Per Cent Ethylcellulose Ciccoil Varnish	38
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ACKNOWLEDGEMENT

The Author wishes to acknowledge the
kind and helpful guidance
of Dr. R. C. Ernst who
directed this research

ABSTRACT

A study was made of pigmented ethylcellulose varnishes containing five different oils, namely: china wood oil, perilla, dehydrated castor oil, siccoil, and linseed oil. The length of each varnish was twenty-five gallons long, except the linseed oil vehicle which was twenty gallons in length.

The effects of various percentages of ethylcellulose on the clear and pigmented vehicles were studied. An investigation of the properties of ethylcellulose varnishes at different cooking schedules and the effects on these vehicles with increased pigmentation was made.

Five gallons of perilla oil were substituted for wood oil in the twenty-five gallon lengths in order to increase the compatibility of ethylcellulose in this type of varnish. Eight per cent ethylcellulose based on total solids of the varnish was the maximum amount that could be cooked in the wood oil - perilla oil combination. This eight per cent wood oil - perilla oil varnish decreased in gloss when pigmented. This was remedied by prolonging the gelatin time of the wood oil with a ten per cent ester gum substitution in the resin formulation. The flow and gloss of an enamel made with this varnish was equal to the blank control enamel.

Typical formulations of excellent standard qualifications were adopted for testing the ethylcellulose varnishes. Each was compared to a blank control. Those formulations used for this part of the investigation were; quick drying, high gloss, brushing enamels, short oil length, dipping, baking enamels, flat wall, and wood and metal primers.

INTRODUCTION

With the introduction of ethylcellulose to the lacquer industry, it was found that many of its physical properties made it a potential raw material for varnish and enamel products. The chief characteristics which pointed to its usefulness in the paint and varnish industry were its ability to increase drying rates and to increase film toughness, flexibility, hardness, and alkali resistance.

It is the purpose, therefore, of this investigation to find the proper means of incorporating ethylcellulose in an enamel product, to determine its effect on the physical properties of the enamel, and its advantages in practical enamel formulations.

The observations made during this work were particularly concerned with the effect of ethylcellulose on the gloss, drying, body, resultant film characteristics, and the application to the various types of enamels.

The inability of obtaining gloss in some of the enamels was the main difficulty, but this was worked out satisfactorily by properly incorporating the ethylcellulose in the varnish cook.

The tests made on the final enamel products were: brushability, dipping, effects of baking, water resistance, abrasion resistance, and package stability. Attention was given to the mixing and grinding or the wettability of the

various pigments in the ethylcellulose vehicles.

Most tests and observations were not measurable. In order to have some method of measurement, each varnish and enamel formulation was compared with a blank varnish or enamel.

HISTORICAL

Cellulose, a widely used material industrially and the chief constituent of the cell walls of plants, has been known for many years, some of its derivatives being discovered in the eighteenth century. The early use of nitrocellulose was in the production of military explosives which were introduced by the British scientist Abel. In 1885 Chardounet (2) made the first artificial silk from a cellulose derivative. We now know it best as the chief constituent of pyroxilin lacquers.

Ethylcellulose is a twentieth century discovery. In 1904-1905, Wilhelm Suida (10), a pioneer in the cellulose industry, unwittingly opened a broad new field in organic chemistry. He was studying, at that time, the tinctorial strength of various dyestuffs in carbohydrate bodies, particularly in cellulose. On January 12th, 1905, he sent a memoir to the "Monatshefte fuer Chemie" of Vienna for publication in which he described the method of the etherification of cellulose.

Very little attention was paid to Suida's discovery, however, for it was not until 1912 that various patents were taken out for the practical production of cellulose ethers. Otto Leuch (10), of Germany, and Henry Dreyfus, a Frenchman, were the first of the original patentees. Because of the hostilities in Europe, Otto Leuch (10) took out a U. S. Patent on August 8, 1917, but it was never used advantageously in this country.

Prior to the World War, the cellulose industry in America was in its infancy. The war, however, was a great impetus to the developement of a number of modern cellulose derivatives.

During the post-war days the explosive producer was forced to do something to meet changing economic conditions. New products had to be born to take the place of gunpowder which had consumed the largest part of cellulose produced each year. The industry then put to work their vast number of research men to find new useful derivatives of cellulose. Through their great knowledge of cellulosic material, which they had obtained during their studies with explosives and nitrocellulose, these men were able to reach their objectives, and they gave to the chemical industry many new materials with which to work. One of these new materials was ethylcellulose.

Ethylcellulose is becoming one of the most interesting of the cellulose derivatives. Although this compound has been known for years, it was not until about 1928 that a practical useful patent was taken out in the United States, for its commercial manufacture. Before 1928 virtually all the ethylcellulose used in this country was imported. Now commercial ethylcellulose is made in increasing amounts by the American manufacturers. The price on to-day's market is forty-eight cents per pound, which is much lower

than the imported material, and it is predicted that it will soon be produced at a much lower cost.

The early use of this new raw material was in the lacquer and plastic industries. Because of its extraordinary characteristics of toughness, flexibility, low flamability, freedom of discoloration by sunlight, heat resistance, solubility in cheap solvents, excellent miscibility in plasticizers, oils and resins, and elimination of surface tackiness, it is a raw material of great possibilities. Some of its other uses are found in adhesives, printing inks, leather finishes, electrical insulation, wax tougheners, and pigment-grinding bases.

The latest work that has been done with ethyl-cellulose as a raw material in the paint and varnish industry is its application to quick-drying finishes.

THEORETICAL

There are numerous cellulose derivatives because the hydrogen of the hydroxyl groups can be replaced with substituted radicals of organic compounds and the metals of inorganic salts. In its simplest formula, $C_6H_{10}O_5$, there are three OH groups which behave, in all their relations, exactly as do the OH groups in alcohols. Cellulose reacts to form organic esters such as nitro and acetyl cellulose, and it is capable of undergoing alkylation to form a number of ether compounds of which methyl, ethyl, and benzyl are the most prominent.

Ethylcellulose is a cellulose ether made by the reaction of ethyl chloride with alkali cellulose. This alkylation product, like other cellulose ethers, is incapable of undergoing hydrolysis which makes it acid and alkali resistant. It will not "blush" in a film because it is non-hygroscopic. The type reaction of its formation is illustrated by the following equations:

The preparation of ethylcellulose is described by Groggins (6) as follows:

"One hundred parts of cellulose is impregnated within a 1000 parts of a 20 per cent sodium hydroxide solution and after standing 24 to 72 hours are pressed until the weight has been decreased to 600 parts. The pressed residue is then disintegrated and after standing from

one to three days is placed in a vacuum shelf dryer or vacuum kneading machine and is dried to a temperature below 10°C . until the test shows that the soda cellulose contains from 10 to 25 per cent of water. The dried alkali cellulose is then placed in an autoclave which is rotated and which is provided with a stirring device, two hundred parts of ethyl chloride is then added and the mixture is heated to 90 or 100°C . for 20 hours. During the reaction the mass is stirred, and the autoclave is kept running.

"After the autoclave has cooled, the contents are mixed with water and are poured into a filter or a decanting apparatus, washed with water, treated with dilute sulfuric or hydrochloric acid, again washed, and then dried. The resultant ethylcellulose is a powdery flocculent substance which is soluble in a number of organic solvents."

The maximum degree of alkylations of cellulose to form ethylcellulose is the tri-ethyl derivative. The most useful commercial grades contain from 2.15 to 2.58 ethoxy groups per glucose unit. This corresponds to an ethoxy content between 43.5 to 49.5 per cent. (3)

The absolute viscosity of these two grades is measured in centipoises of a 5% solution by weight in a 60:40 Toluene - Ethanol mixture. The material used in this investigation is the 49.5% type having a 10 centipoise viscosity. This viscosity is comparable to the 2-2½ seconds viscosity measured by the falling ball method using a 20% solution in 70:30 Benzene-Methanol mixture. The properties of the resultant ethylcellulose treated product depend upon the ethoxy content and the viscosity of the ethylcellulose.

