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I hereby recommend that the thesis prepared under my supervision by Edward Terhune Johnson *entitled* Surface Tension Relationships of Lithographic Inks and Waters.

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy.

Approved by:

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SURFACE TENSION RELATIONSHIPS
OF LITHOGRAPHIC INKS AND WATERS

A dissertation submitted to the
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by

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TABLE OF CONTENTS.

Page

Description of Lithography

Theoretical Section

Experimental Section and Observations

Further Experimental Work

INTRODUCTION

Since at the beginning of this work, only one empirical generalization was available as to the conditions under which the particular paper troubles under investigation arise, and one more was very early obtained as to the conditions accompanying the rather similar ink trouble, the experiments were necessarily of a pioneering nature. The troubles and generalizations will be explained in detail below. The empiricism of the means by which these initial generalizations were reached, the multiplicity of factors involved in lithography, and their unknown interrelationships made it necessary to do a good deal of preliminary surveying of the field. Some of it was done simply to secure a better perspective of the problem, and not with the solution of it as a direct purpose. This was in some cases followed by a quantitative investigation with an eye to peculiarities which might shed light on the problem. Thus, insofar as insufficient theoretical information was available on the basis of which to answer the problems of paper and ink, it was necessary, before crucial tests could be framed, to have an hypothesis, or hypotheses, on which to base them. This is why we found it necessary to search so widely for properties which would serve as clues in an explanation of the results obtained in practice.

The order in which the topics were handled was not exactly that in which they should logically occur, due to the fact that the lithographic press in the laboratory was not available for this work till January, 1932. The checking of our empirical information from the shops had, therefore, to be postponed until that time, and there was no time after that was over to follow up the information gained in the press run.

Description of Lithography--General

In lithography, one prints an ink image from a solid surface in which the inked image area is, in general, neither cut away nor in relief, but is, instead, at substantially the same level as the surrounding, non-inked, non-printing area. The reproduction of solids needs no especial explanation. Pictures are reproduced by representing them as a series of uniformly spaced dots of various sizes. The high lights are achieved by printing very small ink dots, and the shadows by printing relatively large ones, but it is important to note that the largest and the smallest ink dots are intended to be identical as to quality, both on the plate and on the printed picture; the dots vary from large to small, but not from heavy to light, as in rotogravure. This is known as "half-tone" reproduction.

Lithography is based on the fact that grease and water do not mix, and that thus a part of a solid surface may be wet with water, and thereby fail to be wet by the greasy ink which is used, even though the ink be rolled over it quite vigorously. In the same way, the ink can maintain itself on a solid surface regardless of the proximity and contact of water. Of course, the retention of the ink or water by the solid surface depends on the relative wettability of that surface by water and by ink. If the water wets the surface more readily than the ink, any minute mechanical displacements of one liquid by the other will be in favor of the water-wet area, and at the expense of the ink-wet area. Or the reverse may be true, and the work of wetting of the surface by ink may be greater than that by water, in which case the ink will advance by small stages, gradually covering the whole surface.

Thus it would seem best to pick out as a material for the plane surface mentioned above, a substance which would be wet with about equal ease by ink and by water, so that neither could encroach on the area upon which we wished to maintain the other. The first material which Senefelder (1), the inventor of lithography, observed to behave satisfactorily in this respect was a certain limestone found in southern Germany, and it was with a polished surface of this that he began to carry on lithography. While this material was quite satisfactory for use in flat bed presses, flexibility of the printing surface became desirable as a result of the invention of the rotary press with its increased speed. Plates of zinc or of aluminum, the surfaces of which were finely grained, were found to be suitable in that both the ink and the water seemed to maintain themselves fairly well in their original areas on the plate. Copper has, on the other hand, been found to be definitely unsuitable, as it is more easily wet by ink than by water, and the inked area gradually increases on running.

A few of the salient points of press design will be given to aid in visualization of some of the steps of the process and some of the troubles incurred. The plate, having already been prepared with the image on it in ink, is fastened to the plate cylinder of the press. When the press is running, a point on the plate rotates first under the damper rollers, which replenish the film of water on the water-wet, non-printing areas, then under the "form rollers", which replenish the ink on the ink-wet, printing areas. An even supply of ink to the form rollers is insured by quite an extensive roller system through which the ink is fed from the bottom of a trough. Last of all, the point comes to the "blanket", a thin sheet of fabric-backed rubber fastened around another cylinder, the blanket cylinder, which squeezes the blanket into very close contact with the plate. The blanket takes a part of the ink from the plate in the form of the design, and squeezes it against the paper on which we wish to print, which, in turn, is backed by still another cylinder, the impression cylinder. The plate and blanket and impression cylinders are all of practically the same circumference, and the plate and blanket cylinders are mechanically equipped so that the linear velocity of the surface of the rotating plate is the same as that of that part of the blanket which is being furthest depressed by the plate at that instant. This is intended to prevent wear of the plate by the blanket, and doubtless reduces it, at least, to a very low value.

The question of what happens near the water-ink interface when the form rollers and the wet portion of the plate separate involves largely the consideration of surface energy and of viscosity. There are three possibilities:

1) Splitting takes place exactly at interface.
2) " " " in water phase.
3) " " " " ink " .

For 1) Increase in γ, surface energy (free), will be $\gamma_{ink} + \gamma_{water} - \gamma_{interface}$ = (assuming typical values) $35+72-20=187$. ergs/sq. cm.

2) Increase in will be $2\gamma_{water} = 2 \times 72 = 144$

3) " " " " " $2\gamma_{ink} = 2 \times 35 = 70$ ergs/cm^2

The last of these involves the least increase in surface energy, but it also involves a considerable amount of work in overcoming the effect of viscosity. In many tests with an inked hand-roller on a metal plate which was partly water-wet and partly inked, it was found that the surface of the water, after the roller had passed over it, still permitted the spreading of little aggregates of ink left on its surface. The surface is, then, at most imperfectly saturated with the materials of the ink. Probably the third of the possibilities mentioned is not much preferred to the second, by the system. At least, we know that spreading can still take place.

To return to the maintenance of ink and water in their proper areas on the plate, it is obvious that the evaporation of the water, leaving the plate receptive to ink, is a real danger, while that of the non-volatile ink, made with a base of heat-bodied linseed oil, is not. Therefore, it is very important to insure that the water-wet areas of the plate remain water-wet. It would be better if we could have for the water-wet areas a material to which grease would not adhere. We started out, however, with zinc or aluminum as the whole surface, so a coating is the most suitable expedient that we have available. The coating which seems to be most effective is made by exposing to light an aqueous solution of gum arabic and ammonium dichromate, spread on the plate. The solution, on exposure to light, gradually stiffens to a gel. If the change be not permitted to go too far, the gel will remain capable of taking up water, with consequent swelling and weakening, so that any ink which may have come into contact with it and adhered while it was dry can now be removed quite easily (along with part of the gel) by wetting the plate and rolling it with an inked elastic roller. When the supply of gel on the plate is exhausted, there is nothing except the water between the ink and the plate. If the plate should now dry, the ink could come into direct contact with it, and stick so tightly that it would be almost impossible to remove it without removing the whole image also. Thus, that particular plate would be rendered useless.

This protective coating makes it possible to carry on lithography practically, but the coating itself is quite fragile, and may easily be used up, as just described, or worn off, and the ink can then come into direct contact with the plate. A special phase (and the most common one) of this trouble is that the ink sometimes extablishes itself in very small isolated spots in the non-printing areas of the plate. When the ink does become established on the plate in small dots, it is common practice to increase the acidity of the dampening, or "fountain", water and so to remove by reaction of the acid with Zn a small amount of the surface of the plate, thus undercutting the undesirable ink spot, and removing it. The trouble with this procedure is that it also undercuts all other inked areas by about the same linear amount, so that the smallest dots lose the greatest percentage area, and the high lights of the picture become very light indeed, even in comparison with the rest of the altered picture. Also, when catching up of ink on the plate has once started, this treatment will rarely eliminate it, but usually serves only to hold it in check. Sometimes it fails to do even that, and more and more of the ink dots appear on the surface of the plate. These print a tint over what should be the blank areas of the print. When the plate fails too badly in either of these two directions, it must be discarded. Therefore it would be very advantageous if this catching up of ink on the plate could be avoided, for the first of these troubles would be minimized, and the other stopped entirely. This taking of ink on the plate is known in the trade by several names. In this thesis, it will be called"greasing of the plate".

Another allied trouble, sometimes less serious in nature, is known as "blanket scum". It consists of the collection of ink on the non-printing areas of the blanket. This condition is apt, though not certain, to be accompanied by two other troubles--first, printing of this undesired ink on the paper, and, second, greasing of the plate, mentioned above. It is usually corrected in a cut and try manner by changing either paper or ink, or both, till the trouble is stopped. It is possible and not uncommon to have blanket scum without having corresponding ink spots on the plate or even on the paper, but it is, of course, impossible to have greasing of the plate without having the spots carry onto the blanket and thence to the paper.

It has been observed in practice that the use of coated papers seems to be associated, in many cases, with formation of blanket scum. Professor Reed, who suggested and directed this research, has found that those coated papers which give the most trouble along this line seem, in general, to be those which, when extracted with water, give solutions that form the most stable foams, and this led him to determine their surface tensions. He found that the extraction with water, under standardized conditions, of papers which seemed to give trouble in the shops, gave solutions of very low surface tension. Upon investigation he found that in many cases, manufacturers of coated papers used surface tension depressors to prevent the foaming of the alkaline casein sols with which the paper is coated. The theory of this practice is that the "sodium caseinate" which is adsorbed at the liquid-air interface forms a very viscous surface layer, although not one of particularly low surface tension, and this property results in foaming. An anti-foaming material is added, and, being able to cause a greater lowering of surface tension than the casein sol, spreads over the water-air interfaces, displacing the casein, and giving a much more fluid surface film. The foam then becomes unstable and breaks down, giving a smooth and regular coating for the paper.

