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UNIVERSITY OF LOUISVILLE

- I. THE REACTION OF ETHYLCELLULOSE WITH FATTY ACID
AND ITS APPLICATION TO THE VARNISH INDUSTRY
- II. ETHYLCELLULOSE IN PENCIL LACQUERS

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

Albert L. ^{Louis} Kimmel

1945

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AND ITS APPLICATION TO THE VARNISH INDUSTRY
- II. ETHYLCELLULOSE IN PENCIL LACQUERS

Albert L. Kimmel

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February 24, 1945

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REACTIONS OF ETHYLCELLULOSE WITH FATTY ACIDS.

Ethylcellulose was refluxed with Stearic, Oleic, Linseed Fatty acids, and a neutral Mineral Oil in the presence of a solvent. The products recovered were analyzed to determine if any possible reaction had taken place. Conditions for the reaction were carried out so that the temperatures obtained could be in the near range of varnish cooking, that is between 375° and 500°C . The solvents used were diethylbenzene, boiling point 180°C . and tetralin, boiling point 208°C . In each case approximate stoichiometric proportions of the fatty acids and ethylcellulose were used. These were refluxed to a sensible minimum viscosity of solution.

The analysis of the product showed that reaction took place at the hydroxyl groups, the ethoxy groups and also at the oxygen bridge. There was also acid formed due to the breakdown of the ethylcellulose molecule.

The amount of acid reacted at the various groups in the ethylcellulose molecule, as mentioned above, and the amount of acid product of decomposition, seem to depend on the type of acid used and its reactive power.

ABSTRACT

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ETHYLCELLULOSE IN PENCIL LACQUERS

Ethylcellulose was used in a number of standard pencil lacquer formulas, totally replacing the nitrocellulose and very good results were obtained. In all cases the plasticizers and resin content were reduced between 30 and 50% from the amount used in the normal nitrocellulose formula. Pencils were coated in a standard pencil coating machine and were subjected to the tests of tack-free time, hardness, brittleness and aging. These lacquers showed that more cellulose and less plasticizers could be used in formulations and that very successful products can be obtained.

PART I

THE REACTION OF ETHYLCELLULOSE
WITH FATTY ACID AND ITS
APPLICATION TO THE VARNISH INDUSTRY

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INTRODUCTION

The industrial application of ethylcellulose to the varnish industry has long been contemplated and successful varnishes have been made using this material. It has definitely been established that drying properties and structure of the film can be improved by the incorporating of ethylcellulose. Ethylcellulose in varnishes tends to produce a semi-gloss or dull film, however this is not an undesirable property since these types of varnishes are used extensively in the furniture and woodwork industry.

Varnishes are prepared in the conventional manner by cooking natural or synthetic resins and drying oils according to the usual schedule and the ethylcellulose is added as the batch cools. For best results the addition is made at 450°F.

This investigation has been made to try to determine whether ethylcellulose reacts chemically with the functional groups of the polymerized resin oil solutions or if it is merely a physical dispersion.

HISTORICAL

In recent years a certain amount of success has been obtained by using ethylcellulose in varnish formulation. Ethylcellulose, when incorporated in oleo-resinous varnishes, improves the drying time and the initial paint resistance of the varnish film. It improves the through dry and minimizes wrinkling. It also decreases penetrating and produces a tougher dry film than when straight heat body oils are used.

Previous work of reacting ethylcellulose with fatty acids has been done by Worden (9) and Hunter (7), however their work was done at low temperatures. Hulette (6) reacted ethylcellulose with stearic acid at the same temperatures which are reported in this thesis with a reasonable amount of success. However some possibilities were overlooked due to the fact that all products of reaction were not collected and only one acid was used.

All other work except that of Hulette were made by using an ester of stearic acid rather than the pure acid, therefore, the results are not applicable to the varnish industry.

THEORETICAL

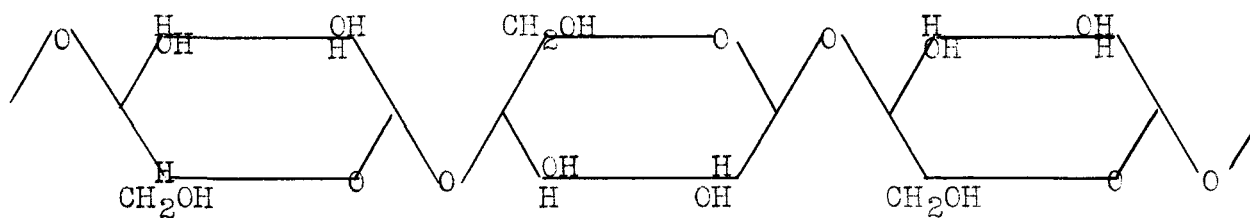
Ethylcellulose is a product of the double displacement reaction between alkali-cellulose and ethyl chloride under certain specific conditions. According to the method described by S. Uschakov and I. Schneer (8) the most favorable conditions for formation are 6 moles of ethyl chloride and 1 of alkali-cellulose heated to 120-130°C. for 18 hours and then followed by mercerization with 50% NaOH solution.

Commercially, we may obtain ethylcellulose with ethoxy contents ranging from 41% to 49.5% ethoxy which is equivalent to a mole ratio of 2.5 ethoxy groups per glucose unit. Accepted structures of cellulose and ethylcellulose are shown in fig.(1). Ethylcellulose may also be obtained in a variety of viscosities depending on the manner in which the original cellulose was treated.

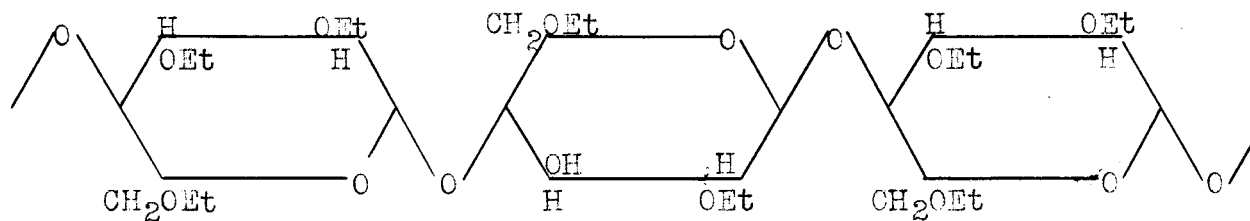
There are four types of reactions which are possible when ethylcellulose is reacted with a fatty acid:

- (1) Esterification with the available hydroxyl groups.
- (2) Reaction with the ethoxy group.
- (3) Cleavage at the oxygen bridge.
- (4) Reaction at the point of cleavage at the oxygen bridge.

If reaction (1) takes place we could expect an amount of water equivalent to the amount of acid reacted.



STRUCTURAL FORMULA FOR THE CELLULOSE MOLECULE



STRUCTURAL FORMULA FOR THE ETHYLCELLULOSE MOLECULE

Fig. 1

If reaction (2) takes place we would expect ethyl alcohol to be liberated. If reaction (3) takes place all we could expect would be a decrease in viscosity of the solution. With reaction (4) we would obtain a decrease in viscosity and one equivalent of water for every 2 moles of acid reacted, assuming a monobasic acid is used in the reaction.

Ethylcellulose has been reacted with stearic acid as described by Worden (9) in British patent 270,347 by reacting one part of ethylcellulose and 7 parts of stearic acid for 6 hours at 150°C. Hunter (7) describes the preparation of ethylcellulose stearates by reacting stearyl chloride and ethyl cellulose in pyradine solutions. The resulting product showed a slight change in viscosity of the unmodified cellulose.

Berl and Schupp (1) report that diethylcellulose is broken down and ethyl groups split off by acetolysis. This type of reaction would be indicated by a decrease in the ethoxy content of the final product and also in the saponification values.

According to Doree (3) cellulose is not affected by heat up to a temperature of 140°C. even after prolonged heating. Increases in temperature however decrease the viscosity on prolonged heating. Furthermore, Birtwell, Clebbins and Geake (2) reacted cellulose with acids at

various conditions and showed that a definite relationship existed between loss of tensile strength and loss of viscosity of the cellulose.

The procedure used in making an ethylcellulose modified varnish is illustrated by the curve fig.(2). Since the temperature of reaction is about 450°F. then the reactions must be carried out in this range. This temperature is above the decomposition temperature of the ethylcellulose so it is expected that products of decomposition will be formed as well as a decrease in viscosity. The decrease in viscosity is very well shown by Hulette (6) who measures the viscosity change as his refluxing progressed.

If any reaction is taking place it would be indicated by the acid number of the solution as the refluxing progressed. It would also be indicated if the products of decomposition were acid in nature.