The degree of ethylation of cellulose depends upon the mol ratio of cellulose to ethyl chloride. This ratio was found (11) to be 1.48. At high temperatures, other constants remaining the same, higher ethoxy values are obtained than at the lower temperatures. Another influencing factor on the alkylation degree is the concentration of the sodium hydroxide. Seldom are the conditions so perfectly adjusted that completely ethylated cellulose molecule is obtained.

Ethylcellulose has many contributing properties for its use in plastic and lacquer products. Those which are of practical use in this investigation are; stability to heat and light, film toughness and flexibility, solubility in cheap solvents, miscibility with most oils and resins, alkali proofness, resistance to acids, and acceleration drying of varnishes.

These are two methods for the incorporation of ethylcellulose in oleo-resinous varnishes. The first and simplest is "cold-cutting" the ethylcellulose in a suitable solvent and adding it to the varnish. The other method which is quite complex, although the more practical of the two procedures, is that of incorporating the desired percentage in the varnish on the down heat. This method is described later in this section and is the method used in this investigation.

Both methods have their advantages and disadvantages. An accelerated drying varnish of low solids content may be desired and can be obtained by cold-cutting the correct amount of ethylcellulose solution in a regular varnish. A varnish of low solids content is not generally adaptable to regular formulations. The cooking method produces a varnish of higher solids and increases the tolerance of the ethylcellulose varnishes for naphthas and other cheap solvents. Its greatest advantage over the cold-cut method is that its resultant varnish is a more homogeneous solution of resin, oil, and cellulose polymers. Therefore, the "cooking-in" method is the most accepted procedure.

The solubility and compatibility of ethylcellulose with various resins, oils, and solvents is of particular importance in the cooking procedure. Although it is compatible in many of the varnish raw materials (3), serious difficulty is encountered when the wrong selection of materials, their proportions, and the incorrect cooking procedure is made.

The ethylcellulose of 49.5% ethoxy content and ten centipoise viscosity is the best type for varnish work. This ethoxy ethylcellulose is soluble in all types of solvents except naphtha, aliphatic hydrocarbons, and polyhydric alcohols. The thinners generally used in this type of varnish are the aromatic naphthas (3). When an

ethylcellulose varnish is thinned with a solvent like Solvesso No. 2 or Union 30, a large portion of the thinner combination can be petroleum naphtha. Equal parts of these two types of thinners are used in most ethylcellulose varnishes and in some cases a higher percentage of naphtha is permissible.

A summary (3) of the compatibility of ethylcellulose with various resins is shown in Table I. It can be seen from this table that ethylcellulose is compatible with most of the common varnish resins.

The oil compatibility of ethylcellulose is quite good; the degree of solubility varying, however, in the different oils. Linseed, soybean, and perilla are easily fortified with ethylcellulose to produce bodied oils of outstanding characteristics. These oils react the same with ethylcellulose when used in varnishes.

TABLE I

SUMMARY OF COMPATIBILITY OF ETHYLCELLULOSE WITH VARIOUS RESINS BY TYPES

COMPATIBLE IN ALL PROPORTIONS

Pure Phenolic

Modified Phenolics

Rosin

Rosin esters

Toluene sulfonamide-formaldehyde

INCOMPLETELY COMPATIBLE

Alkyds:

long oil modified

rosin modified

phenol modified

Maleic-rosin esters

Urea-formaldehyde

Vinyl ester polymers,

copolymers and

acetals

Cycloparaffins

Coumarone-indenes

Most natural resins

Copolymers of acrylic

esters

INCOMPATIBLE

Short oil alkyds

Pure polymers of

methacrylic

esters

China Wood Oil is the most difficult of all the oils to incorporate with ethylcellulose into a varnish. Cicoil reacts similarly but to a less extent. The lengths of these types of varnishes and the percentage of ethylcellulose are the deciding factors in making a homogeneous product.

Ethylcellulose treated oils produce tougher films as compared to regular bodied oils. They also dry more quickly, have less penetration, and are more thixotropic.

The method of cooking ethylcellulose in varnishes does not vary, to a large extent, from the general procedure, but as with other raw materials it requires certain knowledge and experience of the operator. Over cooking of the ethylcellulose in the varnish is as detrimental to its properties as undercooking. Overcooking produces a dark colored varnish of slow drying properties and undercooking renders a high viscosity vehicle which yields a hazy film as the result of incomplete solution of the ethylcellulose. Insufficient cooking will result in the precipitation of ethylcellulose because of improper incorporation.

Ethylcellulose varnish cooking procedures will vary with the resins and oils but the point at which it is added to the cook, regardless of the formulation, is on the down heat and at a temperature between 450° and 500°F.

An example of a typical twenty gallon long

ethylcellulose varnish cook is as follows:

Place in the kettle 100 pounds of resin and 16 gallons of the oil, run the temperature to about 565°F in 30 minutes and check with the remainder of the oil to be between 450 and 500°F. At this point add the desired percentage of ethylcellulose and hold 10 to 30 minutes until a clear pill is obtained on a glass slide. This time limit depends upon the oil and the resin; the formula refers to tung oil. About five minutes after the addition of the ethylcellulose, add 1% lead acetate, based on the oil, to the batch. The varnish is then cooled and thinned to fifty per cent solids with 50:50 mixture of Solvesso No. 2 and Mineral spirits. Naphthenate driers are added in the amounts necessary for the formulation.

This procedure will vary with the oil and resin used in the formulation. For instance, for a linseed oil 100% phenolic varnish, the oil is taken by itself to 585°F and held for body, then checked with resin.

The length of time for holding the varnish, after the ethylcellulose has been added, depends upon the oil compatibility. The time element is important to this part of the procedure. The compatibility of the ethylcellulose, the viscosity of the resultant varnish, and the tolerance for naphtha type solvents are dependent upon the time period at 480°F. The longer the varnish is held at this temperature the lower will be its viscosity.

The behavior of the ethylcellulose molecule on being cooked into a varnish has not been exactly determined. N. R. Peterson (9) asserts that a mixed ester ether cellulose is formed by the action of the resin or oil fatty acids with the hydroxyl group in the ethylcellulose chain. He also states that the solubility of this mixed ester ether would be dependent upon the amount of esterification, and that the reacted ethylcellulose is present in the form of a collidal gel.

This theory is partly substantiated by the results obtained in the present investigation and by the work of Swiss patentees (11) who esterfied ethylcellulose with linseed oil, stearic acid, and oleaic acid to form ethylcellulose linoleate, stearate and oleate. Worden (11) states that such compounds are soluble in a wide range of inexpensive solvents, and that they have the desirable characteristics of both ether and ester compounds leaving or minimizing the undesirable properties of both classes.

When a small amount of metal, such as lead or zinc, is added to the ethylcellulose varnish cook a better solution is obtained. This is attributed to the retardation of the bodying action of the oil, thereby affording more time for the esterfication of the cellulose ether.

Another point that gives credence to this theory is that the viscosity of the resultant varnish is inversely proportional to the time. When the length of time for

holding the varnish (after the ethylcellulose has been added) is increased, a varnish of lower viscosity is obtained. The gel formation, as spoken of before, is produced in a smaller arrangement and the resin, oil, and cellulose polymers are more uniform throughout the varnish.

The pigmentation of varnish vehicles is a problem of a great number of variables and it covers a wide range of complex products. The incorporation of pigments with a vehicle is a good test of the vehicle practicability and of its various physical properties. The objective of a pigment combination is to add opacity and a decorative finish to a surface, and to increase the durability of the product.

It is not the purpose of this section to elaborate upon the fundamentals of the various pigmented formulations but to deal with the effects of pigments on the properties of the vehicle and to discuss the characteristics of the resultant pigmented product.

The first principle in obtaining good mixing of the pigment and the vehicle, is good wetting characteristics of the grinding medium. From the production standpoint and for all practical purposes, a liquid should easily take up the pigment on mixing and should wet the pigment particles with a minimum number of passes through the mill. A poor wetting vehicle will cause the "mix" to slip through the roller mill thereby reducing the "shearing action" on the material between the rolls. A poor wetting vehicle will

yield a seedy, un-ground product. Similar results are obtained when a poorly wetted mixture is ground on a stone mill. In this case the mill is overheated and the grinding time is increased.