The only basis on which we can explain the effect of coated papers on plate and blanket is to suppose that that material in the paper which effects these results is extracted in small amounts by the slight amount of moisture which passes from the plate to the blanket. It then functions on plate, blanket, or in the inking system.

Another group of materials which are often present when trouble occurs is the thin nearly fluid sort of ink. Lithographers assert that an ink which is functioning well can be caused to give greasing of the plate simply by adding to it too much of a reducer, a material which will thin it and render it softer.

While the author was testing the surface tension effect on water of various lithographic varnishes, these being constituents of ink, he happened to try one brand of varnishes, which will be known in this thesis as C#1 and C#3, which gave very unusual results. The results are described below. On inquiry, he found that their history was as follows:

It seemed to lithographers that greasing of the plate could be eliminated in a very obvious way by eliminating from the inks the most "greasy" materials, and these they took to be the fatty acids. A certain ink manufacturer made up this series of varnishes, of varying viscosity, but having in common the characteristic of having in them a very small amount of free acid, less, in fact, than most raw linseed oil, and it was expected that this would be a much better varnish, and that inks made with it would not allow greasing of the plate to occur. An ink was made up with it, and it was found that, instead of decreasing, greasing of the plate was increased. Only this qualitative statement was known to us; no quantitative information was available either as to the composition or the behavior of the ink, but this seemed to be a hint worth following, nevertheless.

There are other inks besides the too-fluid group, which also give trouble of the same sort. Some are curable, while some seem incurable, and all of them are simply known as bad inks, and are not accounted for in any way. Some samples of these were obtained and examined to see whether they also might exhibit some salient peculiarity in the surface tension effects that they caused when dropped on water in small amounts.

It was the purpose of this work to make some advance in our knowledge of the water-ink relationships in lithography, with the explanation of these troubles as a distant objective, and the phenomena mentioned above seemed to furnish a good point of departure.

Inks--General

Inks are composed of lithographic varnishes, pigments, and driers. The varnishes serve as the liquid vehicle for the solid pigment, and consist of linseed oil, heat-bodied at about 600°F to different consistencies. The viscosities range from about 1.75 to 2000 poises at 25°C. Those used as the bulk of the vehicle for the pigment run from about 14 poises (#00) to 60 poises (#1), while both extremes are used in small amounts to alter the consistency of the inks. The numbers of the varnishes given,are, of course, the designations of a certain company.

The pigments usually used are:

Carbon black

Lead chromate

Lakes of organic pigments on

Precipitated hydrated aluminum oxide
" " basic aluminum sulfate

" magnesium carbonate

" barium sulfate

Zinc oxide

All these pigments are used in very finely powdered form.

The drier is simply linseed oil boiled with a metallic oxide, usually cobalt, which goes into suspension or combination in a form which serves as an oxygen carrier in the oxidation of the bulk of the varnish by atmospheric oxygen. All these constituents are ground together very thoroughly to form a mixture as nearly as possible homogenious.

The consistencies of inks are at present compared by a rather crude method of finger testing. They are first compared as to length. The finger is placed on top of a little heap of ink 1 to 3 mm. in height, and pulled gently upward. The ink strings out for some distance and then breaks. The same procedure is carried out for the other ink. Care is taken that the area of contact of finger and ink, and the depth of the pile of ink is about the same in each case. The ink which strings further is said to be the longer of the two. Length is, then, the tendency in the ink to draw out evenly over a considerable distance rather than to accentuate a neck in the string of ink until it becomes a break. As such, it seems to be attributable to two factors:

1. Consistency. It is noticed that the short inks are those which show but little more resistance to flow at high rates of shear than at low. That is, it is <u>much</u> easier to elongate the neck by a given distance in a given length of time than to spread that elongation over the whole length of thread and accomplish it in the same length of time. Consequently, the elongation tends to be concentrated at the neck, which becomes progressively thinner, until it breaks. In the case of the long ink, it is only a little easier to elongate

the neck at a given rate than to elongate the whole thread at that rate. Consequently, breaking of the thread through necking does take place, but not so soon.

2. Another factor, which is not always comparable in importance to the first, is the surface tension of the ink. Within limits, which are set by the shape of the neck, and of its ends, the smaller the cross-sectional area of that part of the thread of ink which is suffering the stretch, the less new surface will be created by a given increase in length. Since the creation of new surface uses energy (surface energy), the formation of a neck, with consequent shortness of the ink, will be more encouraged by high than by low surface energy.

A very rough experiment verified this last statement. A very fluid varnish which had a surface tension of about 34 dynes strung out .3 cm. in air. Its interfacial tension with water was about 16 dynes, and it strung out about .6 cm. under water. It was pulled out to 22 cm. in a solution against which it had an interfacial tension of something less than 1 dyne. These values showed that the influence of surface tension on the length of a varnish is as stated above. The experiment was very rough. Quantity of varnish, area of cross-section at start, and velocity of elongation were only controlled manually and visually, but repeated tests showed that the distance to which the string pulled out was not very sensitive to these factors.

The other two characteristics of ink which are measured by the finger tests are much simpler. Mobility is simply a composite of resistance to flow at various low rates of shear (down to zero). It is tested by rubbing a finger round and round on the surface of a body of ink about .5 mm. thick, and noting the drag on the finger.

Tack is tested by rubbing the ink out very thin on paper, pressing the finger firmly into the ink film, and pulling it sharply upward. The resistance to the pull is noted, and known as tack. Tack seems to be the resistance to flow at very high rates of shear. Not until all these measurements are about equal are two inks considered to have the same consistency. Among a variety of inks, mobility usually varies inversely with tack, but exceptions to this are not uncommon.

Inks are capable of taking up, and holding, as a disperse phase, a considerable amount of water. There is no proven mechanism by which this occurs, but it seems probable that the water is adsorbed on the pigment particles within the ink. As a rule, inks become shorter when water is added. This is about the only nearly consistent tendency to be observed. Inasmuch as inks do run in contact with water on the press, they necessarily take up some of it, and mean values in four cases show inks taken from the lower drums (one roller away from the plate cylinder) to contain 11.0% of water, out of a capacity of 27.1%, the ink at the start of the run containing only 2.2%.

Fountain Waters--General

Fountain waters, as stated before, are usually slightly acidulated solutions of gum arabic and a dichromate, or chromic acid. It became customary to use gum arabic at this point when the desensitization of the non-printing areas was carried out using only a strongly acid concentrated sol of gum arabic(2). At that time the desensitizing film was only adsorbed, according to Riddell (2). Since adsorption is a reversible process, it was necessary to maintain a slight concentration of gum in the fountain water to keep from washing the gum off the plate. Now it may be only a survival. The function of the chromic acid has never been adequately explained, but it continues to be used.

Lithographers in general declare that the use of soap in fountain waters is fatal to the plate--that ink soon sticks to it under such conditions, and cannot be removed. Soap is another very active lowerer of surface tension. This seems to bear in the same direction as the fact that the coated papers whose aqueous extracts foam and have low surface tensions are in general those which cause trouble.

Mechanism of Surface Tension

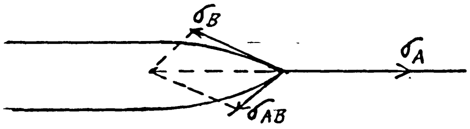
Surface tension is supposed to be due to the assymetric attraction on the molecules at the surface of any liquid, and proportional to the total attraction parallel to the surface of the liquid. Langmuir (3) has quite an elaborate mechanical explanation worked out to account for the surface tensions of classes of organic compounds. (The idea is Hardy's (4), but the particularization and much of the evidence is Langmuir's.) The highest surface tensions are those of metals--Hg 465 dynes/cm. at 20°C. Water is usually listed next, with a surface tension of 72.8 dynes at 20°C. σ, surface tension, for most organic liquids is considerably lower. Langmuir attributes the sidewise pull manifested as surface tension to the secondary valences of the molecules present in the surface. The polarity of molecules is credited to such secondary valences. Water, for instance, is at least one of the most polar non-metallic liquids, and it has a very high surface tension. This obviously fits the hypothesis. But σ of methyl alcohol, still a fairly polar liquid, is only 23.0 at 20°C, and ethyl alcohol at the same temperature has σ of 21.7, while olive oil, which is a mixture of relatively non-polar compounds, has a σ of about 33 dynes, as have other oils. The surprizingly large σ of such oils can be explained, according to the Langmuir theory, by the secondary valences of the long hydrocarbon chains, which, apparently, make up in number what they lack in intensity. He points out that all of the fatty acids have about the same σ, about 34, that is, and that this is not far from the σ of the petroleum fractions of moderate length chains, ca. 32. From this he deduces that the carboxyl "head" of the molecule has a slight σ-raising effect, and that it is the hydrocarbon "tail" that is uppermost. Another angle from which to approach this is that, since the free surface energy, γ, which is numerically equal to σ, tends always to be a minimum, as do other forms of free energy, then the fact that the acids have a higher γ than the hydrocarbons means that the molecules will arrange themselves so as to minimize this increase. It is plausible to suppose that the position nearest the surface is the most critical position, and in that case, the carboxyl, whose presence raises γ, will be relegated to a place as far as possible from the surface. This is confirmed by work done on the compression of fatty acids in monomolecular films on water, as well as the near-coincidence of the value of surface tension plus interfacial tension with that of the film surface tension when a monomolecular film, the orientation of which is known, is present on water.

Hardy (4) points out that it is to be expected from a consideration of the surface tensions at work that there will be three possible modes of behavior for a liquid A when it is dropped upon it a liquid B:

1) A will wet B and spread upon it.

2) B will wet A " " " ".

3) Neither will wet the other. One will float on the other in the form of a lens.



If $\gamma_B < \gamma_{AB} + \gamma_A$, and $\gamma_A < \gamma_{AB} + \gamma_B$, the diagram of vectors as drawn will represent equilibrium, and there will be a lens. But if either of the above conditions is not true, the resultant of all three forces will be a real and positive quantity, and spreading will take place. Hardy found no liquids which did not spread on water.