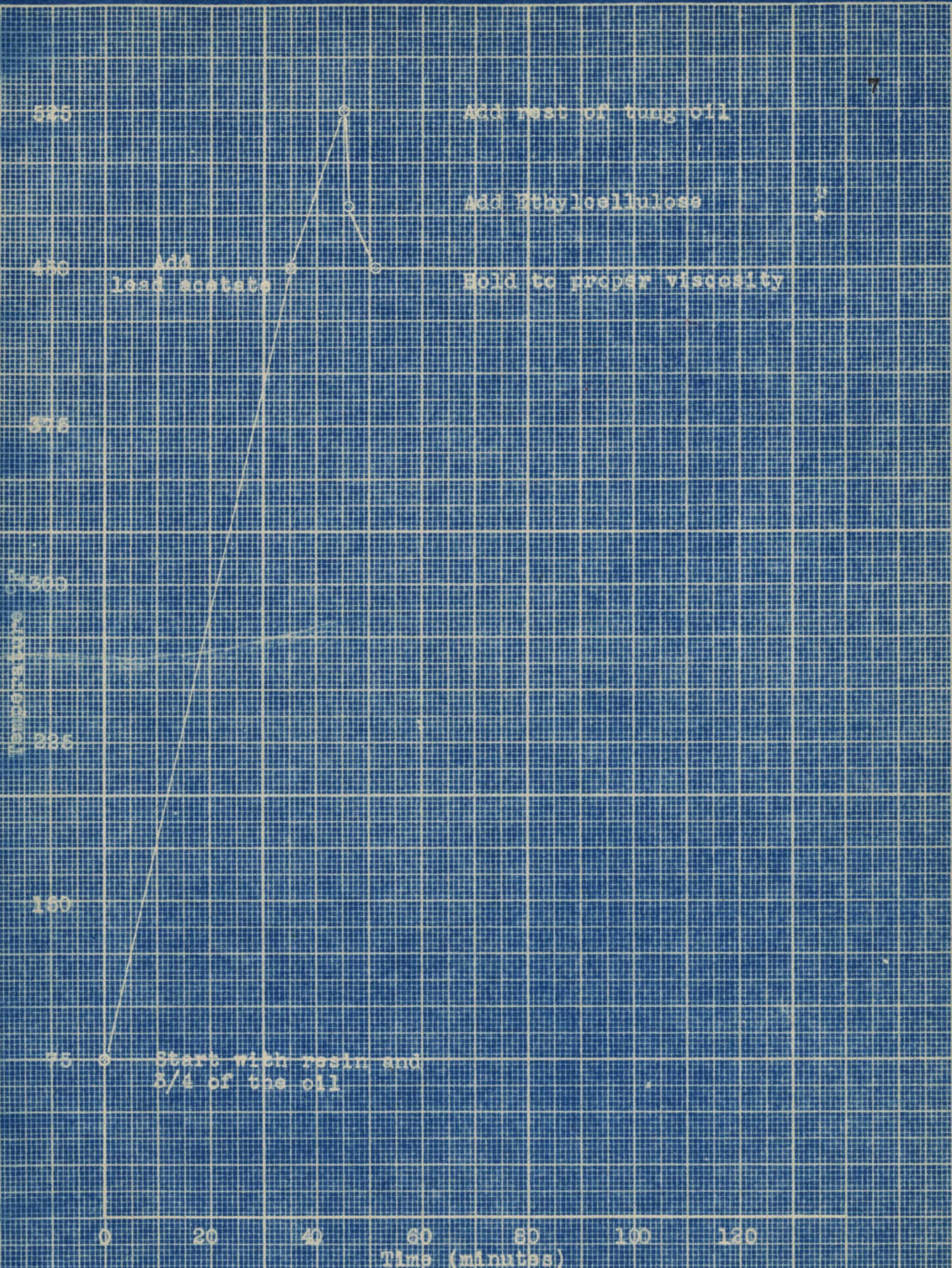


Fig. 2 COOKING CURVE OF AN ETHYLCELLULOSE MODIFIED VARNISH
10 GALLON PERMAC 615 N TUNG OIL VARNISH

EXPERIMENTAL

The ethylcellulose was refluxed with a number of fatty acids in the presence of solvents which had definite boiling points. As the refluxing proceeded, viscosities were determined. In all cases the reaction was carried to a minimum viscosity. It was assumed that the minimum was reached when there was no further change during a 2-hour period of time. In one case acid numbers as well as viscosities were run on the refluxing mixture.

APPARATUS

Apparatus used for the refluxing was a 2 liter, 3 necked flask fitted with a reflux condenser; a thermometer well and a built-in viscosity tube. The condenser was fitted with a water trap attachment making possible direct reading in ccs. All connections to the flask were of ground glass reducing losses to a minimum. When it was desired to collect all the products of decomposition, a draw-off tube and a thermometer were fitted in the top of the condenser and to this tube was connected 2 U-tubes, one immersed in an ice bath to collect any alcohol which might be given off. The other was filled with soda lime to absorb any liberated carbon dioxide. Heat was supplied to the 3 necked flask through a medium of wood's metal which was kept at a molten state by an electric heater.

MATERIAL

The following materials were used in this investigation:

Ethylcellulose - ethoxy (actual) 48.7; viscosity 145 C.P.A. measured at 25°C.; 25% solution in 80:20 toluene ethyl alcohol. It's softening point was 133-138°C. and a melting point of 165-175°C.

Stearic acid - C.P. grade

Oleic acid - C.P. grade

Linseed fatty acids - commercial grade

Mineral oil - S.A.C. 30 (Gulf Refinery).

Diethylbenzene - redistilled.

Tetralin - redistilled and dried over CaCl₂.

Carbon dioxide gas - dry commercial grade.

EXPERIMENTAL METHODS

Solutions containing stoichiometric proportions of ethylcellulose and the fatty acids were made with each of the solvents and refluxed to a minimum viscosity. In the case of the mineral oil, and linseed fatty acids only approximate stoichiometric proportions could be used. More consistent results were obtained with the stearic acid, therefore check runs were made collecting Carbon dioxide and alcohol evolved. Solutions containing solvent and ethylcellulose, and solvent and fatty acids were also refluxed so that any decomposition, change in viscosity, change in acidity, and water present could be detected. Table (1)

shows the weight composition of all solutions refluxed and the materials in the solution.

The ethylcellulose, fatty acid and solvent were heated in a water bath until a clear solution was obtained. These resulting solutions were then refluxed at their boiling point until a minimum viscosity was reached. The final viscosity was then measured at 25°C. Other viscosities measured during the process of refluxing were at the reflux temperature and were recorded in seconds.

In all cases where we were not interested in determining the amount of Carbon dioxide gas given off by the reaction an atmosphere of this gas was maintained over the reacting mixture to minimize oxidation. The Carbon dioxide was admitted to the flask through the viscosity pipette. This also served to agitate the solutions.

When we measured the carbon dioxide evolved, the flask was heated open until the solvent vapor drove out the air. The system was then closed and the high temperature kept the air from reentering the flask.

ANALYTICAL METHODS

In order to analyze the resulting product it was necessary to remove the high boiling solvent. This was accomplished by two methods. First by steam distillation. This procedure left a mixture of ethylcellulose and stearic acid which was redissolved in acetone and

precipitated by pouring in an excess of water. This precipitate was filtered and dried to a constant weight in an atmosphere oven at 110°C . The second method consisted of pouring the reflux mixture in an excess of V.M.P. naptha and boiling the precipitate in four successive volumes of this solvent. This yielded a product free from any excess fatty acid. Both methods were used and will be indicated in the data. The resulting samples were then analyzed for ethoxy content, acid number, and saponification number. The problem of running the acid number and saponification values, due to the dark color of the solution, was solved in using the methods of Gardner (5) and Hulette (6). For the saponification value, the ethyl alcohol was added in the form of 0.5 N alcoholic NaOH, so as not to disturb the solvent combination. The solutions were refluxed one hour and back titrated with 0.5 N HCl. The indicator used was thymol-blue. The color change was from a blue-green to a yellow.

DATA AND RESULTS

The solvents used were first double distilled to free them from any water present or any dissolved foreign matter. During the distillation the first 50 cc. to come off were discarded and the distillation continued until there remained about 100 cc. in the distilling flask. The distilled solvents, about two liters, each were stored in large glass bottles containing about 25 gms. of calcium chloride. After about three days specific gravity and refracting index was run on the solvents and there was shown a high degree of purity.

The following is the procedure used for operations. Ethylcellulose, solvent, and fatty acids were weighed into the 3 necked flask. The flask was heated on a water bath until homogeneous solutions resulted. The condenser, thermometer, and viscosity pipette were then connected and the flask placed in the wood's metal bath. A precision, adjustable electric heater supplied the heat to the system. The first viscosity was taken just as the solution reached the boiling point and every 15 minutes thereafter. In order to check the technique and methods involved, the results obtained from the systems ethylcellulose, stearic acid, tetralin, and ethylcellulose tetralin (runs 1 and 10) were checked with the results of Hulette (6) who conducted a similar project. All materials used were checked for changes

TABLE I
COMPOSITION OF SOLUTIONS FOR REFLUXING

Sol. No.	Fatty Acid	Solvent	Grams of Fatty Acid	Grams Ethyl-cellulose
1.	Stearic	Tetralin	36.0	60.0
2.	Stearic	Tetralin	36.0	60.0
3.	Oleic	D.E.B.**	38.2	60.0
4.	Oleic	Tetralin	38.2	60.0
5.	Mineral Oil	D.E.B.	36.0	60.0
6.	Mineral Oil	Tetralin	36.0	60.0
7.	Linseed F.A.*	D.E.B.	36.0	60.0
8.	Linseed F.A.	Tetralin	36.0	60.0
9.	----	D.E.B.	----	60.0
10.	----	Tetralin	----	60.0
11.	----	Tetralin	----	60.0
12.	Stearic	Tetralin	36.0	----
13.	Oleic	D.E.B.	38.2	----
14.	Oleic	Tetralin	38.2	----
15.	Linseed F.A.	D.E.B.	36.0	----
16.	Linseed F.A.	Tetralin	36.0	----
17.	Mineral Oil	D.E.B.	36.0	----
18.	Mineral Oil	Tetralin	36.0	----

* Fatty Acid

** Diethylbenzene

NOTE: 600 grams of solvent were used in preparing all solutions.

in the ethoxy content, water given off and acidity of the ethylcellulose when no acid was present, changes in physical properties, water given off and acidity of the solvents and fatty acids. The weight composition of the solutions are given in Table I.

The refluxing operation was carried on in the apparatus shown in fig. (3) and the graphs figs. (4-12) show the changes in viscosity during the operations; viscosities were measured at the reflux temperature by means of a viscosity pipette inside the reaction vessel. The refluxing was carried on one hour after a sensible minimum viscosity had been reached.

A study in the change of the acid condition was also made on sample (2) and this is shown in graph fig. (4). This was accomplished by withdrawing a small portion of the solution (3 grams) and titrating in the usual manner to obtain the acid number.

A summary of the reflux conditions and the physical data on the final solutions are given in Table II. This includes the reflux temperature, time of reflux, final viscosity at 20°C., the water collected and the color of the solution.