Theoretically, when a liquid has wetted a pigment particle it has displaced the gaseous interface about that particle. Wettability is dependent upon the surface tension of the liquid and the solid and the adhesion tension between the liquid and solid. C. A. Murray and F. E. Bartell (8) found that the wetting of a solid by a liquid can be evaluated by the determination of the adhesion tension of the system.

The wettability of a liquid can be determined in a practical way by pigmenting it and observing the grinding results. The term "grinding" used here is synonymous to "wetting" because most pigments, received by the paint manufacturer, are capable of passing 95-98% through a 325 inch mesh standard sieve.

Some varnishes cannot handle as high a pigment - vehicle ratio as others. The amount and type of pigment controls their physical properties such as, working qualities, flow, and gloss. A false bodied liquid could not be very highly pigmented and used as a dipping product. Pigments help to increase the "set-up" of the film and, therefore, some fast drying varnishes are undesirable liquids for brushing enamels. Gloss is greatly affected by increasing the

pigment content in highly polymerized vehicles. The reason being that a highly polymerized vehicle has poor wetting characteristics or that the pigment has increased the "Yield value" or decreased the flow of the film.

Yield value has been studied by many investigators. It is described by H. A. Gardner and P. C. Holdt (5) as a force which resists the flow of the paint. The force which causes flow was termed by these investigators as a hydrostatic force. This force is opposed by the combined forces of yield value and the surface tension of the flowing material. A good flowing material will have a low yield value and low surface tension.

Flow is a direct function of yield value. A measurement of flow and the description of the apparatus for its evaluation is in the above mentioned paper (5). It is termed a "flow meter" and is the type of apparatus used in this investigation. This instrument was designed upon the previous work of R. D. Bonney (1). A description of this flow meter is inserted here to make clear the theory of its application. It consist of a glass plate resting on a leveling device and having drawn on its surface a series of concentric circles placed a quarter of an inch apart. On its center, is placed a cylinder whose volume is approximately one fluid ounce. The material to be tested is poured into this cylinder and leveled off at the top. The cylinder is then gently raised and the material is

free to flow over the glass plate surface. A definite time limit is set and the diameter or radius is recorded. The diameter of flow can be recorded at various time intervals and a plot of the two functions, time and flow can be made.

There are several factors which control the flow. The amount of pigment, its particle shape, the degree of wetting of the pigment (fineness of grind) has a lot to do with the flow of the paint. Surface tension and the type of vehicle are of great importance. A raw or bodied linseed oil will have a lower yield value than a spar varnish and again, a spar varnish will have a lower value than some alkyd liquids. A pigmented spar varnish has been found (5) to flow to a greater extent than a pigmented raw linseed oil.

The initial flow caused by the thinness in a vehicle must not be confused with the secondary flow which is governed by yield value. The addition of the right thinner will, in most cases, give the desired working properties, such as good flow under the brush and in spray application, so that brush marks or "orange peel" might be eliminated. Yield value is the measurement of plasticity and the addition of thinner will not decrease its opposing force to the flow of the paint.

In part six under Experiment Data, the flow as influenced by yield value is termed "diametrial flow". This is a common term used in the paint industry.

Poor wetting vehicles will not bring out the full strength of the colored pigments and in some cases cause

flooding. Flooding is influenced by many factors; the vehicle shares a portion of the blame in some formulations.

Stability of the paint product is important to the trade sales divisions of the industry. Highly reactive varnishes and pigments cause "livering" or aging. If the body has not progressed to a complete gel, it does, in some cases, increase to the point of undesirable working properties. Settling is another bad offender and is caused by improper wetting vehicles, extreme low viscosity liquids, improper selection of pigments, and numerous other reasons. A slight soap or gel formation will often eliminate this difficulty.

The foregoing statements on pigmentation are generalities and most of the problems mentioned can be solved either by the addition of a vehicle combination, proper solvent balance, or by a change in the pigment formulation. Often in the development of a problem, one quality is sacrificed to obtain two more important ones. The properties of various liquids are sometimes additive, and proper selection of them net better results.

**MATERIALS AND
APPARATUS**

All raw materials used in this investigation were of standard commercial grades. They were chosen for a particular purpose in a formulation when their individual properties were needed. They are classified here under resins, oils, thinners, driers, pigments, and miscellaneous.

The principal resin used was Durez 210 and was chosen because of its compatibility with ethylcellulose, its water resistance, and its adaptability to enamel formulation. It is a terpene phenolic resin having a melting point of 239°F to 248°F, specific gravity of 1.086, acid number 15-20, and color C-5 (Barnett).

The ester gum has an acid number between 6 and 8, melting range between 149°F - 162°F, and specific gravity of 1.10-1.15.

The China Wood Oil was of average grades having a specific gravity of 0.945, acid number 8, iodine number 163 and gelation time under Brown heat test of ten minutes (4).

Regular alkali refined perilla oil was bodied four hours at 575°F for a body of 2-3 according to the Gardner Holdt scale. No other properties were determined.

The dehydrated castor oil was made by the Sherwin Williams Company, Cleveland, Ohio. This has a trade name of "Dehydrol" and it is claimed to be completely dehydrated.

The Cicoil used in this work is an improved quality of oiticica oil produced by the Brazil Oiticica Oil Company

of South America. The gelling time of this oil if fifteen minutes, it has a specific gravity of 1.509 to 1.513 and an acid value of six (11).

Admolene is a quick bodying linseed oil. It has a specific gravity of 0.933, Iodine value between 175-190, and an acid number of about 0.25.

Diamond K is a special oil designed to increase the leveling and brushability of a pigmented product. It is a blown linseed oil having just enough linoleate drier added for proper drying in eighteen to twenty hours. It is manufactured by the Spencer Kellog Company and has a specific gravity of 0.993, acid number between 6 and 8, and viscosity of Z-3 (Gardner Holdt).

Solvesso No. 2 is a petroleum aromatic naphtha. It has a boiling range between 135°C - 174°C and weighs 7.15 pounds per gallon (3). Mineral spirits are aliphatic petroleum hydrocarbons which have a boiling range between 312°F and 394°F.

The two titanium pigments used were both manufactured by the Titanium Pigment Company, St. Louis, Missouri. The titanot A is a 98.5-99.5% pure titanium dioxide and is the low oil absorption type. The calcium titanium pigment has high oil absorption and contains 30% TiO_2 and 70% $CaSO_4$.

The chrom yellow was made by Kentucky Color and Chemical Company of Louisville, Kentucky. It is the regular

lead chromate pigment having a medium yellow shade. The Monastral Blue was Krebs BT - 100 - D a copper thiocyanide blue.

The inert or extender pigments were Surfix, Albacar, Asbestine, and Celite. The Surfix is a surface treated calcium carbonate and is used principally in primer finishes for extending the film and sealing the covered surface.

Albacar is a precipitated calcium carbonate. It has a high oil absorption value. The regular asbestine was used. It is a magnesium silicate of high oil absorption and has good extending qualities.

Celite 110 is a fine grade of SiO_2 . It has a amorphous nature and porous structure. Its color is white, has an oil absorption according to the Gardner-Coleman test of 170. It has very fine texture retaining only eight per cent on 325 mesh screen. It is used for its high bulking value and extending properties.

All driers used were lead, cobalt, and manganese naphthenates. The concentrated 24% lead, 6% cobalt, and 6% manganese driers were added to the various liquids according to the desired percentage.

Only the ten centipoise ethylcellulose of standard ethoxy content was used in this problem. It was supplied by the Dow Chemical Company of Midland, Michigan under the

trade name of "Ethocel".

A small laboratory buhrstone mill and a small three roller mill were used for grinding all of the batches. The Gardner Flowmeter was used to determine the diametrial flow and a Stormer Viscosimeter was used in determining the viscosities of the various pigmented products.