Harkins (5) puts this forward as one of the current ideas, and then derives a new equation. He says that a liquid will spread if its work of surface cohesion is less, and will not spread if its work of surface cohesion is greater than its work of adhesion. "The spreading coefficient, which - - - - gives a measure of the tendency to spread is defined as $S = W_A - W_c$. W_A is given by the equation of Dupré as

$$W_A = \gamma_A + \gamma_B - \gamma_{AB} \qquad W_c = 2\gamma_B$$

The free energy decrease S which occurs in spreading is obviously

$$S = W_A - W_C = \gamma_A - (\gamma_B + \gamma_{AB})$$

This is simply another way of putting Hardy's statement of the situation, for γ is numerically equal to σ in any given case, having only different units.

Hardy has found that an even film of some water-insoluble materials has a maximum σ-lowering effect at a certain thickness. In general, this thickness is less than one micron. Whatever it is, free surface energy will be a minimum at that thickness, and so such a film will be the most stable film possible. He used Miss Pockels' (6) method of controlling the thickness of his films--compressing them by moving a barrier across the surface of water--and plotted curves of σ against thickness of film. He checked the work of Lord Rayleigh (7), finding that up to a certain thickness of film, σ was practically constant. Then the curve broke sharply, giving very rapid change of σ with respect to thickness of film at first, becoming more nearly horizontal again later. That is to say, up to a very definite point, contamination of the surface makes no difference in the surface tension. That point is now believed to be the point of formation of a monomolecular film. Hardy's measurements were made by balancing with weights the resistance of a group of vertical glass blades to being pulled out of the liquid. This much resembles the Du Noüy ring method.

Various water-insoluble organic liquids exhibit great differences in the films they form. Oleic acid in droplets, or lenses, on the surface of water is in equilibrium with a monomolecular film of the acid covering the whole surface of the water. Other fatty acids exhibit the same property. The film is formed with great rapidity. Paraffin oil, on the other hand, a rather high hydrocarbon fraction of petroleum, spreads slowly and gently over practically the whole water surface en masse, the layer simply becoming thinner and thinner. Lithographic varnishes, a mixture of fatty acids and glycerides, were found by the author to display a behavior somewhat intermediate. They, too, spread en masse, but the bulk of the varnish is preceeded by a number of interference rings, which, on a clean surface, spread almost circularly. These rings, wide at the outside, become narrow as one proceeds toward the center, indicating a shape like this:

This was the pattern followed by other vegetable oils.

Mono-molecular Films

A great deal of work has been done on the "surface pressure" in dynes /cm. of monomolecular films of water-insoluble liquids on water. The major hypothesis that has been developed is that the polar group is dragged into the water--tends to dissolve in it--while the hydrocarbon end resists this solution tendency. The result is that the molecule is oriented with its axis vertical, and the hydrocarbon "tails" uppermost, the same arrangement as we find indicated (above) for the upper surface of organic liquids. Linking these two probabilities is the fact that the surface tension produced by a monomolecular film on water is not far from the sum of the surface tension of the film material and its interfacial tension with water, when both are present in bulk.

Some authors believe that the carbon-to-carbon double bond, as well as carboxyl, nitro, amino, sulfonic, and halogen groups are drawn down to the water as a polar group, but N. K. Adam (8) has done work which indicates strongly that there may be merely a spacial displacement here, due to the bend in the molecule at the double bond, and that the group can hardly be considered as being so polar as that.

Experiments carried out by the author and described later indicate formation of rather unstable films of greater thickness than gives maximum lowering of σ, when a mixture of two or more components of different σ-lowering ability is added to the surface of water if one of them has the property of forming monomolecular films.

Heat-bodying of Linseed Oil

It has been known for a long time that heating of linseed oil is accompanied by increase in the acid number, and by great increases in its viscosity and length, while the iodine number decreases.

Morrell (9) found that linseed oil, tung oil, and poppyseed oil produced two modifications when heated, even in an atmosphere of carbon dioxide, at 260-280°C. The acetone-insoluble portion of the heat-bodied linseed oil was found to contain no linolic (containing two double bonds) or linolenic (containing three double bonds) acid, and did not contain glycerides of them either. He believed that the reason for the formation of acetone-insoluble and ligroïn-insoluble fractions was simply the formation of polymers.

He also found (9) that the iodine number became constant after heating about 30 hours at a constant temperature, but could be further decreased by a further increase in temperature. He found (10) that the longer he allowed the oil to remain in contact with the iodine solution before titrating the excess iodine, the more iodine it would take up. The variation was considerable.

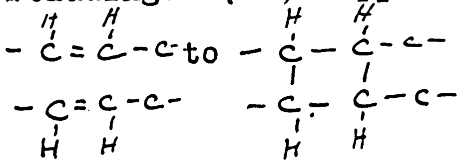
He determined molecular weights by freezing point lowering in benzene, and found them to increase progressively, as high temperature of the oil was maintained for longer and longer times.

Cutter (15) finds that heat-bodied oils, when hydrogenated always yield stearic acid glycerides, and objects on that account to any mechanism of polymerization involving the saturation of the double bonds.

Much objection has been raised by Wolff (11), Bauer (12), and Friend and Alcock (13) to the use of benzene as a solvent, since it is claimed that it causes association of the molecules of that particular solute, but Long and Wenz (14) have since confirmed the increase of molecular weight by use of other solvents.

Wolff claims that neither the fatty acids from the heat-bodied oil, nor even the oil itself show any increase in molecular weight when camphor is used. Bauer claims that even the fatty acids show increase in molecular weight when camphor is used. Schreiber and Nouvel (16), using naphthalene, check the occurrence of increase in molecular weight. Seaton and Sawyer (17) as well as Long, Knauss, and Smull (18) agree that molecular weight of the oil itself increases, though the question of the molecular weight of its fatty acids is not much discussed in the literature at present.

Salway (19) puts forward a theory, on the basis of the work that has been done, to the effect that we get first a dissociation of the glyceride, with the freed fatty acid adding to a double bond in another glyceride molecule by means of its own double bonds. The free valence of the glyceryl radical he believes to combine by an ether linkage with another like itself. He admits, though, that diglyceryl ether has not been found among the hydrolysis products of heat-bodied linseed oil. The method by which this dissociation of the glyceride takes place may be either a regular hydrolysis or an anhydrous dissociation, which seems to be able to take place at temperatures above 250°C, according to Salway.

Staudinger (20) supposes polymerization to take place from  with subsequent rearrangement to eliminate the unstable 4-carbon ring in favor of a 6- or 8-membered ring. Schreiber (21) suggests both polymerization at the double bonds, and condensation at the glycerol groups formed by hydrolysis, as probabilities.

The suggestion has been made that glycerine oxidized to acrolein (which is present among the volatile decomposition-products formed in the heat-bodying of linseed oil). But Salway (22) points out that it is not formed by the oxidation of glycerine, but rather by the oxidation of linolenic acid. He does not mention, however, that acrolein may be formed by dehydration of glycerine.

Wolff (23) states that heat-bodied linseed oils contain mucillaginous material visible by ultra-microscopic mothods. Vollman (24), however, says that at 180°C, the foreign matter in the linseed oil coagulates, having been seen in an early stage by Wolff, and that he (Vollman) has removed it with a collodion ultra-filter, but that that still proves nothing.

Wolff believes the change in iodine number on standing with iodine to be evidence of steric hindrance, due to a very close-packed gel, but it might equally well be due to the time required for the unstable 4-membered carbon rings to break down and react with the iodine. If these rings do rearrange, as suggested by Staudinger, into 6- or 8-membered rings, the rate of increase of apparent iodine number in any one determination, as well as the maximum iodine number obtainable, should decrease upon ageing of the heat-bodied linseed oil. No one seems to have done or suggested this, but it seems to be a possible angle of attacking the problem.

Lewkowitsch (25) states that in ordinary litho varnishes, the hexabromide number (depending, in the analysis of acids, on the percent of acids present which contain three double bonds, and in the analysis of glycerides, upon the percentage of glyceride molecules present containing six to seven double bonds) falls to very low values, even among the lighter varnishes, thus following the same course as Long, Knauss, and Smull (18) (see below) find in the polymerization of what they claim to be mono-linolenin. Morrell (9) found that olive oil, when heated under the same conditions as obtain in the heat-bodying of linseed oil, no acetone-insoluble portion was formed. Olive oil contains little, if any, acid radicals having more than one carbon to carbon double bond. He also found that in the heat-bodying of linseed oil, no fatty acids containing either two or three double bonds were left after heating about seven hours at 260°C.

Long, Knauss, and Smull (18) attempted the following synthesis of monolinolenin: The fatty acids of linseed oil were treated with bromine in a cold ethereal solution, and the insoluble hexabromides thus obtained were heated in a container with zinc dust at 125-35°C, wwhich was supposed to regenerate the original acid. This was carried out in the presence of dry glycerol saturated with HCl, to effect esterification. They got an iodine number of 176, whereas it should have been 216.2, theoretically. Hazura (26), working toward linolenic acid itself by the same method except for his omission of the glycerol, got a product having 89.7% of the theoretical value, instead of the 81.5% obtained by Long, Knauss and Smull. Hehner and Mitchell (27), by the same method, got a product with 88.5% of the theoretical iodine number.

By treating the hexabromides with alcoholic KOH, the same authors obtained viscid yellow oils which did not dry after being exposed to the air for a week, and which were, therefore, "neither the hydroxy acids which result from oxidation by permanganate, nor the less saturated products which would have resulted from an elimination of 6 HBr from the molecule." At the same time, the oil absorbed iodine from Hübl's solution "to the extent of 61-63%". After titration of the excess of iodine added, the solutions rapidly became blue again from the further liberation of iodine. This reminds one of Morrell's determinations of the iodine number of heat-bodied linseed oil, which took so much time to proceed. This reaction, instead of doing that, turns out to be reversible.