The final acid number of the solutions were then run, and the product steam distilled to remove the high boiling solvents. The solid products obtained were then dissolved in acetone, reprecipitated by pouring into an excess of distilled water, filtered and then dried to a constant weight.

in an atmospheric oven. Since a portion of the acids were retained in the steam distilled product, it was again necessary to run the acid number in order that the true ethoxy content could be calculated.

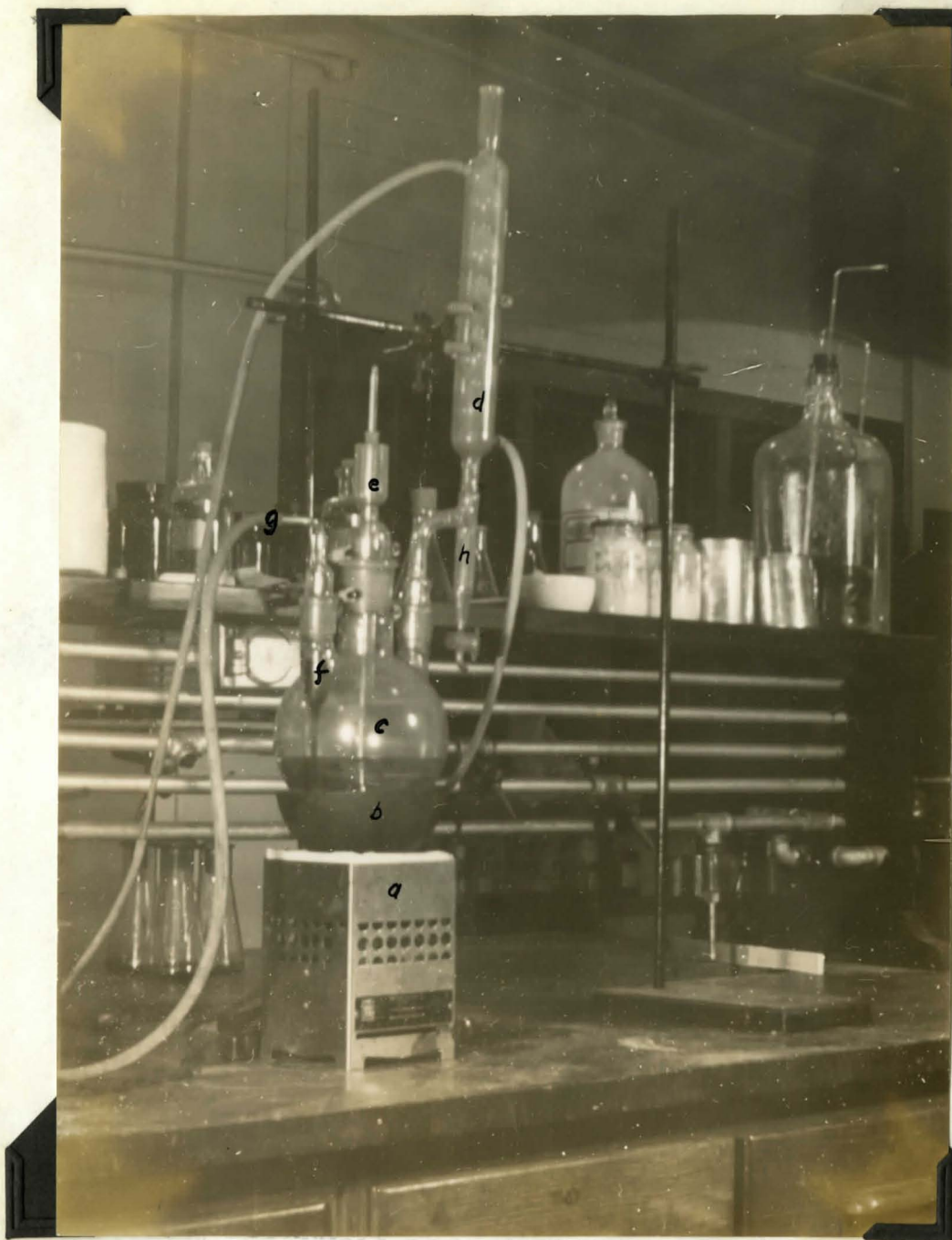


Fig. 3 Apparatus for Refluxing Solutions

- | | |
|--------------------------------|-------------------------------------|
| a. Electric Heater | e. Thermometer and thermometer well |
| b. Wood's Metal Bath | f. Viscosity pipette |
| c. Three necked Reaction flask | g. CO ₂ inlet |
| d. Condenser | h. Water trap |

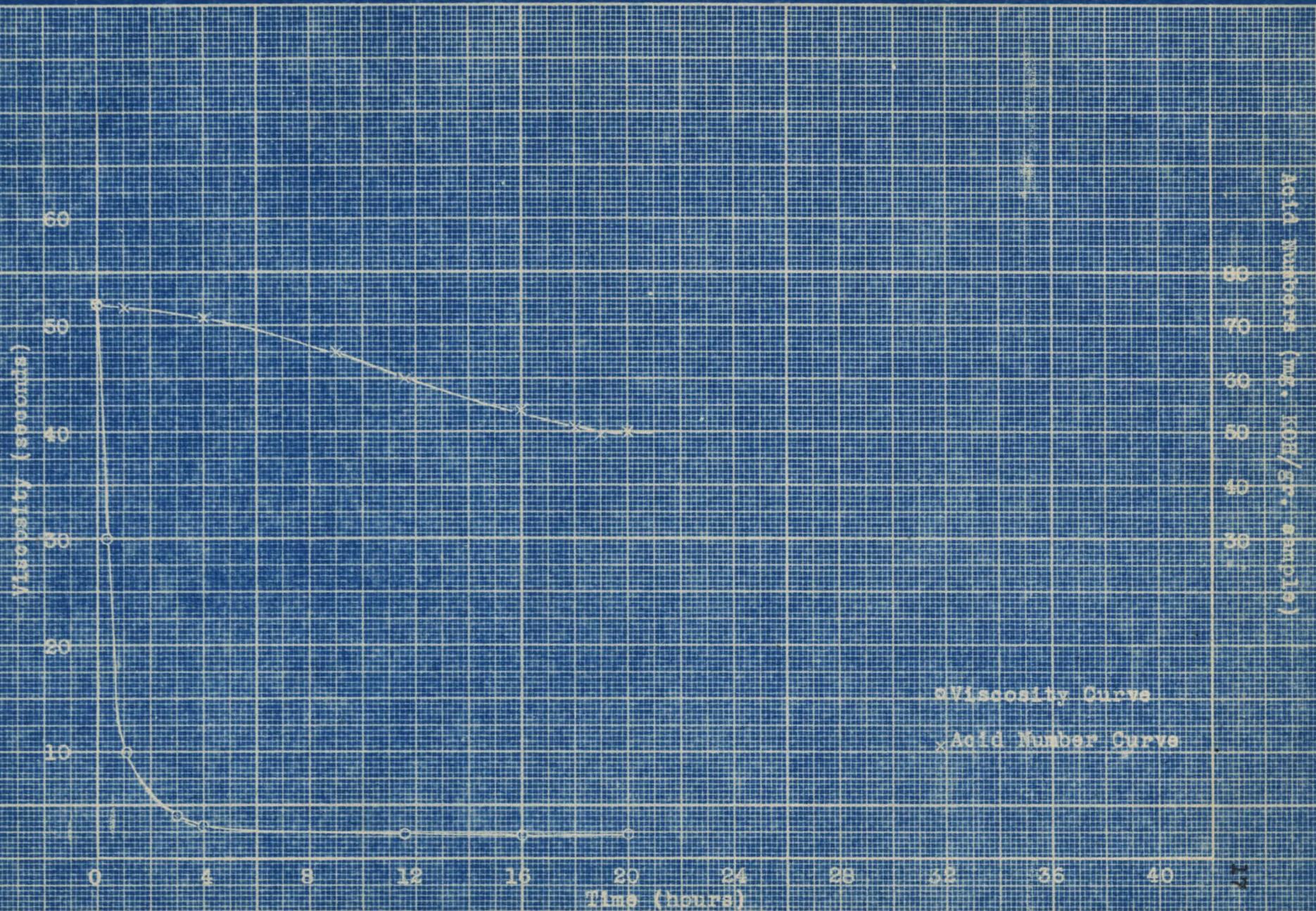


Fig. 4 Viscosity-acidification curves
(Stearic acid, ethylcellulose, benzene in solution)