The experimental work of this investigation was done in the laboratories of the Charles R. Long Jr. Company.

EXPERIMENTAL

PRELIMINARY EXPERIMENTAL

A pigmentation problem of this type requires certain fundamental formulations for the final experimental part so that the scope of the problem will remain within reasonable limits.

Enamel formulations were of greatest interest and for this reason most of the varnishes were constructed on the twenty-five gallon length bases. For other formulations, such as flat wall and primer products, varnishes of twenty gallon lengths were made.

It was first necessary to become familiar with ethylcellulose and to determine the best cooking procedure for incorporating it into the various oils, resins, and oil length vehicles. This preliminary work also included the determination of the most practical percentage of ethylcellulose to use in the enamel liquids.

To facilitate this work, and to simplify the problem, only one resin was chosen, varying the types of oils. A terpene-phenol resin, Durez 210, was chosen because of its compatibility with ethylcellulose, its water resistance, and its general adaptable properties for enamel finishes. With resin, five types of varnishes were cooked using china wood oil, perilla, dehydrated castor, Ciccoil and linseed oils. A blank varnish similar to each of these was cooked for control purposes.

Considerable difficulty was encountered when trying to cook the ethylcellulose into the twenty-five gallon long wood oil varnish. Because of the low compatibility with wood oil, 8% ethylcellulose (based on total solids) was the maximum amount that could be cooked into a wood oil varnish of this length. Better compatibility was obtained when five gallons of the wood oil was substituted with bodied perilla. In this combination ten per cent would yield a clear pill but on cooling, it would form gel like particles and settle to the bottom of the kettle. The ethylcellulose was added on the down heat at 480°F and held until a clear pill was obtained. (see formula No. 1) The higher the percentage of ethylcellulose the longer it was required to hold this heat for complete solution. Where a "kick out" of the ethylcellulose occurred the gelation time of the wood oil would not permit the varnish to be held long enough for the ethylcellulose to form stable solution. For example, the blank varnish (20 gallons wood oil and 5 gallons bodied perilla) was held at 500°F for body, fourteen minutes; the five per cent ethylcellulose varnish was held five minutes at 480°F and a clear solution on cooling was obtained; the eight per cent was held ten minutes and a clear varnish resulted. The ten per cent addition was tried several ways to render it compatible. In one case the ten per cent varnish was held to the point of gelation and then quickly cooled with water. Lead acetate (1% based on the oil) was

added to another cook after the addition of the ethylcellulose and held thirteen minutes. A clear pill was obtained but on cooling the ethylcellulose precipitated.

The working properties of the above varnishes were tested and, the most practical percentage of ethylcellulose was chosen by making four floor enamels using the blank, the five per cent, the eight per cent, and a blend of the eight per cent with the blank to make a five per cent mixture. There were no differences between the five per cent and the blended products. The eight per cent showed the greatest increase in drying and toughness, but had a noticeable decrease in gloss. These and other proportional differences of the eight per cent over the blank indicated that this percentage should be chosen for the study of ethylcellulose in wood oil finishes. The decrease in gloss was particularly studied and the results of the same are reported in part three of this section.

Similar to the above procedure, cooks were made using the other oils namely: dehydrated castor, perilla, and Cicoil, and it was decided that in these varnishes since ten per cent was compatible in each oil, that this would be the desired percentage to study.

VARNISH FORMULATION

All varnishes in the twenty-five gallon length series were formulated as closely as possible to a standard

procedure. This was done to obtain comparative results and to reduce the number of varnishes. The following formulas, charts and cooking schedules are inserted here to make plain the comparison between the different formulations. Effort was made to keep the non-volatile of the varnishes the same (50%) but, in doing this the viscosity of the blank was several bubbles lower than the ethylcellulose varnish. The drying of the ethylcellulose varnishes was not greatly increased over the blank in this twenty-five gallon length series. The increase was between one and two hours which was sufficient to warrant further investigation of these varnishes.

All precautions mentioned in the Theoretical section were taken, and, to insure solution stability, fifty per cent of the thinner was Solvesso No. 2. The remainder of the thinner combination was mineral spirits. The blank varnishes were thinned with straight mineral spirits because the Solvesso No. 2 was not needed to increase the stability of the varnish.

The eight per cent ethylcellulose wood oil varnish rendered a clear pill in ten minutes. A clear pill in the dehydrated castor and perilla oil varnishes was easily obtained; it only required five minutes at 480°F in both cases. It was necessary to add 1% lead acetate (based on the oil) to the Cicoil batch to obtain clarity.

FORMULA NO. I

V-18-D*

8% Ethylcellulose, 25 gallons long
(20 gallons Wood Oil, 5 gal. perilla)

100 lbs.	Durez 210
20 gal.	China Wood Oil
5 gal.	Perilla (body Z-3)
24 lbs.	Ethylcellulose (16 cps.)
23 gal.	Solvesso No. 2
26 gal.	Mineral Spirits

PROCEDURE: 100 pounds of Durez 210 and 20 gallons of China Wood Oil are heated together to 565°F in 30 minutes. The batch is then checked with 5 gallons of bodied perilla to 480°F at which time the ethylcellulose is stirred in and kept at this temperature until a clear pill is obtained. The batch is then cooled to 400°F and thinned. Lead and Cobalt naphthenates in 0.5% and 0.01% proportions, based on total solids, respectively are added to the cooled batch.

The blank varnish is cooked similarly except after the batch has been checked, it is held at 500°F, 14 minutes for body.

COOKING LOGS

TEMPERATURE	ETHYLCELLULOSE VARNISH	BLANK VARNISH
Start	0 minutes	0 minutes
300°F	11 "	12 "
400	19 "	19 "
500	26 "	27 "
565	31 " Checked	32 " Checked
500		36 "
500		46 "
480	44 " ethyle. in	
480	54 "	
400	62 "	56 "

* This designation signifies a varnish (V) with Wood oil (1) 8% ethylcellulose (8) and Durez 210 as a resin (D)

FORMULA NO. 2

V-210-D

10% Ethylcellulose, 25 gallons long
Dehydrated Castor Oil

100 lbs.	Durez 210
20 gal.	Dehydrol
5 gal.	Dehydrol
30 lbs.	Ethylcellulose (10 cps)
23 gal.	Solvesso No. 2
26 gal.	Mineral Spirits

PROCEDURE: 100 pounds of Durez 210 and 20 gallons of Dehydrol are heated together to 565°F in about thirty minutes. The batch is held there for a few minutes and checked with the remaining five gallons of dehydrol to 480°F. The ethylcellulose is stirred in and kept at this temperature until a clear pill is obtained. It is then held at this temperature for body, cooled, and thinned at 400°F. In this case a clear pill was obtained after five minutes and the batch was held 30 minutes. The longer an ethylcellulose varnish is held at 480°F, the lower the resultant viscosity. Lead and cobalt naphthenates were added in the percentages of 0.5 and 0.01 respectively.

In the blank cook, all the resin and oil were taken to 565°F in 30 minutes and held there one hour for body.

COOKING LOGS

TEMPERATURES	ETHYLCELLULOSE VARNISH	BLANK VARNISH
Start	0 minutes	0 minutes
300°F	8 "	10 "
400	15 "	19 "
500	24 "	27 "
565	30 "	31 "
565	50 "	91 "
480	57 "	
480	87 "	
400	97 "	97 "

FORMULA NO. 3

V-310-D

10% Ethylcellulose, 25 gallons long
Bodied Perilla Oil

100 lbs.	Durez 210
20 gal.	Bodied Perilla (Z-3)
5 gal.	Bodied Perilla (Z-3)
30 lbs.	Ethylcellulose (10 cps)
23 gal.	Solvesso No. 2
26 gal.	Mineral spirits

PROCEDURE: 100 pounds of Durez 210 and 20 gallons of the bodied perilla were heated together to 565°F in thirty minutes and held for forty minutes, then checked with remaining five gallons to 480°F and the ethylcellulose was added. The temperature is held at this point until a clear pill and the desired body are obtained. In this cook a clear pill was obtained after about five minutes and the batch was held for thirty minutes for body. Lead and Cobalt naphthenates were added as before, in the percentages of 0.5 and 0.01 respectively.