Hehner and Mitchell found also that on rebromination of their acid, HBr was evolved, and the original hexabromide was not reproduced. "In this particular it behaved like the acids from boiled linseed oil."

All this points to the conclusion that the double bonds are involved in the reactions involving the heat-bodying of linseed oil, and the concensis of opinion seems quite strongly in favor of actual increase of molecular weight. Schreiber and Nouvel (16) find that benzene seems to give consistently a constant and exact multiple of the molecular weight obtained in naphthalene. Provided it is consistent, the relative results are as good as ever. Also, the work with naphthalene as a solvent backs up the conclusion that molecular weight does increase.

The work and reading on surface tension and other surface phenomena has led to one definite conclusion on the subject as well as to some interesting speculations, all of which will be described below.

Surface Phenomena

It was found in the course of these experiments that the author has carried out on the surface tension effect of lithographic varnishes on water, that, for thick films, at least, σ is dependent on the age as well as on the thickness of the film. σ-time curves will be found for a series of varnishes in Plate I, near the end of the thesis. σ_f will be used to express the observed resistance to rupture of a film of the material in question, on water unless otherwise specified, while σ_i will express the interfacial tension of the material in question with water or any other phase which may be specified.

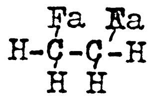
Perhaps the most salient feature of this group of curves is the great difference between that for raw linseed oil and that for boiled oil. The viscosities, as determined by C. J. Opp, using the falling ball method at 25°C, are given in Table III, with approximate end values for σ_f. Therefore, with such a small difference in a nearly-equilibrium value between #7 varnish and boiled oil, whose viscosities are as 1440 to four and with such a large difference between boiled and raw linseed oil, whose viscosities are in the ratio of 4 to 1¼, the change is apparently chemical rather than physical in basis.

See table 4. The data in it is all taken directly or derived (columns 8, 10, and 11) from an article by Long, Kittleberger, Scott, and Egge (28). It refers to the heat-bodying of linseed oil at 293°C. The following interpretation is that of the present author. A search was made for some variable which should show the same sudden break very early in the boiling process as is exhibited by the values of σ_f and perhaps account for it. Columns 8, 9, 10, and 11 all wobble uncertainly, and show no definite trend. Columns 2, 5, and 6 show a definite, but steady trend. Columns 3 and 4 show decided breaks at first. The break in Column 3, however, means an increase in free acid, which is hardly to be expected to fall in the same place as a rise in σ_f, but rather the reverse. It was not apparent what the break in the iodine number curve meant in terms of σ_f. Column 7 shows a slight break, followed by a gradual average decrease. Just as one would expect, weaker adhesion of the oil to the water surface is accompanied by greater interfacial tension, or, in other words, the tendency of the molecule to dissolve is less. This relationship seems rather fundamental.

The measurements on surface films were carried out by compressing on the surface of water, in a trough, a film composed of a known number of molecules of the water-insoluble material, and measuring the force/cm. of length necessary to do the compressing. Compression is carried out by means of a movable barrier, which sweeps the surface of the liquid. Thus, the area on which the known number of molecules is distributed is known. The compressive force is measured by a torsion balance which must be weighted for a reading so that the movable float which confines the liquid on the fourth side shall remain at the zero mark. Thus, curves can be plotted of area per molecule against compressive force. The curves usually begin at the lowest measureable compressive force, (area per molecule = A_0), and proceed along a smooth curve to a sharp break. It is generally agreed that this represents the point at which the monomolecular film becomes as closely-packed as possible, which results in some of the molecules' being pulled out of the film and out of contact with the water. The area per molecule at that point is designated in the table by A, and the force is the crumpling force F. It is the force, as Long puts it "necessary to pull the molecule up by the roots".

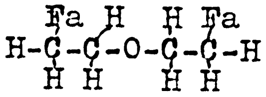
Since neither A_0/A nor $A_0/$ mol. wt. increases on heat-bodying, there cannot be any hedgehog arrangement of fatty acid groups taken on at the double bonds and sticking out in all directions.

Also consider the following formulae, in which Fa- represents a fatty acid radical:



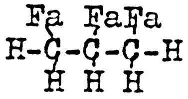
$H-\underset{H}{\overset{Fa}{C}}-\underset{H}{\overset{Fa}{C}}-H$

Ethylene glycol ester
F=14



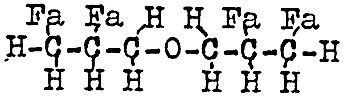
$H-\underset{H}{\overset{Fa}{C}}-\underset{H}{\overset{H}{C}}-O-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Fa}{C}}-H$

Diethylene glycol ester
F=18.4



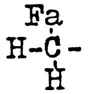
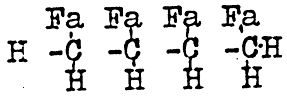
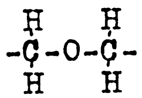
$H-\underset{H}{\overset{Fa}{C}}-\underset{H}{\overset{Fa}{C}}-\underset{H}{\overset{Fa}{C}}-H$

Glyceryl ester
F=12



$H-\underset{H}{\overset{Fa}{C}}-\underset{H}{\overset{Fa}{C}}-\underset{H}{\overset{H}{C}}-O-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Fa}{C}}-\underset{H}{\overset{Fa}{C}}-H$

Diglyceryl ester, Salway's suggested heat-polymer of linseed oil.

This data is to be found in table V. It is also taken from Long, Kittleberger, Scott, and Egge (28). Diethylene glycol (di)ester has a crumpling force F greater than ethylene glycol ester. At first sight it appears that the tetra ester of diglycerol would certainly have a higher F than the tri ester of glycerol, analogously to the difference in F for diethylene glycol ester compared to ethylene glycol ester. At second glance, it is seen that in the case of the glycerides, we are inserting $-\underset{H}{\overset{H}{C}}-O-\underset{H}{\overset{H}{C}}-$ between two $H-\underset{H}{\overset{Fa}{C}}-\underset{H}{\overset{Fa}{C}}-$ groups, whereas before we inserted the group between two $H-\underset{H}{\overset{Fa}{C}}-$ groups. Thus, we would expect that the increase due to the $-\underset{H}{\overset{H}{C}}-O-\underset{H}{\overset{H}{C}}-$ would not be so much as in the case of the glycol. Considering the mannitol esters, we can arrive at a provisional conclusion as to the effect of the extra $-\underset{H}{\overset{Fa}{C}}-$ group present in the diglyceryl ester as compared with the diglycol ester, which latter has the same number of fatty acid groups linked to it as before, if it is considered that ethylene glycol ester is polymerized to diethylene glycol ester by Salway's suggested mechanism. There is much more extrapolation than there should be, in this line of thought, but the idea was conceived too late to add to the data available. The matter is represented graphically in Plate II. The "mixed acids" are the mixed acids of linseed oil. The three curves shown converge, two of them to the end, and the third as far as it goes. This indicates at least the same general form for the curves. A crumpling force of 14 cynes/cm. is required for ethylene glycol ester, while that for the triglyceride is 12. This gives an interval of 2 dynes/cm. due to the addition of  $H\text{-}\overset{Fa}{\underset{H}{C}}\text{-}$. If this were continued as one proceeded along the series, mannitol hexaester should require a crumpling force of 12-3(2)=6. This is a plausible point for the mannitol ester curve, though perhaps a little low. Also, it is a general rule that the higher one goes in a homologous series, the less the differences in properties between successive members. So it would be expected that  $H\text{ -}\overset{Fa}{\underset{H}{C}}\text{ -}\overset{Fa}{\underset{H}{C}}\text{ -}\overset{Fa}{\underset{H}{C}}\text{ -}\overset{Fa}{\underset{H}{C}}H$ would require a crumpling force of not less than 10 dynes/cm. If the effect of inserting  $\text{-}\overset{H}{\underset{H}{C}}\text{-}O\text{-}\overset{H}{\underset{H}{C}}\text{-}$ between the halves of the glycol ester molecule is an increase of 4.4 dynes, it would be expected that, even though the group on each end is now twice as heavy as in that case, the characteristic ether group would still have considerable influence in increasing the crumpling force. If it did so, the crumpling force would be raised above that of the barely-boiled linseed oil, (10.2) by almost that amount--by almost the whole amount of the effect of the ether group, that is.

This is all very speculative, but one thing is shown very definitely by the present work. Even in boiled oil, the free fatty acid is no longer in its original form, as is shown by the fact that it fails to lower the surface tension of water, when placed upon it in a thin film, anywhere nearly as much as in the case of the raw oil, and that this change takes place in the first boiling by more than half of the amount of the change in the formation of the heaviest litho varnish. This means that the acid is no longer free to migrate through the varnish and become adsorbed at the varnish-water interface, or else that its tendency to do so is destroyed or reduced. The latter is unlikely, for, according to the theory of orientation of films on water, a carboxyl group always tends to dissolve in water on account of its polarity. Titration shows more acid present than ever. This acid must be chemically combined, so that it loses the mobility of its molecules, for titration indicates that its polar groups are still present. These molecules must be combined, either with other acid molecules, or, more likely, with bulky glyceride molecules which thus gain a strongly polar group, but greatly reduce its mobility, and, consequently, its adsorption in any particular case. As a check on this, it can be shown that addition of fresh free acid restores much of the σ-lowering power of the varnish. All this might be due to colloid formation, as suggested by Wolff, but if so, it is a very well-oriented and arranged colloid, in the formation of which the third double bond of linolenic acid is covered up and removed from reactions very early in the process, and its second bond (double) as well as that of linolic acid is also rendered incapable of reacting, in quite a short time. Also, computation shows, in a number of cases, that more double bonds are rendered unreactive by the first doubling of molecular weight than by the second doubling, while the number of double bonds rendered unreactive is also somewhat more than enough to account for those used up in the reaction of one molecule with another. The excess, where noticed, is usually attributed to intramolecular condensations. It would be expected that a polymerization through the double bond would use up more of the iodine capacity of the oil per unit increase in molecular weight when the molecular weight was small--that is, when there were many junctions to be made--than when it was large, and the iodine number behaves according to this, rather than according to the colloid supposition.