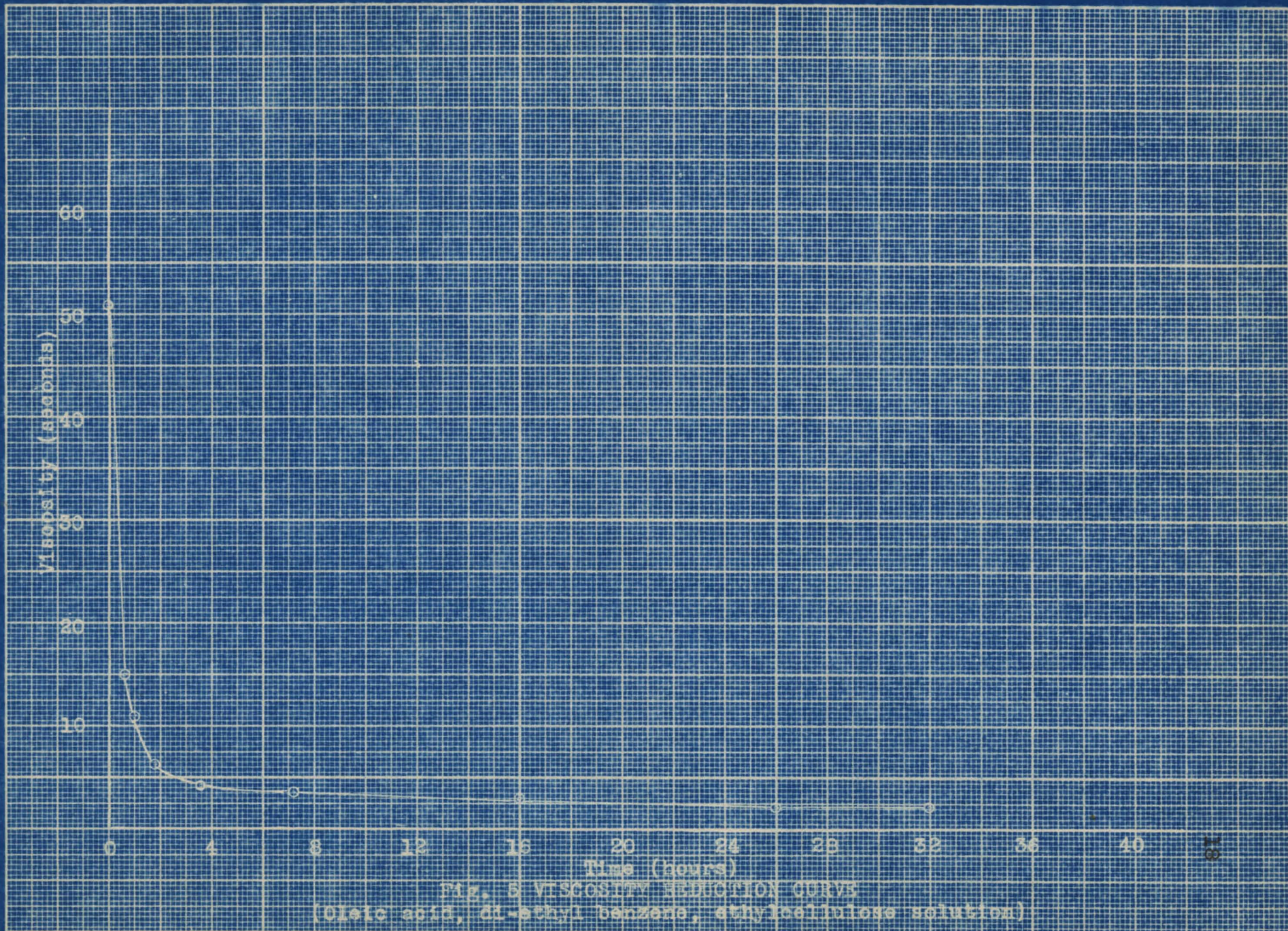
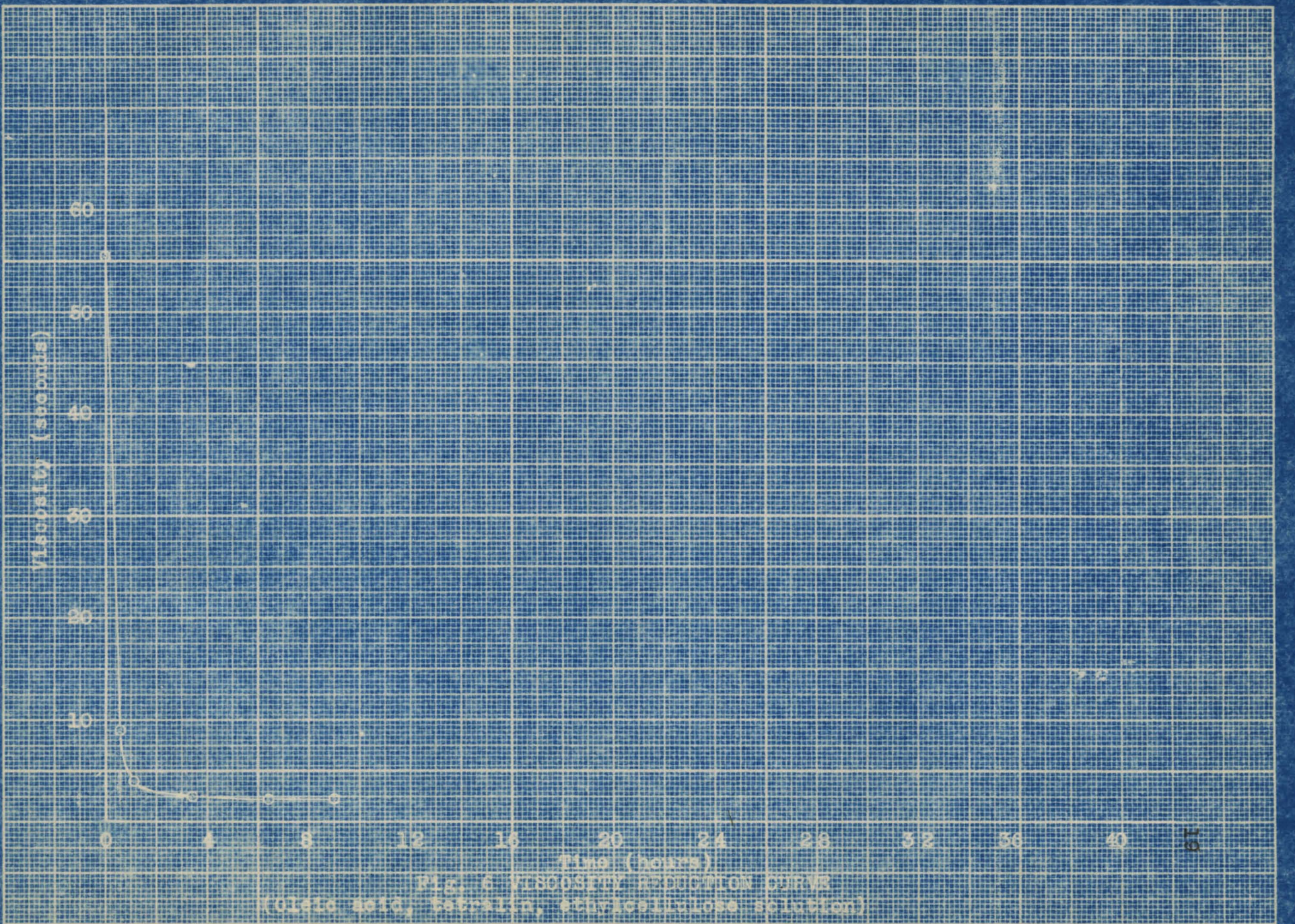


Fig. 5 VISCOSITY REDUCTION CURVES
(Oleic acid, dl-ethyl benzene, ethylcellulose solution)



Time (Hours) 0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40

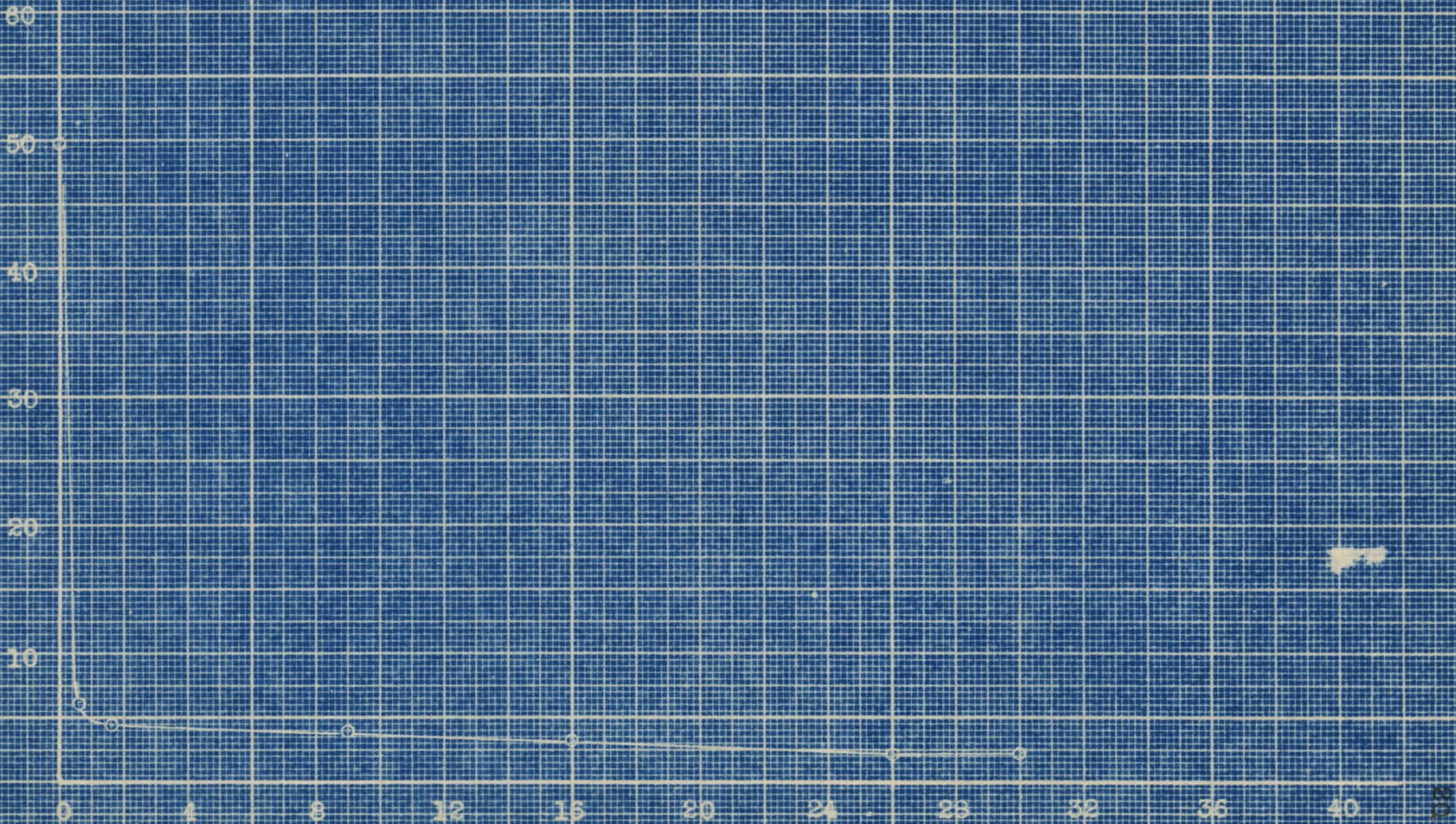
Velocity (m.p.h.) 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

Scale: 1 cm = 10 hours, 1 cm = 10 m.p.h.