In the blank cook, all the oil was heated with the resin to 565°F and held there for 2 hours and 45 minutes for body. Formula was the same in all other respects.

COOKING LOGS

TEMPERATURE	ETHYLCELLULOSE VARNISH	BLANK VARNISH
Start	0 minutes	0 minutes
300°F	7 "	9 "
400	15 "	16 "
500	24 "	28 "
565	30 "	32 "
565	70 "	2-hours 45 min.
480	75 "	
480	105 "	
400	120 "	3-hours

FORMULA NO. 4

V-410-D

10% Ethylcellulose, 25 gallons long
Cicoil Varnish

100 lbs.	Durez 210
25 gal.	Cicoil
30 lbs.	Ethylcellulose (10 cps)
2 lbs.	Lead Acetate (1% on Oil)
23 gal.	Solvesso No. 2
26 gal.	Mineral spirits

PROCEDURE: 100 pounds of Durez 210 and all the Cicoil are heated together to only 460°F in thirty minutes and held there for twenty minutes. The ethylcellulose was added at this temperature and held for fifteen minutes when the addition of 1% lead acetate was necessary to obtain a clear pill. The batch was then continued at 460°F for ten more minutes and cooled. The driers were added in the amounts of, 0.2% lead naphthenate, 0.04% cobalt, and 0.06% Manganese, all based on the oil weight.

The blank varnish was cooked the same way only the batch was held one hour at 460°F for body.

COOKING LOGS

TEMPERATURE	ETHYLCELLULOSE VARNISH	BLANK VARNISH
Start	0 minutes	0 minutes
300°F	11 "	11 "
400	16 "	22 "
460	30 "	30 "
460	50 " (ethylc.)	90 "
460	65 " (Pb. Ac.)	
460	75 "	
400	83 "	98 "

The varnish formulations containing the above mentioned oils, were pigmented in enamel formulas and the properties of these resultant products were studied. The pigment was proportioned according to the base in the liquid. For every pound of base, one pound of lithopone and one-eighth pound of asvestine was ground into the varnishes on a stone mill. Films of these enamels were flowed using a 0.002 inch doctor blade. Table II contains some of the results obtained from the various tests of these films. The toughness and the hardness was increased in the ethylcellulose varnish while the drying and the Sward-Rocker hardness was not so greatly increased. The gloss in every enamel was equal to that of its blank control except in the eight per cent ethylcellulose, wood oil-perilla oil enamel.

STUDY OF THE LOSS OF GLOSS

The flatness which occurred in the ethylcellulose wood oil-perilla oil (V-18-D) enamel films was not like the dead flatness that is exhibited by a flat wall, or a primer finish, for it possessed a definite angular sheen. This angular sheen increased as the angle of reflection increased. When the human eye observed the film at an angle of about ninety degrees with the surface of the finish the sheen appeared to be dead flat. At an angle of about ten to fifteen degrees, a regular light reflection could be observed.

TABLE II

PROPERTIES OF PLAIN AND PIGMENTED ETHYLCELLULOSE VARNISHES OF 25 GALLON LENGTH

1st SERIES

NO. OF ENAMEL	VARNISH	DRYING		GLOSS	SWARD-ROCKER HARDNESS			
		TOUCH	TACK FREE		4 HR.	8 HR.	12 HR.	24 HR.
1	V-100 D	1 Hr.	4 Hr.	1	28	28	40	46
2	V-18 D	3/4 Hr.	3 Hr.	Dull	36	36	38	46
3	V-200 D	1-1/2 Hr.	7-1/2 Hr.	3	11	16	26	32
4	V-210 D	1-1/4 Hr.	7 Hr.	3	16	18	26	34
5	V-300 D	1-1/2 Hr.	6 Hr.	3	14	18	26	44
6	V-310 D	1-1/4 Hr.	5 Hr.	2	20	20	30	40
7	V-400 D	1 Hr.	5 Hr.	2	24	26	30	36
8	V-410 D	1 Hr.	4 Hr.	3	26	26	30	38

The dull appearance of the film was no doubt caused by the diffusion of the light rays. The degree of diffusion of the light rays, as they impinge on the surface, depends upon the condition of that surface. The more irregular, or the rougher the film, the greater are the rays dispersed into space.

This dispersion of the light rays or the roughness of the film was accredited to one, or all, of three causes, namely; the poor wetting characteristics of the vehicle, the "throw-out" of the ethylcellulose from solution during the pigmentation process, or the improper flow of the film.

The wetting of the pigment by the vehicle occurs on the mill. Therefore, two enamels were made containing a total of six per cent ethylcellulose based on total solids of the vehicle. The same pigment combination as before was used. The six per cent vehicle was made by the combination of the blank (V-100-D) and the eight per cent ethylcellulose varnish (V-18-D). The one enamel was mixed, ground in the blank and thinned with the eight per cent varnish. The other enamel was made by grinding the pigment in the eight per cent varnish and thinning with the blank. By this method the grinding was done by both liquids and the results showed, in a comparative way, their relative wetting characteristics. These enamels were flowed on panels using a 0.002 inch doctor blade and their gloss

properties were studied. There were no differences in gloss between these two films. No gloss measuring instruments were used in this investigation. Therefore, this property was measured by comparative observation.

The next step taken to test the validity of the wettability theory was the incorporation of wetting agents with the pigments which were subsequently ground out with the paste. Aerosol O. T. 100% and Nuodex zinc wetter were added to the mix in the amounts of 1% and 5% based on the weight of the pigment respectively. A very slight increase in gloss over the straight ethylcellulose enamel was observed. This increase being only slight was not enough to prove the theory; it was, however sufficient to lend prospects to the solution of the problem later on in the investigation.

In the preliminary work of this investigation, it was discovered that ethylcellulose was compatible in 25 gallon wood oil-perilla oil varnishes up to and including eight per cent. All the work done heretofore was with 25 gallon lengths containing 20 gallons of wood oil and 5 gallons of bodied perilla. If the low gloss was caused by incompatibility, then a varnish in which the ethylcellulose stays in solution should give an enamel of good gloss properties.

A series of varnishes was made in order to study the relationship between the length and compatibility of

straight wood oil varnishes, keeping the percentage of the ethylcellulose constant at eight per cent based on total solids. Durez 210 was again used in this series and 5, $8\frac{1}{2}$, $12\frac{1}{2}$, 16, 20, and 25 gallon length varnishes were cooked for this study.

The cooking procedure of these varnishes was similar to the above mentioned 25 gallon wood oil-perilla oil varnish. The only difference in the general procedure was the method of checking the batch. Being a straight wood oil varnish, seventy-five pounds of the gum and all the oil were taken up to top heat and checked with the remaining twenty-five pounds of gum; the ethylcellulose was then added as before at 480°F.

No trouble at all was experienced in cooking the ethylcellulose into a 5, $8\frac{1}{2}$, and $12\frac{1}{2}$ gallon batches. Several days of aging caused the ethylcellulose to precipitate in the $12\frac{1}{2}$ gallon varnish. This could have been remedied by holding the batch at 480°F longer after the addition of the ethylcellulose. The 16 gallon batch gelled before a clear pill could be obtained, and in the 20 and 25 gallon batches the ethylcellulose would not go into solution.

This same series was repeated using the same oil combination as was used in the 25 gallon wood oil-perilla oil varnish (V-18-D). In the five gallon varnish, one gallon of bodied perilla was used to check the batch; in the $12\frac{1}{2}$ gallon batch, $2\frac{1}{2}$ gallons of bodied perilla was used, and

so on with the rest of the series. One per cent lead acetate was added to each batch after the ethylcellulose had been introduced to increase the compatibility and stability of the varnish. All of these varnishes turned out satisfactorily. The 16, 20, and 25 gallon cooks yielded clear uniform varnishes but it was observed that a little more difficulty was met in getting the ethylcellulose into solution.