The crumpling force is very interesting. If this problem is pursued further, esters of diglycerol might be prepared, and their crumpling forces determined. Also, the crumpling forces of mixtures of these esters and the glycerides present in linseed oil should be determined, to make sure that the crumpling force does not pass through a minimum with such mixtures. It is difficult to see why it should, but if it did, this might account for the decrease found as a result of the heat-bodying of linseed oil.

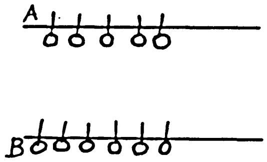
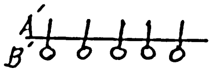
The acids liberated during polymerization, according to Salway's idea, attach themselves to the polymerized molecule through the double bond, but one molecule of acid should come from every molecule of glyceride concerned, and that much acid is not actually found. For instance, a doubling of the mean molecular weight would mean that one acid radical out of every three should be liberated.

The acrolein noted as a volatile product of the heat-bodying of linseed oil may, as Salway suggests, come from the oxidation of linolenic acid, or it may come from the dehydration of glycerine in the glycerides, with the consequent liberation of fatty acids. This suggestion is not new, and neither is the suggestion of the polymerization of the glycerides through the double bonds, but both are an integral part of the explanation of polymerization on a basis other than that of ether linkage, to which the present work has attempted to add a little, and so must be included.

The Spreading Coefficient, S

Since one of the important individuals among surface tension effects is the spreading of one of two mutually insoluble liquids on the other, the spreading of inks and of varnishes on a solution of a γ-lowerer seemed to be indicated as a topic for study.

Theoretically, one would expect that a varnish would spread whenever γ at the interface plus γ of the varnish is less than γ of water, that is, whenever it could lower the surface energy of the system by so doin, and not otherwise, and that inks would also behave in this way except insofar as their being plastics instead of fluids might prevent it. This is approximately true. The surface energy criterion should be absolutely true, since it is based on thermodynamics. The first statement of the matter is not, and doesn't seem to be exact. The difference is that γ_i plus γ_{oil}, with both phases present in bulk, does not necessarily equal the γ_f actually produced. The film, if monomolecular, as in the case of a pure fatty acid, has been found in at least one case--that of oleic acid--to have a lower surface energy than the sum of the interfacial energy water-oleic acid and the surface energy of the oleic acid. In terms of the current theory of surface tension, and the idea of oriented surface films, the polymolecular film that we have when the material is present in bulk is possibly partially oriented more than one molecule from each surface.

At least we have  rather than 

The effect at surfaces A and B is almost exactly the effect at A' and B' respectively, but we have also the other end of each of the molecular layers shown in the first sketch. Unless secondary valences are entirely satisfied by the nest layer of molecules below A or above B, there will be some residue of surface tension here, and, even if they should be, there should be considerable orientation of this next layer. It would be remarkable if none of the secondary valences except at the planes A and B found satisfaction in their own layers. That they do is indicated by the fact that, for oleic acid, various authors find a difference between the surface tension of the film on the one hand, and the sum of the surface tension and the interfacial tension of the oil against water, both phases being present in bulk, on the other, the film surface tension being the smaller value. (See Table VI).

The spreading coefficient, S, which can be equated to $\sigma_A - (\sigma_{AB} + \sigma_B)$, thus is not exactly applicable, any longer to all cases, but if we substitute for $(\sigma_{AB} + \sigma_B)$, σ_f, the "surface tension" of the film, (which is equal to the sum of the surface tension and interfacial tension of whatever film is formed), the formula again becomes applicable, and the statement that a liquid will spread on another liquid if its spreading coefficient is equal to or larger than "a small positive quantity" tells us the whole truth. Otherwise, the formula understates the case. Let us call this new value of the spreading coefficient "S_f". Harkins (5) mentions the possibility of formation of "composite" films, in which the interface AB and the surface of B are not distinguishable from each other, so that a surface C, which has been denoted in this work by the subscript f, might be substituted for AB plus B. He says only this about the idea, however, and omits using it in a table in some parts of which, at least, it would be the correct one to use (5).

Thus it is perfectly true that if $S =$ a small positive quantity, spreading will take place, but it should also take place if $\sigma_A - (\sigma_{AB} + \sigma_B)$ were equal to a small negative quantity, provided only that $\sigma_A - \sigma_f =$ a small positive quantity, and both of these conditions may be true at the same time, since $\sigma_f < \sigma_{AB} + \sigma_B$ in at least some cases. Probably spreading with $S =$ a negative quantity is limited to those cases in which the negative quantity is a small one, because it is not to be expected that the departure of σf from $\sigma_{AB} + \sigma_B$ will ever be very large, and it is this difference that has to abolish the negative value and furnish as a remainder, a small positive value. Let us consider, in the experimental part, only S_f., the actual spreading coefficient of a film already established.

As to the mechanism of starting the spreading of a film under such conditions, it must be such that the effective σ against which σ_A has to pull is less than σ_A .

This is possible, for consider what happens to the triangle of forces in such a case. Were σ_B and σ_{AB} unaltered by variation in the thickness of the film of B, we would have the conventional diagram of Hardy, sketch A, below.

A

But when the negative value of S is very small, alpha, the internal angle of the edge of the drop, must also be small, to allow the resultant of vectors σ_B and σ_{AB} to balance the vector σ_B . But since this decrease in alpha makes the edges of the droplet thin, and that decreases the arithmetic sum of σ_B and σ_{AB}, which must cause a further decrease in alpha, the system is caught in a vicious circle, and in many special cases the edges may be thinned down to a monomolecular film, still without being able to achieve equilibrium. If this occurs, spreading of the monomolecular film will take place.

It was found that when turkey red oil was used as a σ-lowering solute in aqueous solutions, oleic acid would spread whenever σ of the solution was substantially greater (.2-.3 dynes) than the value which oleic acid would produce on water. Also, oleic acid produces in such cases σ_f not far from that which it produced on water, indicating that the interfacial tension of oleic acid and aqueous turkey red oil solutions of concentrations below .065% did not differ greatly from that of oleic acid and water. Agreement was as close as could be expected without thermostatic control.

It was interesting that oleic acid spread upon a 1% solution of Nekal, a naphthalene sulfonic acid. The original surface tension of the solution was 38.8 dynes/cm., and the oleic acid lowered it to $\sigma_f = 35.1_3$ dynes. The addition of oleic acid in bulk gave two layers. The mean of three determinations of σ_i was .62 dynes/cm., while the mean of four determinations of the surface tension of this layer of oleic acid was 34.70 dynes/cm. $\sigma_f = 35.13$; $\sigma_i + \sigma_{oil\ phase} = 35.3_2$. These values can be compared with Harkins' values (see Table VI) of σ for oleic acid and σ_i of oleic acid and water, and with Miss Pockels' values of σ_f for oleic acid on water. These are, respectively, 32.27, 16.05, and 43; $\sigma_f = 43$, $\sigma + \sigma_i = 48.32$. It will be seen that the difference in one case is .2 dynes, and in the other, 5.3 dynes. The author's value for σ of oleic acid, not contaminated with Nekal, is 34.3--2 dynes above Harkins' value,--but he checks Miss Pockels' 43-dyne value for σ_f of oleic acid on water. Also, independent of the question of a constant error involved in the author's determination of σ for oils in general, the determination of σ of oleic acid by the ring method has given at least consistent results, the determination of σ_f in one case

[illegible]

has checked Miss Pockels' result, and the interfacial tension in the case now under consideration is so small that a large accidental error would hardly escape unnoticed, while not even the severest critics of the ring method predict large systematic absolute errors that would be found under these conditions.

Then we can say that the disparity in value between σ_f and $\sigma + \sigma_i$ has been greatly decreased--almost eliminated by the presence of a large amount of σ-lowering materials. We can also say that most of the elimination of this disparity must have occurred via the interface, since σ is very little changed by the presence of the Nekal.

Certainly Harkins' value of σ of oleic acid cannot be applied here, for if so, $\sigma + \sigma_i < \sigma_f$, which is not understandable from known theoretical considerations, and no case of which has been seen by the author in the literature. If this assumption be correct, and the author's values be also taken as being correct, at least as to their magnitude relative to each other, most of the disparity between σ_f and $\sigma + \sigma_i$ will have been eliminated through the interface. Then it must have been in the interface at first. According to present theory, this means that sidewise attraction between molecules in the interface when the oil phase is present in bulk is, in this case, very nearly equal to the sidewise attraction between the lower ends of molecules in the mono-molecular film.

Experimental Method

The ring method of Du Noüy (29) for determining surface tension was used in the work done in this thesis. The principle is that a measurement is made of the force which is necessary to pull a ring of known radius out of the liquid. If the ring is not too small, the slope of the liquid surface outside the ring will equal the slope inside, so that the mean circumference of the two surfaces broken will be the mean circumference of the ring. If the ring is too small, there will be capillary rise inside, and that will spoil the symmetry of the system. The rings provided with the Du Noüy tensiometer have, commonly, a mean circumference of 4 cm. It is necessary to measure the maximum pull, the reading at which the ring barely begins to accelerate its movement upward.

The ring method has been much criticised by Harkins (30), but in the study of σ_f, drop weight and drop volume methods are almost entirely out of the question, and when time of standing of the film is also introduced as a factor, the method becomes completely impracticable.

When an effort was made by the author to determine σ_f of oleic acid by the capillary method, a fine and a coarse capillary gave 35.78 and 35.38 dynes respectively at 25°C. Very good checks on these values were repeatedly obtained, so, since they are about 7 dynes low, the capillary method was no longer considered. The ring method seemed the best possibility left. It was also very rapid and convenient, compared to the others mentioned. Instead of the Du Noüy tensiometer, a chainomatic specific gravity balance was used, with the ring replacing the bob, and all these results were obtained in that way.