Viscosity (seconds)

Time (hours)

Fig. 7 VISCOSITY REDUCTION CURVE
(Mineral oil, di-ethyl benzene, ethylcellulose solution)



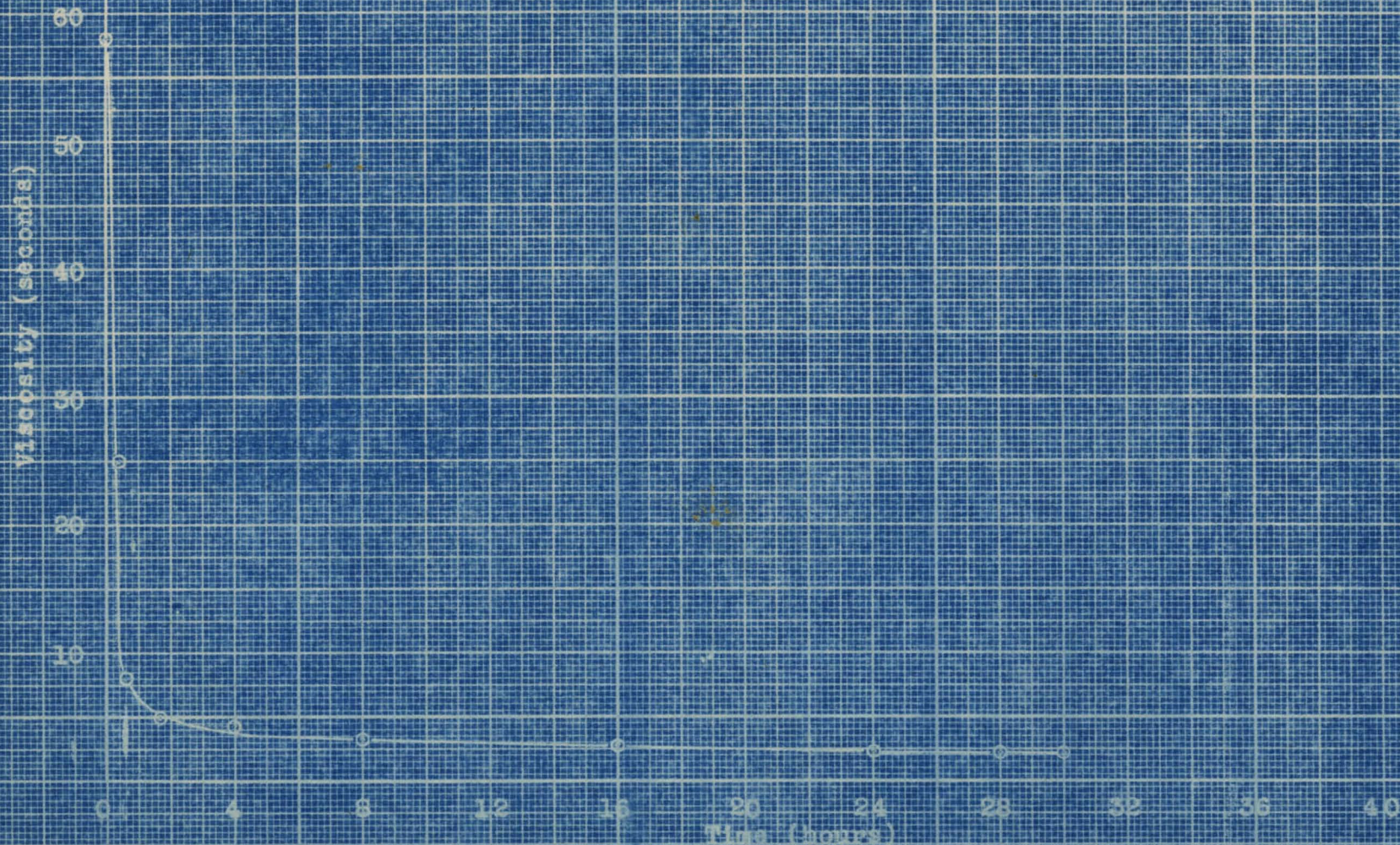


Fig. 3. VISCOSITY REDUCTION CURVE
1% hyaluronidase solution in 0.1% sodium chloride solution

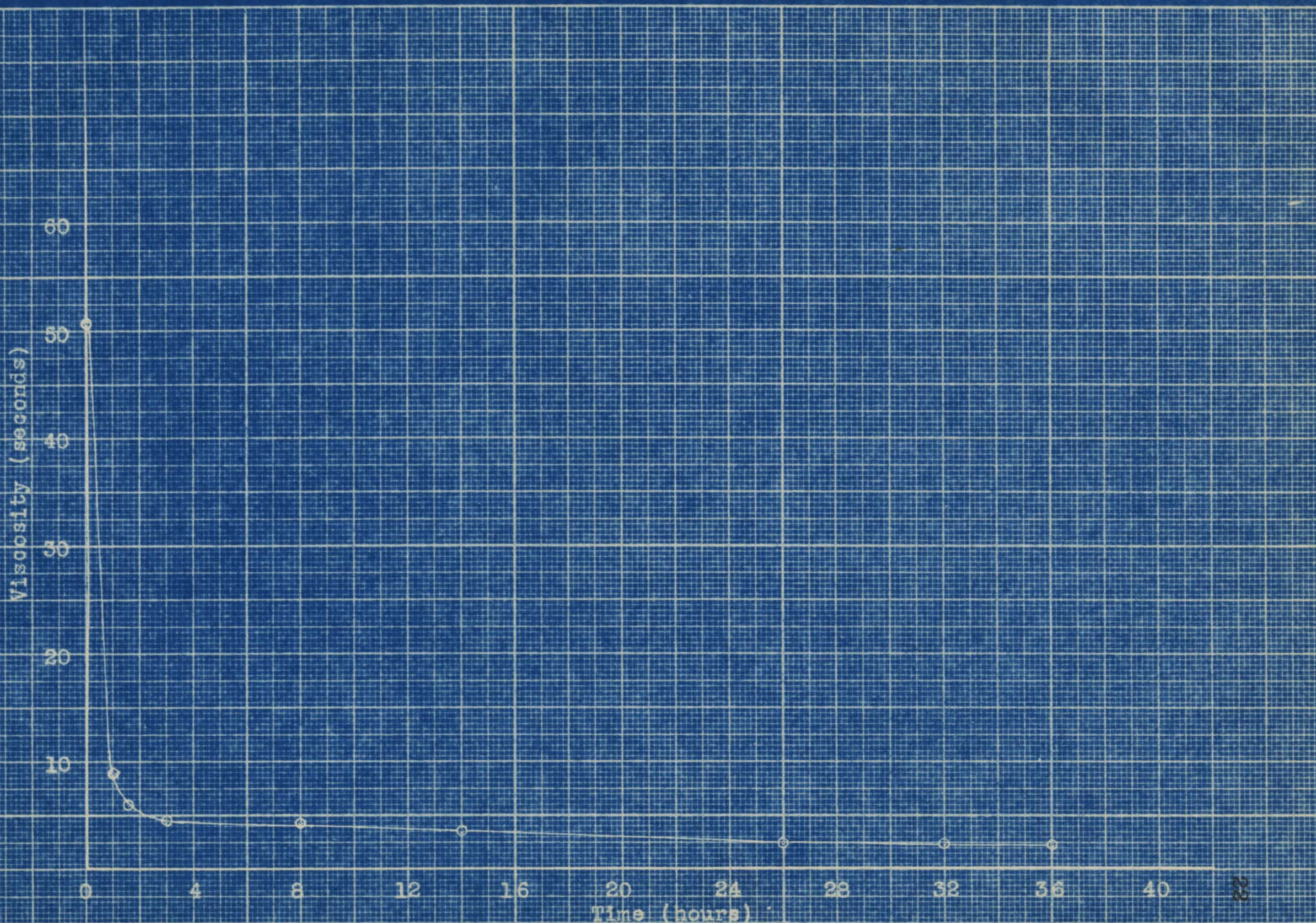


Fig. 9 VISCOSITY REDUCTION CURVE
(Ethylcellulose, linseed fatty acid, di-ethyl benzene solution)