All the ethylcellulose varnishes made for this investigation were thinned with a fifty-fifty mixture of Solvesso No. 2 and mineral spirits. Solvesso No. 2 is an excellent solvent for ethylcellulose while mineral spirits is a poor one, but to increase the solubility of the varnish as a whole and to have an even evaporation rate of one solvent, a straight reduction with toluol was used in another varnish cook; similar to the V-18-D. This eliminated the possibility of a poor solvent remaining in the film after the evaporation of the good solvent which would cause a throw-out of the ethylcellulose from solution. An enamel of the same pigment combination as before made in a ball mill with this varnish and its characteristic properties were studied. The film of this enamel dried to a dull sheen, the same as resulted in the other V-18-D enamels.

The results of the pigmentation of the above 5-25 length series were important to the compatibility and gloss problem. The pigment combination was switched from the floor enamel type to the plain gloss formulation and,

at first, straight titanium dioxide at two and three quarter pounds to every four pounds of varnish base was ground into the six different liquids in the series. The gloss of the films of each of these enamels was studied and it was found that each one except the 25 gallon enamel, had good gloss qualities as compared to the regular 25 gallon blank enamel. Disregarding the twenty-five gallon ethylcellulose enamel, the other five had a very good general appearance for enamel application. They possessed a nice body, flowed well, did not skim, had good color, and dried tack free in thirty minutes for the 5 gallon product to one hour for the longest enamel.

Although the 5-20 gallon formulations had good gloss appearance, the pigment-solids ratio was too small to show a definite demarcation of the affects of the pigment on the various lengths. The pigment was increased to four pounds of titanium dioxide to four pounds of vehicle base. Films of these enamels were flowed with a 0.002 inch doctor blade and their gloss properties compared. The results were as expected. The enamels made with the 5, 8 $\frac{1}{2}$, and 12 $\frac{1}{2}$ gallon long varnishes were high in gloss and equal to the 25 gallon blank. The 16 and 20 gallon enamels began to show a let down in gloss; the latter showing the greater difference between the two. Again the 25 gallon enamel dulled off in gloss and to a more marked degree than the lower pigmentation series. These results helped in sub-

stantiating the compatibility theory since there was a similarity between the decrease in solubility and the diminution of gloss beginning in the varnish lengths above 12½ gallons long.

Examination of the clear films under the microscope showed no trace of undissolved particles of ethylcellulose. It was difficult to observe any appreciable difference in the wetting of the pigments by the various liquids in question. However, the microscopic study of the dried pigmented films proved both interesting and helpful to this investigation. The films that had good gloss properties revealed good, clear, smooth surfaces. Those having low gloss showed, what may be called, a small minute "orange peel" affect which was only slight in the 16 gallon enamel and increased with the 20; being quite noticable in the 25 gallon varnish pigmentation.

Figures 2, 3, and 4 illustrate this affect as observed under the microscope. These photomicrographs were made of the 12½ gallon ethylcellulose enamel, the 25 gallon ethylcellulose, and the 25 gallon blank enamel. Particles of dirt can be seen in these pictures but they were purposely found in the film to show that the microscope was in focus. Otherwise it would have been difficult to illustrate the smoothness of the films in the 12½ and the blank enamels. These photomicrographs were taken at 75 magnifications. This microscopic study showed that the

decrease in gloss of the 16, 20, and 25 gallon ethylcellulose enamels was the result of improper flow of the film.

Enamels of the four pound titanium dioxide formulation were made with the substituted oil varnishes and the diametrial flow (as described in Theoretical, Part IV) of these enamels and the 5-25 series enamels was determined. The substituted oil series enamels and the 25 gallon blank were used as the standard of comparison for the amount of flow. The results obtained by the Gardner "Flowmeter" (5) are recorded in Table III and shown graphically in figure 5. The flow for all materials was taken after a period of ten minutes and at 77°F.

Table III and figure 5 show that the substituted oil varnish enamels flowed out to about the same value. The ethylcellulose enamels of this series varied only one-eighth of an inch from their blank enamel. The 5, 8 $\frac{1}{2}$, and 12 $\frac{1}{2}$ gallon ethylcellulose-wood oil enamels flow approximately to the same distance as did the 25 gallon blank enamel. The variance is within experimental error. The 16 gallon enamel flowed to a radius of 2 $\frac{5}{8}$ inches which is a decrease as compared to the blank. The flow further decreased in the 20 gallon enamel and the 25 gallon pigmentation showed quite a drop to 2 $\frac{1}{16}$ inches. These results follow, very closely, those obtained from the microscopic study and theory of the decrease in gloss.

The affect of wetting agents on the gloss and flow of the 25 gallon ethylcellulose enamel, was demonstrated

Fig. 2 Photomicrograph of 12 $\frac{1}{2}$ Gallon
Enamel Film, 8% Ethylcellulose Mag.75x

Fig. 3 Photomicrograph of 25 Gallon
Enamel Film, 8% Ethylcellulose V-18-D
Liquid. Mag. 75x

Fig. 4 Photomicrograph of 25 Gallon
Blank Enamel Film, V-100-D Liquid. Mag. 75x

by the addition of 5% Nuodex zinc wetter and 4% benzoic acid based on total weight of the pigment. The gloss was slightly increased but, under the microscope, there still could be seen the small orange peel effect. The effect was not as prominent as before and this was further illustrated by the fact that the benzoic acid and the zinc wetter increased the flow to 2 5/8 and 2 3/8 respectively.

These results showed that gloss was directly proportional to the flow of the film, and, that those varnishes in which ethylcellulose was easily cooked had produced enamel of high gloss. This study also showed if the 25 gallon ethylcellulose varnish (V-18-D) could be cooked in such a way that a more homogeneous product could be obtained, then a better flowing enamel could be produced.

A varnish (formula 5) similar in formula and cook to V-18-D was made substituting ten per cent of the Durez 210 with ester gum, and after the addition of the ethylcellulose in the cook, 1% lead acetate was stirred into the batch. The cook was held at 480°F for thirty minutes which is twenty minutes longer than the original 25 gallon varnish (V-18-F).

There was not much change in the various properties of this varnish over the original V-18-D. The pigmentation of the varnish gave a product which had a gloss equal in every respect to the blank enamel. The determination of its flow showed a three inch radius on the flowmeter and upon observation under the microscope there

TABLE NO. III
DIAMETRIAL FLOW

Substituted Oil Enamels	Varnish	Radius of Flow	
	V-200-D	2 $\frac{1}{8}$	inches
	V-210-D	2 $\frac{3}{8}$	inches
	V-300-D	2 $\frac{1}{8}$	inches
	V-310-D	2 $\frac{1}{8}$	inches
	V-400-D	2 $\frac{1}{8}$	inches
	V-410-D	2 $\frac{3}{8}$	inches
5-25 Wood Oil Enamels	5 gal.	2 $\frac{13}{16}$	inches
	8 $\frac{1}{2}$ Gal.	2 $\frac{7}{8}$	inches
	12 $\frac{1}{2}$ gal.	2 $\frac{11}{16}$	inches
	16 gal.	2 $\frac{5}{8}$	inches
	20 gal.	2 $\frac{1}{2}$	inches
	25 gal. (V-18-D)	2 $\frac{1}{16}$	inches
	25 gal. Blank	2 $\frac{13}{16}$	inches
25 gal. Ethylcellulose Enamel & Wetting Agents	5% Nuodex Zinc Wetter	2 $\frac{3}{8}$	inches
	4% Benzoic Acid	2 $\frac{5}{8}$	inches
Reformulated 25 gal Ethylcellulose Enamel	(V-18-DE)	3	inches

FORMULA NO. 5

V-18-DE

Re-formulated 8% Ethylcellulose Wood Oil,
Perilla Oil Varnish

90 lbs.	Durez 210
10 lbs.	Ester Gum
20 gals.	China Wood Oil
5 gals.	Bodied Perilla
24 lbs.	Ethylcellulose (10 cps)
2 lbs.	Lead Acetate
23 gals.	Solvesso No. 2
26 gals.	Mineral spirits

PROCEDURE: All the gum and the 20 gallons of wood oil are taken up to 565°F in 30 minutes and checked as before with the 5 gallons of perilla. At 500°F, the ethylcellulose is added and held at 480°F for solution. After ethylcellulose is in about three minutes the lead acetate is stirred in to promote the solubility. When the ethylcellulose had been in for thirty minutes and a clear pill was obtained, the batch was cooled and thinned. Lead and cobalt naphthenates were added in the same percentages as before, 0.5 and 0.01 respectively.