Ring Method for σ_i

It is not possible to obtain very accurate values for large interfacial tensions by the ring method. The specific gravity of the aqueous and non-aqueous layers (in this work at least) are usually close enough together so that a considerable volume of water has to be raised above the normal interface level to overcome the interfacial tension and break the ring through the interface. The quantity of water raised is so large, and the capillary rise within the ring so great under the decreased action of gravity, that instead of the theoretical circular ridge, a plateau is formed, and the break comes only around the outside of the ring. A film of water is often left on the ring as evidence of this. The result is that the length of the break is much less than the theoretical $4\pi r$, though somewhat over $2\pi r$, and this gives a low value for interfacial tension.

When the real value of interfacial tension is very low, the plateau-forming tendency is not found, since it is possible to form above the normal interfacial level, a circular ridge of water which will contain a large enough volume, V, of water so that $V(D_{water} - D_{oil})$ will counterbalance the small interfacial tension without the necessity of forming a plateau. From the normal form of the ridges formed in measuring the interfacial tensions of water solutions against varnishes, it is estimated that the readings were within the limit of error in other directions, as a rule, when the interfacial tension being measured was less than 3 dynes.

σ_f of Ink Films on Water

Since the varnishes known as C#1 and C#3 had been found, as mentioned above, to give trouble in the plants when made into inks, and since they were notably different from other varnishes in their behavior when allowed to spread on water, it was thought that this deviation from the normal might be the cause of the trouble. The peculiarity was that they did not lower the surface tension of water nearly so far, when allowed to spread over it in a film, as did the normal varnishes. That is, its σ_f was higher (see Table XI). Accordingly, samples of ink were collected and the surface tension produced when small amounts of them were placed on water was noted. The first troublesome ink obtained was tried in this way, and it was found that at the end of 2 hours, it had decreased the surface tension of the water on which it was placed by an amount of about 14 dynes. This and a set of corresponding values for other inks is shown in the accompanying table.

The underlined inks, 9 and 10, were samples of inks which gave trouble in the plant. A series of points, giving σ-time curves, were taken for the lettered inks. The missing letters represent those inks which came to an approximate equilibrium in less than 2 hours, and on which further readings were not taken. All inks but 9 and 10 were satisfactory, so far as behavior on the presses was concerned.

Tables I & II

Ink	seconds' contact with water	σ-lowering	σ-lowering at end of 2 hours.
1	20	8.8	12.8
2	20	7.2	13.4
3	6	9.1	14.9
4	9	9.7	14.1
5	9	9.1	14.6
6	9	12.0	18.2
7	8	12.0	13.9
8	5	12.4	25.7
9	12	0.0	15.5
10	15	- 0.4	2.5
A			20.9
B			22.1
G			16.4
F			14.1
H_1			14.9
H_2			18.1
I_2			15.8

Ink	Time at which equilibrium nearly established	σ-lowering
C	50 min.	17.1
D	70 "	19.4
E	70 "	20.0

The second column simply states the length of time that ink on a glass rod was allowed to remain in contact with the water surface, and the third column, the result. The results may be somewhat misleading, as stated, for all of the inks were able to remain in contact with the water for a little length of time before they caused any measurable effect, and Ink 9 did, finally, cause a lowering of surface tension, as seen in the fourth column. Ink 10, however is not much misrepresented in the third column.

In retrospect, it seems that it was a mistake to abandon the practice of taking readings like those in columns 2 and 3. The method was supplanted by the plotting of σ-time curves for water surfaces on which had been dropped

Small threads of ink, of approximately known weight, because it was considered that such results would be more quantitative in nature and that the procedure could be more definitely controlled than that of the former method. But the results yielded by later samples of bad inks, while exhibiting a definite tendency, were not strikingly distinctive, like the figures in the third column of the above table. This may have been due to the particular samples of ink obtained, or to the method, but the former method should at least have been carried concurrently with the latter.

σ-time curves for the lettered inks and some of the inks studied later will be found on Plates III A and B.

Effect of Age of Film on σ_f

It is well known that the surface tension of aqueous solutions varies with the age of the surface. This variation, within ordinary time limits, is most marked in the case of dilute solutions of positively adsorbed materials, and especially so if the material is in a colloidal state. Obviously the same should be true of the interfacial tension between water and a system of two water-insoluble oils, miscible in all proportions with each other. Positive adsorption of that oil which is the more active in lowering interfacial tension should take place at the interface. The more nearly homogenious the oil, the more quickly a state very close to equilibrium will be attained. Oleic acid, one compound, reaches a constant σ_f quite quickly (in about ten minutes, within the limit of accuracy of the ring method--.1 dyne, accirding to Du Noüy (29)). Paraffin oil, a mixture of hydrocarbons all having approximately the same σ and σ_i against water, practically reaches equilibrium almost as soon. "Linoleic acid", a mixture of the fatty acids present as glycerides in linseed oil, is slower in reaching an equilibrium, within the limits of accuracy, probably because the actual change due to rearrangement is greater.

This matter came up in connection with the lowering of σ of water by inks and varnishes. As mentioned above, there seemed to be a clear coincidence, in all cases studied, of abnormally slow lowering of σ under such conditions with the formation of blanket scum by inks. It was thought that addition of a free fatty acid to these inks would of course increase their speed of lowering ,and, if slow lowering of σ were in any way the cause of the blanket scum, as seemed quite possible, merely from the coincidence of the two properties, the trouble might be eliminated.

At the start, two acids were considered as possibly suitable for addition to the inks--oleic acid, and "linoleic acid". In the following table, Sample 1 was varnish C#3, Sample 2, the same, plus 6% oleic acid, by weight, Sample 3, the same, plus 100% by weight of oleic acid.

Sample	Time of standing	σ_f produced
1	10 min.	50.7
2	10 "	49.1
3	5 "	46.7

The extent and reason of the dependence of σ_f on time of standing for such solutions was not realized at this time, and so equilibrium values were not obtained.

Qualitatively similar results were obtained by the addition of linoleic acid. It was indicated that upon addition to an oil of film-forming water-insoluble materialswhich were more efficient lowerers of σ than was the original oil, the surface tension caused by a film of the mixture is less than that caused by a film of the original material. This is to be expected for thoeretical reasons.

As would be expected from the theory of adsorption, the σ_f-concentration curve for two-component oils is not a straight line, but is deeply concave upward, taking the lowest value of σ_f on each time- σ_f curve as the value to be plotted. (See Table XIV for values)

This was brought out by experiments on the effect of adding linoleic acid first to varnishes, then to paraffin oil, finally to castor oil. The effect on varnishes was the point of interest; paraffin oil was taken as a material the change in whose properties on addition of linoleic acid would be more accentuated than it was in the case of varnishes, because the nature of the two components would be further apart. Thus, trends should be more clearly perceptible. The trouble with paraffin oil was that, while linoleic acid was easily emulsifiable in it, only an emulsion, not a solution, was formed, and since the emulsion was not completely stable, a film of the mixed oil placed on the surface of water would separate into the components, which would form separate layers, with linoleic acid,simply due to gravity, on the bottom. It was observed that σ_f of a film of this mixed oil was very nearly σ_f for linoleic acid, and depended almost none on the concentration of the acid in the oil, as it did in the case of linoleic acid in varnishes.

There was also another purpose in view. It was desired to know whether heat-bodied linseed oil had any peculiar effect on acids which were introduced into it, such as restraining them from migrating to the interface, which would show up as a failure of the surface tension to fall in the same way as it did for natural vegetable oils when the same acid was added to them. In other words, it was thought that such experiments might tell whether the acids of linseed oil were directly,or indirectly,involved in the heat-bodying of the oil.

Castor oil was quite satisfactory, since linoleic acid was soluble in it in all proportions tried, and the original σ_f was somewhat above that for varnishes, giving more distance through which the values might fall.

The determination of σ_f of different materials was troublesome, because, since the oils and varnishes were of greatly varying consistency, the surface tensions at given lengths of time would probably not represent analogous conditions for different varnishes. Increased accuracy became desirable when work on the effect of addition of more active to less active σ-lowerers was begun. Thermostatic control had not been used before because only relatively large differences were being examined, and it was not called in later because for some time the above-mentioned trouble made such refinements useless. Because of the trouble, it was considered necessary to get nearly-equilibrium values in order to have results that would be at all comparable in any two cases. Carrying a series of deter determinations even to approximate equilibrium often takes three hours, and sometimes more than that. Therefore, it seemed that it might be worth-while if an empirical relationship could be found which would permit extrapolation of the equilibrium value from a short series of readings.

The first attempt was to pick out by inspection the line that a given curve was approaching asymptotically. Little was expected and nothing gained here.

Several type formulae were then tried. The type $(t+a)(\sigma_f+b)=c$, in which $t=$ age of the oil surface, gave fair results, but there was a good deal of apparently desultory departure of the points from a straight line when $t-t_k$ was plotted against $(t-t_k)/(\sigma_f-\sigma_{fk})$, where t_k and σ_{fk} refer to any particular point. This plot will give a straight line insofar as this formula is applicable. $\sigma_f = ab^t$ was then considered. If this formula were applicable, log σ_f would be a linear function of t. Plotting log σ_f on the vertical axis, it was found that the curves were uniformly concave upward and outward. This at once suggested that the lower end might be dropped, straightening the line, by subtracting a constant from σ_f before taking the log. This was done, selecting the constant at random, and brought the curve much closer to a straight line, but did not completely rectify it. The value of the constant was finally worked out by rule of thumb as the one which gave the closest approximation to a straight line. This makes up a linear equation in t and log (σ_f-c).

ln (σ_f-c)=At+B, where A, B, and c are constants. Taking a derivative on each side,

$$\left(\frac{d\sigma_f}{\sigma_f - c}\right) = Adt$$

$$\frac{d\sigma_f}{dt} = A(\sigma_f - c).$$

This is very much like the equation for a first-order reaction: $\frac{dx}{dt}=k(a-x)$. The difference is that in the term (a-x), a is the constant and x the variable, whereas σ_f is variable and c constant. Also, A is a negative quantity, whereas by ordinary convention, k is positive.