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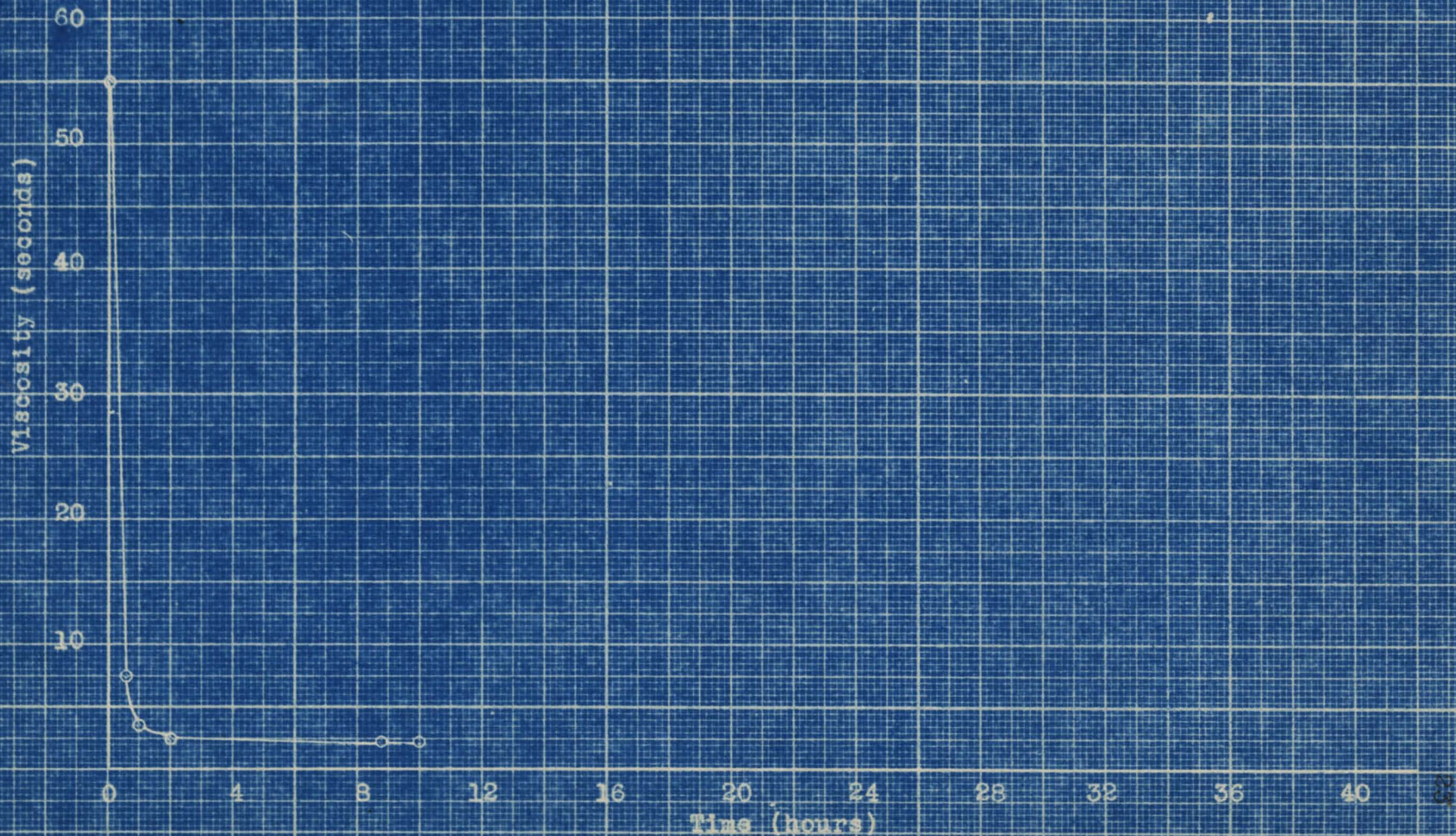


Fig. 10 VISCOSITY REDUCTION CURVE
(Linseed fatty acid, tetralin, ethylcellulose solution)

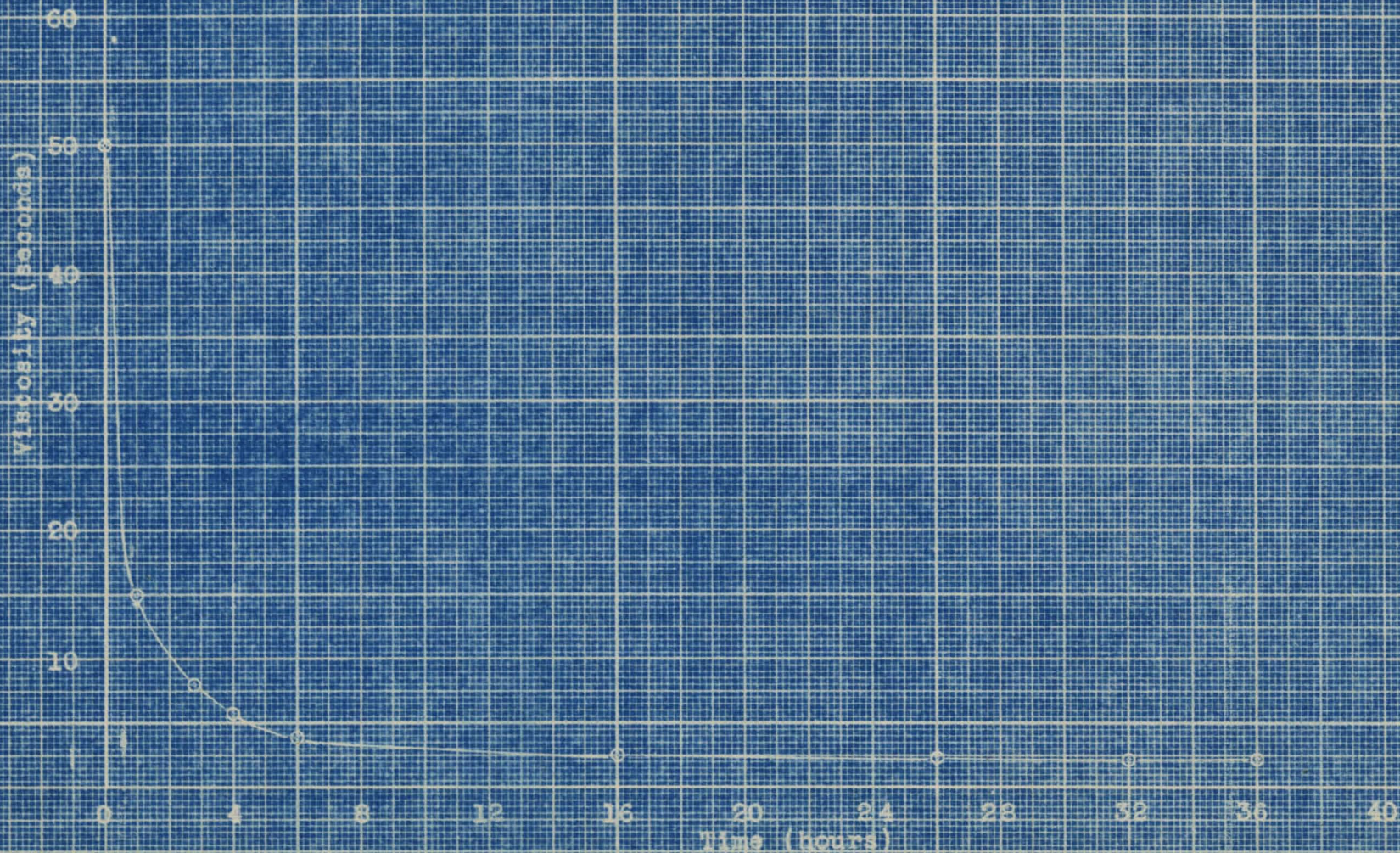


Fig. 11 VISCOSITY REDUCTION CURVE
(Cetylcellulose, di-ethyl benzene solution)

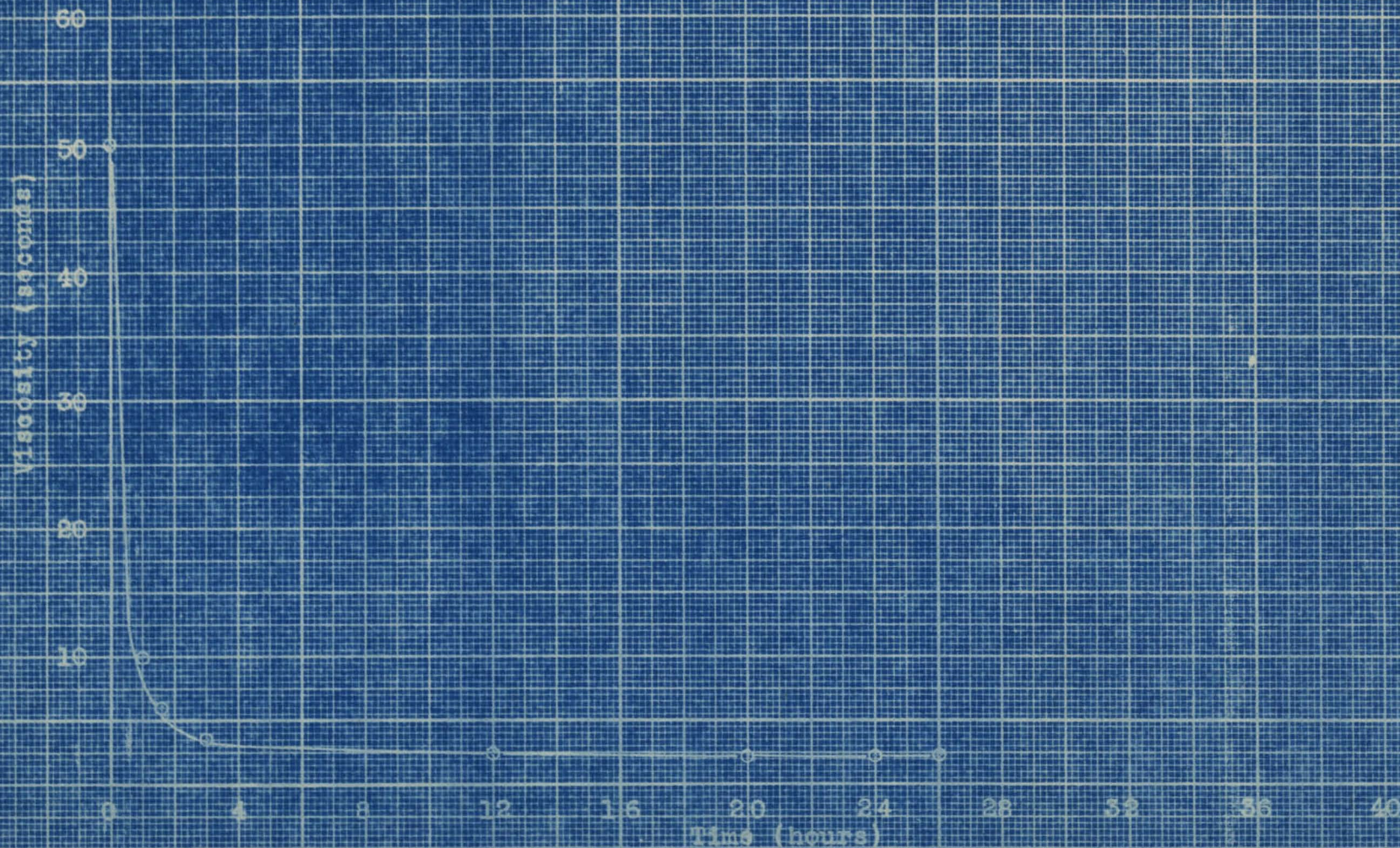


Fig. 18 VISCOSITY REDUCTION CURVE
(Kyalcellulose, tetralin solution)