COOKING LOGS

TEMPERATURE	ETHYLCELLULOSE VARNISH	BLANK VARNISH
Start	0 minutes	0 minutes
300°F	14 "	11 "
400	20 "	16 "
500	26 "	27 "
565	31 "	32 "
500	36 "	34 "
500		59 "
480	39 "	
480	69 "	
480	79 "	75 "

appeared no orange peel effect; the film had a clear smooth surface. A photomicrograph of this film taken at seventy-five magnifications is shown in figure No. 6.

PRACTICAL PIGMENTATIONS

The statement made before that the true test of the practicability of a varnish is by pigmenting it and observing its various properties is substantiated here in this section. A number of formulations were made using the previous formulated varnishes in high gloss enamels, short length dipping and baking enamels, flat wall finishes, and wood and metal primers.

Formula 6 is a typical formulation for a onecoat, high gloss, general utility enamel used on furniture, wood work, and for other household purposes.

The addition of the thinner was made to adjust the brushability and only a very small addition of thinner to the ethylcellulose enamels was needed as compared to that added to the blank enamels. As a whole the working properties of all the ethylcellulose enamels were very good.

The same pigment combination and concentration was used in every enamel of this series and quite a marked degree of difference in flooding was observed between the ethylcellulose enamel and its blank. In all formulations, except the cicoll enamel, the flooding was less uniform but to a lesser extent than the blank enamels.

Fig. 6 Photomicrograph of 25 Gallon Enamel Film, Reformulated 8% Ethyl-cellulose Wood Oil-Perilla Oil Varnish, V-18-DE Liquid. Mag. 75x

FORMULA NO. 6

One Coat, High Gloss, Quick Drying Enamel

3 lbs.	Titanox A
1 lb.	Chrome Yellow
1/8 lb.	Monastral Blue
1 gal.	Varnish

This pigment is proportioned to a vehicle containing 3.6 pounds of base per gallon. Mineral spirits was used as the thinner and added to the enamel for good brushibility.

The drying was increased in each ethylcellulose formula and in the dehydrated castor and perilla oil ethylcellulose enamels the skinning was completely eliminated. The initial drying time was appreciably decreased and the final dry was reduced two hours in the wool oil enamel, three in the dehydrated castor and perilla oil enamels (the perilla enamel dried faster than the dehydrated castor enamel), and one and one-half hours in the Ciccoil enamel.

There were no differences, in the observation by the thumb-nail method, in the hardness, adhesion, or toughness in any of the ethylcellulose enamels over their blanks.

Can stability was observed over a months period with no variance in the Stormer viscosity reading in any enamel. The panels containing the various enamels were placed in water and observed at intervals of 24, 48, and 72 hours. At the end of 48 hours, all were equal to their blanks with no blistering, except the Ciccoil formulation which showed signs of beginning failure. At the end of 72 hours, both Ciccoil enamels showed blistering; the blanks slightly better, and the dehydrated castor oil enamel showed slightly more failure than its blank.

The desirable properties of ethylcellulose were exhibited more in shorter length varnishes than in the longer ones. For this reason a 12½ gallon dipping enamel was formulated both for an air dry and baking procedures.

This particular type of formulation can be used on toys, metal parts, and metal furniture where quick drying toughness, and hardness are the essential properties. Longer lengths are generally required for most metal furniture pieces but this type formulation has many applications in that industry.

Two enamels were made using as the liquids, the 12½ gallon blank wood oil-perilla oil varnish and the 8% ethylcellulose control of this varnish. An equivalent of two pounds of titanox A and one half pound of Monastral blue was ground into a gallon of varnish. This amount of pigment gives good hiding when used in a vehicle containing about 3.8 pounds of base per gallon. The blue was added to observe the color change on baking and to watch the flooding tendencies in the dipping process.

These two enamels were reduced four parts of enamel to one part of Solvesso No. 2 and dipped on metal panels for the baking and air drying procedures. The ethylcellulose enamel air dried in forty-five minutes while the blank control took two hours to become tack free.

The ethylcellulose enamel dipped very smoothly and was better than its blank in both procedures for flow, flooding, and fullness of film.

Three sets of dipped panels were baked for one-half hour at 200°F, 250°F, and 340°F. In every case the ethylcellulose came out better than its blank. In the

200°F bake the ethylcellulose enamel was tack free; the blank seemed to need more baking. Outstanding was the color retention of the ethylcellulose enamels in the high baking schedules. They far surpassed the blank enamels in every case.

Another outstanding feature of these ethylcellulose enamels was their retardation of flooding. In each dip, the ethylcellulose had a clear smooth film free of any pigment flood.

The film of the ethylcellulose enamel was much harder and tougher than its blank. However, the hardness of the film should be watched, for on age it might have a tendency of becoming brittle sooner than the blank.

It is difficult to substitute China Wood Oil with linseed oil because of the great difference in their drying properties. The increase of the drying time of linseed oil by the incorporation of ethylcellulose could be used advantageously in flat wall finishes and primer products.

A 20 gallon long linseed oil, 10% ethylcellulose varnish (see formula 7) (V-510-D) was formulated and flat wall finishes, wood and metal primers were made using this liquid as part of the vehicle combination.

A twelve per cent ethylcellulose varnish was made similar to V-510-D, holding the varnish, after the ethylcellulose had been added, thirty minutes instead of

FORMULA NO. 7

V-510-D

10% Ethylcellulose, Linseed Oil Varnish
(20 gallons long)

20 gal. Adomolene

100 lbs. Durez 210

26 lbs. Ethylcellulose (10 cps)

20 gal. Solvesso No. 2

24 gal. Mineral spirits

PROCEDURE: The Admolene was heated to 585°F and held there for two hours. It was then checked with the 100 pounds Durez and held at 500°F until solution was complete. The ethylcellulose was then added and the batch was held 15 minutes, cooled and thinned at 400°F. Lead, cobalt, and manganese naphthenates were added in the percentages of 1.4, 0.0675, and 0.02 respectively.

In the blank varnish, a five-hour (585°F) bodied adomolene was used instead of the straight oil. It was taken to 585°F and held there for 35 minutes for heavy string. The gum was then added and held at 500°F for solution, cooled, and thinned at 400°F. Driers were added in same proportion as in the ethylcellulose varnish.

COOKING LOGS

TEMPERATURE		ETHYLCELLULOSE VARNISH		BLANK VARNISH
Start		0 minutes		0 minutes
585°F		25 "		30 "
585	2 hrs.	25 "		65 "
500	2 hrs.	38 " (ethyle. in)		67 "
500				77 "
480	2 hrs.	40 "		
480	2 hrs.	55 "		
400	2 hrs.	65 "		87 "

the fifteen as shown in formula 7, cooking schedule. This longer cooked varnish had to be abandoned because the properties of ethylcellulose were destroyed and no apparent differences were observed between it and the blank linseed oil varnish.

The difference in the length of cooking time for the ethylcellulose varnish with respect to that of its blank is a point in favor of the use of ethylcellulose in this type of varnish. It was necessary to start with a pre-bodied oil for five hour procedure to obtain a good body. The drying time of V-510-D was between two and three hours for tack freeness while the blank took six and one-half hours.

A typical, well balanced flat wall formula was chosen for trying the pigmentation of this varnish. The general flat wall formulation (formula 8) has a vehicle combination of forty gallons length and forty per cent base. The pigment volume - non-volatile volume ratio is about 1.5.