For castor oil alone, the rectification gives, throughout, a straight line, either within or barely without the limit of accuracy of the method. Castor oil with linoleic acid dissolved in it, gave, instead of a straight line, a curve, concave upward at the left, but turning into a straight line further down. The more linoleic acid was present, the longer and steeper was the curve preceding the straight line. (See Plates IV, V A-F, and VII A and B). The values of c are lower when acid has been added to the oil than when it has not. The resemblance of the above expression to the equation for a first-order reaction is really suggestive. $\frac{d\sigma_f}{dt}$ is proportional to the distance that σ_f still lies above a constant. Apparently something is being used up. Of course that part of σ_f which lies above c is being used up, but there must be one or more physical counterparts. Two things suggest themselves--1) the supply of acid molecules in the oil, 2) the supply of space at the interface into which the acid molecules may move. Is the first power of ($\sigma_f - c$) that is involved just a product of the effect of the concentration of the acid and that of the concentration of the acid and that of the concentration of the free spaces in the interface which are open, at the time, to the acid? The fact that σ_f approaches a different c when a large amount of acid is present than when only a small amount is present indicates that the concentration of the acid is important, even after the beginning. On the other hand, the concentration of free spaces in the interface should, from separate kinetic considerations, decrease asymptotically toward zero, just as σ_f decreases asymptotically toward c, as soon as the concentration of the acid in the neighborhood of the interface has recovered from the first great drains on it. But that still leaves the question of whether σ_f varies from the value for the original oil to the value for pure acid proportionally to the fraction of its interface composed of acid molecules. It seems quite likely, but that is all. It would have taken much equipment and time, as well as being rather off the track, to determine whether this linear relationship existed, so the subject was carried no further.

There is still another period after this--the period of reticulation, in which σ_f falls considerably below the value which it was already approaching asymptotically, and many fine droplets of oil are seen upon the surface of the aqueous layer, though a homogenious thick film was present before. This, apparently, is the period of formation of a much thinner film, possibly even monomolecular. Whatever sort it is, we can at least say that, since it formed spontaneously, it necessarily has a lower σ_f than the original thick film, and is more stable than the latter was. If, by any disturbance, the surface of this thin film were momentarily bared at any point, the thick film would not be able spontaneously to reëstablish itself over that point, since that would involve the raising of the free surface energy of the system without compensation. In short, a thick film existing under such circumstances is not in a state of stable equilibrium, since the free surface energy may undergo lowering by the adsorption of a thin film of free acid followed by reticulation of the rest of the material comprising the thick film.

It was noted that, even with addition of linoleic acid, σ_f for the lithographic varnishes was did not reach the low values given by raw linseed oil. Comparison of the results given by lithographic varnish and castor oil showed quite similar results. 5% linoleic acid, added to castor oil and to the varnish being studied, gave in both cases, values of c between 43 and 44. 2% linoleic acid in the varnish gave c equal to about 47, while in castor oil, it gave c equal to 49. This difference is not surprizing, for castor oil without linoleic acid does not give such a low σ_f as does the varnish without added linoleic acid.

The curves for castor oil which had linoleic acid added to it, it will be remembered, could not be rectified through-out. The shape of the curved top of the line suggested that it might be possible to rectify it independently by the same method, using a different, larger constant for c. This proved possible. That, in turn, suggested the idea that an intermediate portion of the curve might be rectified by the use of an intermediate constant, which would mean that our constant was probably varying continually, and was rather an artificial thing. This was tried, but only very short portions of the curve could be rectified by any one intermediate constant, while the whole curve from 15-20 minutes on, could practically always be rectified by the lowest constant, the value of c obtained at first. The curves appeared to go around quite a definite corner at about 10-15 minutes, and beyond that, σ_f appears to approach its lower limiting value at a lower rate of speed. (See Plates VI, A-C.)

Water-soluble σ-reducers.

Turkey red oil was the water-soluble σ-lowering material in which we were most interested. Also, it is representative of a large class of σ-reducers, so it was first studied.

It is partly the sodium salt of the sulphonated acids of castor oil. There may be a small amount of glycerides present, but not much, for the addition of ammonia to an aqueous solution of the substance removes completely any turbidity that may be present, suggesting soap formation, rather than emulsification.of the ordinary sort. The organic salt is practically a soap. That the fatty acid is sulfonated seems to be the main difference between it and most soaps.

Experiments showed that turkey red oil is a very efficient lowerer of the surface tension of water in which it is dissolved. The series of solutions was not carried to the concentration that gave the lowest values of surface tension, but the reading after one minutes'standing was 41.2 dynes, while the value, near equilibrium, was 40.7 dynes for a .316% solution, whereas a 1.60% solution gave 36.95 and 36.5 dynes respectively under those conditions. That is, surface tension is not very sensitive to concentration at these concentrations.

No attempt was made to apply to turkey red oil the empirical formula which applies to oils on water, because each reading seriously damaged the adsorbed film of solute at the surface. If two readings were taken in rapid succession, σ was apt to be higher in the second than in the first. This is not true of oils, and especially of varnishes, owing, probably, to their high viscosities and the thinness of the films which were used.

The effect of addition of acids to an aqueous solution of turkey red oil is in the direction of liberation of the acids. It therefore has a slight σ-raising effect on concentrated solutions, and a σ-lowering effect on dilute ones, the tendency, at least, in both cases being toward the surface tension produced by a film of the free acid of which turkey red oil is a salt--sulphonated ricinoleic acid. The data obtained on turkey red oil solutions are in Table VII.

Surface tension readings on solutions of Nekal, saponine, and sodium oleate were also taken. The data are contained in Tables VIII, IX, and X, respectively. The only remarkable thing about Nekal is that its concentrated solutions have very low interfacial tension against oleic acid and varnishes.

Saponine forms plastic films on the surface, when in aqueous solution. Oleic acid spreads very slowly on a .04% solution which has stood for some time, even though the value of S_f may be three or four dynes. It makes cracks in the surface film, and gradually widens them, and in one case, it took the oleic acid fifteen minutes to sweep the film from 4/5 of the surface of the liquid in a liter beaker.

Effect of Varnishes on Nekal and Turkey Red Oil Solutions.

Early in the work on turkey red oil solutions, it was found that, when a drop of oleic acid was placed on the surface of the solution to see whether it would spread, a turbidity formed around the drop when it had been standing overnight in those turkey red oil solutions on which spreading did not take place, and, in general at least, this turbidity was not perceptible around a drop of oleic acid in those more dilute solutions on which the acid did spread. This was interesting, and raised the question of whether the point of spreading represented an absolute dividing-line, as to spontaneous emulsification, between two sorts of solutions, or whether it simply happened to coincide with the point at which spontaneous emulsification took place perceptibly within 16 hours.

It was thought that longer standing might cause emulsification of oleic acid even by some of the slightly more dilute solutions. If so, it would be certain that it was only a particular fact that had been noted, and not a general rule. As long as the tests were being made, it was decided to try out several other materials along with the oleic acid. The tubes were corked and sealed.

The results at the end of three months were as follows, where e stands for emulsification, and c for clarification:

Material	1.60% soln.	.32%	.064%	.013%
Oleic acid	Strong e.	Some e.	No change	No change.
Raw linseed oil	A little c.	Some c.	Strong c.	Nearly complete c.
Normal #1 varnish	Some c.	Strong c.	Nearly complete c.	Apparently complete c.
C#3 varnish	Strong c.	Nearly complete c.	Apparently complete c.	"

Blanks were also run containing simply turkey red oil solutions of these concentrations. It was found at the end of three months, by comparing them with solutions of the same concentrations, freshly made up, that the blanks of the two more concentrated solutions had increased in turbidity. This means that, if anything, the clarifying effect of the varnishes on the turkey red oil solutions was being underestimated.

Nekal solutions were made up in concentrations of 15%, 4%, 1%, .2%, and .04%, and the same thing tried on them with three months' standing likewise. (Table on next page.)

While clarification was in progress, it was thought that perhaps all of the Nekal was being removed--dissolved by the varnish or oil--but when it was practically complete, the brown of the Nekal was still present.

Oleic acid: at start,	at end
15% soln, clear brown.	½cm. layer of curdy material at top of liquid. Drop considerably depleted.
4%, somewhat turbid, light brown	slight general increase in turbidity
1%, turbid, very light tan	considerable increase in turbidity.
.2% more turbid, colorless	slight c.
.04% less turbid, colorless	" "

Raw linseed oil,

Soln.	Effect
15%	Slight turbidity.
4%	Slight general increase in turbidity.
1%	Almost complete c.
.2%	Apparently complete c.
.04%	" " "

Normal #1 varnish,

Soln.	Effect
15%	No visible effect
4%	Slight c.
1%	Apparently complete c.
.2%	" " "
.04%	" " "

C#3 varnish

Soln.	Effect
15%	No visible effect
4%	Slight c.
1%	Apparently complete c.
.2%	" " "
.04%	" " "

The non-volatile material in the various tubes of approximately 1% solution was determined by drying at 105 C. The drops of varnish and of oleic acid were avoided in drawing out the samples. The results were as follows:

Tube containing:	% solids and non-volatile liquids
Blank	.941%
Oleic acid	.947%
Raw linseed oil	.897%
Normal #1 varnish	.829%
C#3 varnish	.815%

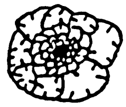
5.0% of the Nekal had been removed from an aqueous solution by an ether extraction some time previous to this. The extraction left the solution clear. The raw linseed oil has, in the case of the 1% solution of Nekal, removed 4.7% of the Nekal present, almost completely clearing it, while the normal #1 varnish extracted 11.9%, and C#3 varnish, 13.4%, and the oleic acid gave up as an emulsion .6% of the weight of the Nekal present.