TABLE II

CONDITIONS AND PHYSICAL DATA ON REFLUX SOLUTIONS

Sol. No.	Temp. Degrees C.	Reflux Time hrs.	Viscosity Final min.	Water in cc.	Color of Solution
1.	208	12.50	9.00	1.50	dark straw
2.	208	13.00	9.08	1.55	dark straw
3.	180	30.00	12.00	1.11	straw
4.	208	8.91	8.00	2.11	dark brown
5.	180	30.00	6.70	0.05	light straw
6.	208	30.00	11.11	0.80	straw
7.	180	14.00	15.00	1.30	pale straw
8.	208	9.75	13.00	1.90	light straw
9.	180	56.00	12.00	0.50	straw
10.	208	40.00	9.00	0.90	light straw
11.	208	40.00	9.00	0.90	light straw
12.	208	5.00	-----	-----	-----
13.	180	5.00	-----	-----	-----
14.	208	5.00	-----	-----	-----
15.	180	5.00	-----	-----	-----
16.	208	5.00	-----	-----	-----
17.	180	5.00	-----	-----	-----
18.	208	5.00	-----	-----	-----

The chemical data taken on the refluxed solutions is given in Table III. This includes the water of esterification, the alcohol liberated (theoretical), calculated from the ethoxy, the acid number on the steam distilled product, and the percent true ethoxy.

Table IV is an acid balance on the product containing initial acid content of the solution, free acid in the steam distilled product, total free acid, free and reacted acid, acid reacted at OH groups, acid reacted at the ethoxy, acid reacted at the Oxygen bridge, acid formed by decomposition of the ethylcellulose and acid of decomposition due to acid present.

The total free acid, and the free and reacted acids were calculated from the acid number of the solution, and the saponification value respectively.

The acid reacted at the OH groups, was obtained from the water collected during the refluxing after it had been corrected for the water normally given off when no acid is present.

The acid reacted at the ethoxy groups, is the acid equivalent of the difference between the Ethyl alcohol given off when the solutions of ethylcellulose were refluxed with and without an acid present.

The acid reacted at the oxygen bridge is the difference between the total reacted acid, the acid reacted at the OH and ethoxy.

The acid of decomposition was calculated from the total free and reacted acids, and the acid originally present in the solutions.

The acid of decomposition due to acid present is obtained from the total acid of decomposition in the solutions containing no acid.

TABLE III

CHEMICAL DATA ON SOLUTIONS

Sol. no.	Water of es- terification cc.	Alcohol ac- tually col- lected gr/ gr. sample	Alcohol li- berated gr/ gr. sample	Acid no. mg. KOH/gr. sam- ple taken on solution	Saponifica- tion no. mg. KOH/gr. sam- ple	Acid no. steam dis- tilled pro- duct mg. KOH per gr. sam- ple	Ethoxy per- cent
1.	0.400	-----	1.640	49.50	76.80	49.0	42.2
2.	0.450	0.530	1.550	50.00	76.00	-----	43.5
3.	0.160	-----	0.955	52.30	77.30	25.2	43.1
4.	0.260	-----	1.960	43.40	77.00	35.3	41.0
5.	0.000	-----	-----	2.70	2.72	-----	45.4
6.	0.000	-----	-----	2.72	2.73	-----	45.0
7.	0.100	-----	0.626	52.80	64.40	15.6	44.2
8.	0.250	-----	1.075	42.80	66.20	36.7	42.3
9.	0.000	-----	0.713	0.93	0.940	-----	46.3
10.	0.000	-----	0.865	1.18	1.230	45.8	45.8
11.	0.834	0.042	1.150	1.20	45.90	-----	45.9

TABLE IV

ACID BALANCE ON THE PRODUCT OF REFLUXATION

Sol. No.	Initial acid content of the solution	Free acid in steam distilled product	Free acid indicated by acid number	Free & reacted acid indicated by saponification number	Acid reacted at OH group	Acid reacted at O ₂ bridge	Acid reacted at ethoxy	Acid formed by decomposition of ethylcellulose	Acid formed by decomposition of ethylcellulose due to acid present*
1.	.3750	----	.2510	.3815	.0645	.0156	.0510	.0064	.0070
2.	.3750	----	.2535	.3850	.0727	.0080	.0462	.0062	.0051
3.	.3980	.125	.3081	.4150	.0262	.0090	.0654	.0161	.0100
4.	.3980	.190	.2335	.4141	.0445	.0120	.1340	.0107	.0060
5.	.3750	.235	.3780	.3811	-----	-----	-----	.0047	-----
6.	.3750	.240	.3811	.3811	-----	-----	-----	.0061	-----
7.	.3750	.084	.3144	.3851	.0190	.0032	.0474	.0091	.0026
8.	.3750	.205	.2550	.3891	.0475	.0054	.0812	.0141	.0076
9.	-----	-----	.0047	-----	-----	-----	-----	.0047	-----
10.	-----	-----	.0060	.0063	-----	-----	-----	.0063	-----
11.	-----	-----	.0058	.0061	-----	-----	-----	.0061	-----

* Acid products of decomposition expressed on a basis of acid used in solution
 NOTE: All units grams per gram sample

INTERPRETATION OF DATA

The time required to reach minimum viscosity has been found by Hulette (6) to be an inverse function of the temperature. This is true, however, only when there is no acid present. The data definitely indicates that the properties of the acid present greatly influence the time required to reach minimum viscosity.

A study of fig. (4) indicates that the acidity of the solutions decrease due to reaction until decomposition of the cellulose begins, then the acidity curve begins to flatten and on prolonged heating should gradually rise.

The color of the solutions in all cases darkened as the time of refluxing increased.

The acid balance Table IV indicates that we have reaction at all places and the percent reacted at the various places are given in Table V. The theoretical amount reacted at the OH groups would have given off 2.35 cc. of water (density 0.98) and in no case was this amount accounted for. If the acid had completely reacted with ethoxy groups we should have obtained 29.85 grams of ethyl alcohol, this also, was never obtained as shown in Table III, runs numbers 2 and 11. In connection with the above we may state that the amount of reaction of the various groups depends largely on the time of reaction, the acid present and the temperature of reaction.

TABLE V

PERCENT REACTION AT THE VARIOUS
GROUPS IN THE ETHYLCELLULOSE MOLECULE

Sol. No.	% Reacted at OH	% Reacted at Ethoxy	% Reacted at Oxygen bridge	% Acid of Decomposition*
1.	17.20	13.60	4.51	1.84
2.	19.40	12.30	2.13	1.33
3.	6.57	16.40	2.26	2.40
4.	11.20	33.60	3.08	1.45
5.	-----	-----	-----	-----
6.	-----	-----	-----	-----
7.	5.10	12.25	0.86	0.67
8.	12.80	21.80	1.45	1.95

* Percent acid of decomposition due to acid present, based on acid present.

CONCLUSIONS

When Ethylcellulose is incorporated in a varnish it may be concluded that three things will take place. First, there will be reaction between the free fatty acids in the oils and resins with the ethylcellulose at the Oxygen bridge and cleavage points, at the hydroxyl groups, and the ethoxy groups. Second, the acidity of the varnish during the incorporation period except on prolonged heating. Third, the decomposition of the ethylcellulose at the bodying temperature will darken the varnish depending on the time it is held. Since all these factors are a function of time and temperature they can be controlled. The fatty acids present in the oils and resins also would exert an influence on the three factors mentioned above. Studies of the different varnishes would be necessary to determine the optimum conditions.

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PART II

ETHYLCELLULOSE IN PENCIL LACQUERS

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INTRODUCTION

A survey of technical literature reveals that there has been no previous attempts to use ethylcellulose in pencil lacquers. However the use of ethylcellulose in lacquer formulation has been studied for the past few years both by the industrial producers of the material and lacquer manufacturers. Successful formulations have been produced using ethylcellulose in lacquers for clear furniture finishes and a pigmented coating of various types.

These lacquers may be prepared in the conventional manner and the best methods found for incorporation of pigments is by grinding in a ball mill or a rubber mill.

The plastic properties of the ethylcellulose film are better than those of nitrocellulose therefore it has been possible in all previous investigations to use less plasticizers in the finishes.

This investigation is an attempt to use ethylcellulose in pencil lacquer formulation and to make a comparison of it with a standard nitrocellulose pencil finish.

HISTORICAL

Lacquers have been used extensively for many years for their decorative properties in coating pencils. Pencils receive anywhere from a minimum of three to a maximum of fifteen coats of lacquer depending upon the price of the pencil and where it is to be sold. These lacquers may be clear, as in some of the cheaper pencils, or highly pigmented and a coat of clear on top for the more expensive varieties. They must dry in a few seconds and have a high viscosity that they may be applied with a coating machine.

From the physical properties of ethylcellulose it should be ideal to use in the type of lacquer desired for pencil finishing. To the author's knowledge there has not yet been any work done in this field therefore the following work is an attempt to indicate the uses of ethylcellulose in pencil finishes.

THEORETICAL

The formulations for pencil lacquers is more or less standardized throughout the country. Half second nitrocellulose being the chief constituent of the vehicle. In itself it is very brittle so it is necessary to add oils to make it more plastic and resins to give binding power and gloss. The thinners must be volatile enough to be thrown off in a few seconds and there must be no solvent retention in the dried film. These lacquers dry solely by evaporation and there must be enough nitrocellulose present to give a tack free film with the oil and the resin. Therefore the formulation must be perfectly balanced in all these respects.