When this formula was properly proportioned the ethylcellulose product was tested along side the blank and under the same conditions. A freshly plastered wall was made and a coat of each, together with a nationally known brand flat wall, was brushed a day after the application of the plaster to the wall. The second coat was applied the following day.

FORMULA NO. 8
Flat Wall Finish

600 lbs.	Calcium Titanium Pigment
300 lbs.	Surfex
360 lbs.	Precipitated Calcium Carbonate
3½ lbs.	Aluminum Stearate
70 gal.	Varnish
15 gal.	Diamond K. Linseed Oil
5 gal.	Kettle bodied Linseed Oil
45 gal.	Mineral spirits

It was quite hard to designate the best product from this test because each had good and bad qualities and, the completion of the problem would take a considerable amount of time which this investigation did not permit.

The ethylcellulose flat wall sealed some better than the blank and the drying was increased. Solvent retention kept it from drying through as good as the blank in the second coat. These are about the only differences that could be observed. It is believed, that the highly pigmented products lessen the effectiveness of the ethylcellulose addition.

A wood and metal primer formulation was made according to formula No. 9.

The high pigmentation of the ethylcellulose varnish in this formula also reduce the effectiveness of ethylcellulose properties, however, the drying time was reduced an hour and a half over the blank.

The two products were applied on wood and metal by brushing and again both were sprayed on metal and baked forty-five minutes (275°F).

Over the wood, the sanding properties were the same; the ethylcellulose sealed slightly better. It brushed with a little more pull, and its hardness and adhesion were slightly better than its blank. The same differences were observed in the air dry metal finish, and neither lifted on the application of lacquer thinners to its surface.

FORMULA NO. 9

Wood and Metal Primers

320 lbs.	Calcium Titanium Pigment
160 lbs.	Surfex
80 lbs.	Celite
120 lbs.	Asbestose
42½ gal.	Varnish
13 3/4 gal.	Mineral spirits
13 3/4 gal.	Kerosene
2½ gal.	50% Ester Solution

Pigment Volume	1.4
Non Volatile Volume	1

The ethylcellulose baking primer sanded better, baked harder and added slightly better fullness to a baking stove enamel film which was applied over its surface and baked forty-five minutes at 275°F.

The differences between the ethylcellulose products and the blank controls were few and small in amount in some formulations but there were indications present to show possibilities for further work. Also, the above formulations are considered very good in general practice and for this reason too, the degree of difference would be small. They were good tests, however, of the working characteristics of ethylcellulose varnishes.

CONCLUSIONS

Twenty-five gallon length varnishes are generally used in enamel formulations and for this reason most of the vehicles were made on that basis. It was found that eight per cent ethylcellulose based on total solids was the maximum amount that could be incorporated in a twenty-five gallon Wood oil-Perilla oil varnish. This combination contained five gallons of bodied perilla to insure stability.

The resin used in practically all varnishes was Durez 210 and was chosen for its adaptable properties with ethylcellulose. The substituted oils such as, dehydrated castor, perilla, Ciccoil, and linseed oil, were used in other twenty-five gallon length varnishes having an addition of ten per cent ethylcellulose. For each ethylcellulose product made there was a similar one formulated without the ethylcellulose to serve as a check or a control for comparative purposes.

The affect of the cooking time on the varnish, after the addition of ethylcellulose, was shown by the twenty gallon linseed oil formulation. When this varnish was held at 480°F, for fifteen minutes the maximum benefit of the ethylcellulose addition could be obtained. However, when this time was doubled the affect of the addition seemed to be destroyed and there were no apparent difference between the resultant varnish and its blank.

Time would not permit this investigation to study the pigmentation of various oil lengths, but in the 5-25

length series a definite increase in the affects of ethyl-cellulose was exhibited in the short oil varnishes. The 12½ gallon varnish was observed to give quite a noticeable trend in this respect.

The decrease in gloss of the wood oil varnish pigmentations presented a problem which dominated the work of this investigation. The compatibility of ethylcellulose in this type of varnish was not so much retarded in lengths up to and including 12½ gallons as much as it was in longer oil varnishes of 16, 20, and 25 gallons. The decrease in gloss beginning with the 16 gallon varnish and dulling off completely in the 25 gallon varnish seemed to correlate the compatibility results. This affect increased as the amount of pigment increased.

Microscopic study of the dry pigmented film showed small minute orange peel which formed by improper flow. This irregular surface dispersed the reflecting rays thereby decreasing the gloss.

When the flow of 5-25 gallon enamel series was determined by the Gardner Flowmeter it was shown that a marked decrease in flow began with the 16 gallon enamel and fell off considerably in the 25 gallon enamel. Wetting agent helped slightly to improve both the gloss and flow but did not solve the problem entirely. The gloss of the substituted oil enamels and the enamels made with the 5, 8½, and 12½ gallon length varnishes were equal and their

flow as determined by the flowmeter, were about the same.

The flow and the degree of compatibility, or the ease with which ethylcellulose goes into solution with a varnish, were found to be contributing factors to the cause of low gloss products. This was further proven by the formulation of a vehicle whose gelation time was prolonged long enough for the ethylcellulose to form a homogeneous solution with the resins and the oils. This was accomplished by substituting ten per cent of the Durez 210 with ester gum and holding the cook longer at 480°F. Such a varnish produced an enamel which would flow better than any if the previous products and whose gloss was equal to the standard in all respects.

These results and conclusion about the causes of gloss decrease in wood oil varnishes substantiates the theory (stated in part IV) that a gel formation occurs when ethylcellulose is cooked into a varnish. On prolonged heating, a better solution of smaller polymers was obtained.

Ethylcellulose does not decrease the wetting characteristics of the vehicle. It added the necessary tack to a varnish to help the grinding process when roller mills were used. The fact that wetting agents only slightly increased the gloss and the fact that no change in gloss was observed when the blank and the ethylcellulose varnishes were used interchangeably as the grinding medium, gives full proof that there is no change in the grinding

characteristics.

All of the blank formulations chosen for this investigation were made with high quality materials and to high type working properties. In doing this, however, some of the formulations had to be held too closely to the standard and a little variance could have produced a better formulation.

The 25 gallon long quick drying, one coat enamels used ethylcellulose to advantage in drying and non-skinning. Its addition in the Ciscoll enamel reduced the flooding affect. Ethylcellulose's greatest use in enamels of this type is in rapid drying products for general household work.

The shorter oil length ethylcellulose varnishes could be used best in the industrial formulations both in air dry and baking procedures. The properties of ethylcellulose are more effective in the short lengths. Chief of its properties which are helpful to these lengths are rapid drying (30 minutes to one hour) hardness, non-skinning, non-flooding, good dipping qualities, excellent color retention on baking at high temperatures.

Like long oil varnishes, high pigmentation of ethylcellulose varnishes reduces the effectiveness of its properties. For this reason the flat wall finishes made for this problem did not show the expected results. Drying and sealing properties of these flat wall finishes revealed the trend of its use in this type of formulation and showed

that it can be used to an advantage.

In primer finishes the high pigmentation lessened the affects of the ethylcellulose. However, it can be used to a great extent in primers where increased drying or hardness on baking is desired.

The results of this investigation show that ethylcellulose can be used advantageously in enamels to increase drying time, and hardness, decrease skinning of dehydrated castor and perilla oil varnish enamels; and to decrease flooding and discoloration of baking enamels. The formulations made in this investigation indicate that the best use of ethylcellulose is to speed up drying, however, they show that its addition has no particular advantage in long oil varnishes and highly pigmented vehicles. Some of the results obtained, such as, the decrease in flooding, skinning, and discoloration, could be obtained by the addition of other paint materials which are less expensive than ethylcellulose.

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ACKNOWLEDGEMENTS

The author wishes to express his appreciation to the Dow Chemical Company for sponoring this investigation.

He is indebted to Mr. Otto J. Militi; general superintendent of the Charles R. Long Jr. Company, for his kind assistance and advice on this work of this problem.

The author wishes to thank Henry L. Beakes, of the Kentucky Color and Chemical Company, for helping him with the photomicrographs and the microscopic study in this investigation.

VITA

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