Materials available for this study were blown linseed oil, blown soy-bean oil, and paranol, 4541 resin. These materials are somewhat new in the lacquer industry as far as pencil lacquers are concerned. Of the two oils mentioned, blown linseed seemed to give the better properties.

Ethylcellulose has a larger bulking value than nitrocellulose therefore it is possible to get a larger amount of cotton in the dried film. Since its plastic properties are much better than those of nitrocellulose it should be possible to decrease the amount of oil, plasticizer and resin in the final formulation.

RAW MATERIALS

Ethylcellulose

Standard ethoxy grade 48.5-49.5 ethoxy; viscosity 7 C.P. as determined on an 80-20 toluene (5%) ethyl alcohol solution at 25°C.

Oil

Solinox Z; a blown Linseed oil with a viscosity of about Z-6 on the Gardner Holdt scale.

Plasticizers

Dibutylphthalate and Tricresylphosphate, standard lacquer grade.

Hercules Powder Company.

Resins

Beckasol, 1324, 50% solution in Xylol.
Reichold Chemical Company

Paranol, 4541.
Paramet Chemical Company.

Pigments

Titanium dioxide, Titanox R 610.
Titanium Pigment Company

Chrome Yellow medium, no. 2283.
Chrome Orange, no. 2810.
Kentucky Color and Chemical Company.

Iron Yellow, Lemon Yellow, no. 1149-L.
George S. Mephram Company.

Lithol Red, Lithol Red toner, no. 1033.
Kentucky Color and Chemical Company.

Multifex MM, a specially treated calcium carbonate material.

R.T. Vanderbilt Pigment Company.

Solvents

Ethyl alcohol, ethyl acetate, butyl alcohol, butyl acetate, isopropyl alcohol, and acetone, standard lacquer grade.

U.S. Industrial Chemical Inc.

PROCEDURE

The pencil lacquers were prepared in the conventional manner. The pigments were first ground in the oil, resin and plasticizer on a standard three roll paint mill to form a heavy paste. About three passes were necessary to obtain a smooth grind. The ethylcellulose was then dissolved in the solvents and the pigmented paste added to complete the lacquer.

The standard nitrocellulose lacquer formula shown in Table I was used as a basis for starting this investigation. Lacquers were prepared substituting ethylcellulose for the nitrocellulose. These lacquers proved to be too soft and did not dry very rapidly. The film was mushy and was not tack free even after thirty minutes. The plasticizer and resins were then reduced in the preceding formulae until desired drying and film properties were produced. The thinner combinations were then adjusted to improve drying. This method was followed in both the clear and pigmented lacquers. The lacquer given in Table I is a typical pencil lacquer sold by a reliable manufacturer and it has given very good results over a long period of time. Due to wartime conditions some of the raw materials are new, but they have been found to be successful substitutes for the ones originally employed. The pigments used were representative of all types which may be encountered in pencil lacquer formulations.

TABLE I

STANDARD NITROCELLULOSE LACQUER FORMULA

Material	Percent*
Chrome Yellow	16.22
Chrome Orange	4.95
Iron Yellow	1.67
Multifex	5.01
Beckasol 1324 50% solution	7.88
Castor Oil	2.57
Dibutylphthalate	3.15
Ethyl Alcohol	9.64
Acetone	4.72
Butyl Alcohol	1.95
Butyl Acetate	3.13
Isopropyl Alcohol	7.01
1/2 sec. Nitrocellulose	32.10

* Percent by weight.

NOTE: Standard red and white pencil lacquers use the same vehicle combination. The only change in the formula being that the proper amounts of red and white pigments are added to give sufficient covering.

To prepare the lacquers for testing, pencils were coated in a standard pencil coating machine under regular production conditions. They received from three to five coats and some received a clear top coat. The clear lacquer was also tested by itself.

METHODS OF TESTING

The properties desired in a pencil lacquer are: a hard tough film which will not go brittle in aging, a rapid tack free dry (about 30 seconds) and a high covering power.

The hardness is tested by cutting the film with the end of the finger nail and then examining the cut for cracks. The brittleness is tested in the same manner after about 3-6 months.

The tack free drying is tested by taking a hand full of the finished pencils, squeezing them together and then dropping them from a height of about 12 inches. If all the pencils completely separate, they are considered tack free. The covering is determined by comparing the number of coats necessary to give complete covering with a standard pencil lacquer formula.

RESULTS

The data and results obtained on the pencil lacquers prepared are given in the following tables. Lacquers made with white pigments are given in Table II, those containing red in Table III, and those containing yellow in Table IV, and the clear top coats are given in Table V.

The finished lacquers were tested according to the schedule listed under methods of testing, and then compared with a standard pencil lacquer. The results of these tests are also given in Table VI.

TABLE II

FORMULAE FOR WHITE PENCIL LACQUERS

Pigment	1 Percent*	2 Percent	3 Percent
TiO ₂	15.59	16.23	16.81
Lithophone	4.74	4.94	5.11
Beckasol 1324 50%	13.57	8.49	4.82
Silinox Z	4.10	2.82	3.37
Solvesso #1	-----	1.85	1.92
Isopropyl Alcohol	11.25	11.76	12.16
Butyl Acetate	2.44	2.54	2.62
Butyl Alcohol	4.50	4.66	4.82
Ethyl Acetate	11.46	11.93	12.36
Acetone	6.54	6.81	7.05
Ethylcellulose 7 c.p.	26.80	27.95	29.00

* Percent by weight.

TABLE III

FORMULAE FOR RED PENCIL LACQUERS

Pigments	1 Percent*	2 Percent	3 Percent
Lithol Red Toner	3.37	3.66	3.73
Chrome Orange	6.03	6.54	6.68
Multifex**	6.03	6.54	6.68
Beckasol 1324 50%	14.81	10.60	10.90
Silinox Z	4.04	2.93	2.99
Dibutylphthalate	3.37	1.92	-----
Ethyl Alcohol	11.12	12.20	12.32
Butyl Alcohol	2.42	2.59	2.67
Butyl Acetate	4.44	4.82	4.92
Ethyl Acetate	11.52	12.32	12.58
Acetone	6.47	7.03	7.17
Ethylcellulose 7c.p.	26.60	28.90	29.43

* Percent by weight.

** Ppt CaCO_3 .

TABLE IV

FORMULAE FOR YELLOW PENCIL LACQUERS

Pigments	1 Percent*	2 Percent	3 Percent
Chrome Yellow	15.87	13.10	13.92
Chrome Orange	4.84	3.96	4.25
Iron Yellow	1.63	1.61	1.72
Multifex**	5.88	5.79	6.22
Beckasol 1324 50%	13.62	13.39	10.38
Solinox Z	6.79	6.69	6.02
Dibutylphthalate	3.37	3.33	-----
Isopropyl Alcohol	11.44	9.39	10.05
Butyl Acetate	4.56	3.74	4.01
Butyl Alcohol	2.48	2.03	2.18
Ethyl Acetate	11.68	9.57	10.25
Acetone	7.97	5.46	7.02
Ethylcellulose 7 c.p.	-----	22.08	24.10
Ethylcellulose 22 c.p.	10.03	-----	-----

* Percent by weight.

** Ppt. CaCO₃.

TABLE V

FORMULAE FOR CLEAR TOP COATS

Material	Percent*
Ethylcellulose 7 c.p.	50.40
Tri-Cresyl Phosphate	2.80
Lacquer Naphtha	7.48
Butyl Acetate	5.10
Butyl Alcohol	1.94
Ethyl Acetate	13.44
Ethyl Alcohol	9.22
Acetone	6.82
Paranol 4544	7.80

* Percent by weight.

TABLE VI

RESULTS OF TESTS

Sample	Tack-Free Time	Hardness	6 Month Age*	Remarks
Red #1	55 sec.	soft	O.K.	Too much plasticizer, slow dry, mushy film.
Red #2	35 sec.	medium	O.K.	Good dry; good film
Red #3	30 sec.	good	O.K.	Good dry; good film
Red. std.	25 sec.	good	O.K.	Std. Nitrocellulose formulae.
White #1	60 sec.	soft	O.K.	Too soft; too long dry.
White #2	30 sec.	good	O.K.	A good film
White #3	15 sec.	granular	---	Not very good.
White std.	20 sec.	good	O.K.	Std. Nitrocellulose formulae.
Yellow #1	50 sec.	mushy	----	-----
Yellow #2	50 sec.	soft	----	-----
Yellow #3	35 sec.	good	----	Good film; good drying time.
Yellow std.	30 sec.	good	O.K.	Std. Nitrocellulose formulae.
Clear	30 sec.	very good	O.K.	Excellent film.
Std.	30 sec.	good	O.K.	Std. Nitrocellulose formulae.

NOTE: 3 coats gave sufficient covering with the exception of white #1, 5 coats being necessary in this case. For the clear coat only one coat was used.

* Test for brittleness.

CONCLUSIONS

From the tests on the drying and film properties of the ethylcellulose pencil lacquers we may conclude that when proper balance of solvents, plasticizers, oils, and resins are used we can successfully make good pencil lacquers. In the comparison with the nitrocellulose lacquers some of these ethylcellulose lacquers may be considered as good as the former. The clear top coating lacquer worked exceptionally well and probably will be used for this purpose in the future whenever price permits.

RECOMMENDATIONS

The work indicates that it is highly possible that suitable pencil lacquers may be made from ethylcellulose. Therefore an investigation of other oils and resins would be adviseable as soon as they are again commercially available. Some other resins and oils would probably be more suitable. Possibilities are blown castor oil, blown synthetic oils of the malaic acid type and non drying resins such as Paraplex R.G. 2, Paraplex G20, and Duraplex N.D. 75. It might also be adviseable to use demar gum in the clear finishes.

A better combination of thinners might also be found since ethylcellulose has a wider range of solubility than the nitrocellulose.

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V I T A

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