That is to say, the varnishes dissolve the water-insoluble material in the Nekal, whereas the oleic acid, and in some cases the raw linseed oil are emulsified in the Nekal solution. The oleic acid contains fatty acid in much higher concentration than does raw linseed oil, and so the tendency toward emulsification in an alkaline, neutral, or nearly neutral solution would be stronger in the case of the oleic acid. Also, the oleic acid is the less viscous, so the mechanical inertia opposing the emulsification of it would be less.

A difference between oleic acid and raw linseed oil can be noticed in their behavior in the 1% solution of Nekal. The raw linseed oil had a considerable clearing effect on the solution, the oleic acid, quite the reverse. This indicates that there is no hard and fast line of surface tension of a solution relative to the σ_f produced by an oil, at which emulsification of the oil in the solution begins, since the σ_f produced by raw linseed oil is slightly below that produced by oleic acid. A rule dependent directly and only on σ would require that the raw linseed oil emulsify slightly more readily than the oleic acid. And, if the σ_i with the solution be taken as the criterion, they should still be in the same relative position. So, in the easily-emulsified one, a high concentration of free fatty acid molecules in the water-insoluble phase is combined with low viscosity. Also, since both are found in the greater degree in the liquid which emulsifies more strongly and on less provocation than the other, it is not possible to separate them by simple observation and get even a rough idea of which effect preponderates. It would have been interesting to know, but at the time it did not seem imperative, nor even important, so the matter was not followed further, for it has been found out that either emulsification or clearing could take place in such a system, and an outline had been obtained of the behavior of representative materials in this respect.

Reticulation of Ink

When ink is placed on water, it usually spreads rapidly out. If it is a long ink, it spreads out with areas of clear surface separated by fine lines of ink. The clean surfaces expand, and the threads break and contract, making the remaining threads thicker, as in the sketch.



If there is sufficient water area, the whole supply of ink does this, and later draws up into thicker threads, and, finally, into a compact mass, which is roughly in equilibrium with the surface. When the ink is very active in lowering σ of water, this mass can be picked up and placed on a new water surface, and it will repeat the performance, but will not lower σ so far as previously. Sometimes this can even be repeated again. This drawing together, whether much or little, or into large or small masses, is known as reticulation.

If the ink is short, the particles are shot off separately from the edge of the ink drop. They later drift together and reticulate weakly on a small scale.

Probably this whole phenomenon is comparable to the drawing-together of the bulk of an oil containing acid, where the oil spread with the acid at first, though the resultant film in this case has a better chance of being more than one molecule thick.

Another sort of reticulation has also been observed. As described above, it was noticed, as expected, that oleic acid would spread only on those solutions whose surface tensions it could lower by so doing. The author doubted the reality of the corresponding situation, i.e. that a film of an oil on the surface of water should prevent the adsorption of an adsorbed film of a σ-lowerer in solution in the water. It was impossible to imagine a plausible mechanism by which such a prevention would operate, so it was doubted whether it existed.

The case was tried out with normal #1 varnish on the surface of water. The bottom of a funnel projected below the surface, and, after the establishment of a film of the varnish, a very concentrated saponine solution was poured down the funnel in sufficient quantity to have given a value of σ, in water alone, below the value produced by the varnish. The water solution was stirred in some cases by the rotation of an L-shaped glass rod which had been introduced before the varnish was added, in others, allowed to go unstirred. The unvarying result was that the film of varnish broke in one or more scattered points, drew gradually back from them, and was finally gathered together into little drops. The meaning of this is simply that σ of the saponine solution is less than σ_i plus $\sigma_{varnish}$. Whether or not a monomolecular film of varnish-material, fatty acids in particular, was or was not left behind was regarded as being a question that was probably immaterial.

Ink Strips on Blanket

Another miscellaneous observation which seemed relevant is that strips of ink are often--almost usually--found on the blanket around the area where it is shoved most tightly against the plate by packing behind it. Apparently it is due to loose ink's being swept, along with the loose water, off the surface of the plate by the rolling of the blanket tightly against the plate. This agrees with the fact that it is more pronounced when there is excess water on the plate. This explanation certainly necessitates the existance of loose ink, either in or on the water on the plate. It gives no clue as to whether the ink is present as a film, as surface droplets, or as an emulsion.

Also, in some cases, ink deposits are formed on the blanket just outside the area which prints on the paper. This seems to be just an ordinary blanket scum which has not been kept thin by being given an opportunity to make contact with paper.

Hypotheses

With the aid of the knowledge now at hand, three hypotheses were formulated to explain the phenomena of blanket scum and, very provisionally, greasing of the plate.

1. Emulsification of the ink in the damping water, due to the presence of σ-lowering material in the water. (Most σ-lowerers are also emulsifying agents, and turkey red oil is known to be one.)

This is very simple and direct. It fits in beautifully with one empirically determined cause of blanket scum--σ-lowering material in the water. On the other hand, the other empirical statement at our disposal is that the same trouble is caused by varnishes of high σ_i against water, and inks whose films on water give high values of σ_f (which usually means high σ_i, since surface tension against air is quite uniform). This does not agree with the hypothesis of emulsification, since emulsions are most easily formed and most stable when σ_i is low, since the total free interfacial energy = $\sigma_i \cdot$ area of interface. But here we find our trouble growing worse as σ_i increases. It is true that what appeared to be one trouble--blanket scum--might have been several troubles with only an apparent similarity, but it was decided to look further for explanations before forsaking the idea that the two kinds of blanket scum could be accounted for under common principles.

2. The next hypothesis was that reticulation of the ink occurred on a small scale during the revolution of the plate cylinder. The evaporation of water is a force constantly tending to concentrate the solution and lower the surface tension. The passing of a water area of the plate under any roller breaks up the adsorbed film and tends to increase σ, but this effect might be obscured by other changes taking place at the same time. The addition of water also tends to raise σ. The passing of the blanket roller, bearing surface tension depressor, will remove water and add some of the surface tension depressor, if there is any basis at all to the empirical statements concerning coated papers. Both of these tend to decrease σ. Putting it in terms of the spreading coefficient, S is a maximum just after the damper rollers have passed over the particular water area. Then, if ever, the ink should spread. By the time the same point passes under the form roller, σ will be somewhat less than when it passed under the dampers. Experiments mentioned above indicate that if the surface tension which a solution would have, were the surface free of ink, is below that produced by an external film, the external film is unstable. Such a film will not persist indefinitely if it is already in existance when σ of the solution under-reaches it, nor will it be formed at all when the solution has already its low σ. Also,

agitation and disruption of the surface film will tend to take place every time the particular plate area which we are considering passes under a roller, and the strong air currents in the vicinity of the rapidly-moving plate will tend to do the same. That is, there are rather strong influences tending to break down the metastability of the ink film after its σ has been under-reached by the solution.

The former part of this statement is the more pertinent. Suppose that ink is available from the dots of the image to spread over the wet surface of the plate whenever the σ of the damping water on that part of the plate rises to, or above, that value which will permit the spread of ink. Ink cannot be seen to spread from the dots, but the water can be seen to draw back from them, and often, in rolling with a hand roller, ink can be seen by microscopic examination to spread from little flecks of ink accidentally deposited on the surface of the water. It is certain that ink does , in many cases at least, spread on the water.

Suppose also that the σ of the solution becomes decreased very rapidly by evaporation and adsorption of the σ-lowerer at the surface, during the ensuing time before this part of the plate reaches the blanket. The ink can reticulate to little droplets, or at least to aggregates. These should be picked up by the blanket.

All this is possible, but it is rather unlikely, for at ordinary speeds, the plate cylinder rotates at 60-70 r.p.m., and the time elapsing between a given spot's striking the form follers and the blanket is only about $\frac{1}{2}$ second. This is a very short time for spreading, change of σ, and reticulation to take place. Also, a rather delicate control of σ of the fountain water and σ_f produced by the ink would probably be required to cause scum. This might happen, but it should be very easy to change conditions in either one direction or the other far enough to prevent the scum, whereas in fact, the tendency to scum is often--even usually, very difficult to stop.

This hypothesis was retained, therefore, as being a possibility, but hardly a likelihood.

3. a) To recapitulate, it seemed, from the empirical data available, that a low σ of the aqueous layer, and the inability of the ink, even when spread, to cause a large lowering of σ, were two of the factors in causing blanket scum. The thing to which both of these tends is a low value of S, the spreading coefficient. The outstanding consequence of this is that spreading will be slower, other factors being constant, where S is low than where it is high. It was thought that this might in some way be, or be related to, the reason for scum.

b) It was noticed that when Carl Opp, in the Lithographic Research Laboratory, covered with lithographic varnish two rollers set in bearings, and ran them in contact with each other, the varnish pulled out into threads, and many flying droplets were visible. When inks were used here, both the threading and the atomizing were much reduced, and in some cases the atomizing was no longer visible, but there was always some threading. On the press, the upper rollers showed distinct threading, but the press was so constructed that such an observation could not be made on the form rollers, which run in contact with the plate. The form rollers showed a rough ink surface, and the surface was roughest in those places, measuring across the press, where the plate contained most ink area. These observations were simply visual and had to be made on short cylindrical sections of the form rollers, because the motion was so rapid that it was impossible to observe individual spots. Photographing the threading was considered, and had to be rejected for the same reason. The criterion of smoothness was the relative brightness of reflection of a light above the roller from the various parts of the ink surface on the roller. The aggregate of all these facts was regarded as reliable evidence of at least some threading of the ink between form rollers and the ink-bearing portion of the plate. Also, the tendency to form threads and droplets in Carl Opp's machine, mentioned above, is most marked in the most fluid inks, which are characterized in the shops as being, in general, a class of inks which is apt to cause scum.

c) It was noted that the blanket could have on it some ink in the non-printing areas without printing it on the paper. This ink seemed always to be very dry--to contain much pigment and only enough varnish to hold it together. In extreme cases, it could be broken from the blanket in microscopic flakes, which is unrecognizably far from the ordinary behavior of ink. This was accounted for on the basis of absorption of most of the oil by the blanket, leaving the pigment almost dry, close-packed, and hard--not plastic enough to be removed by contact with the paper.

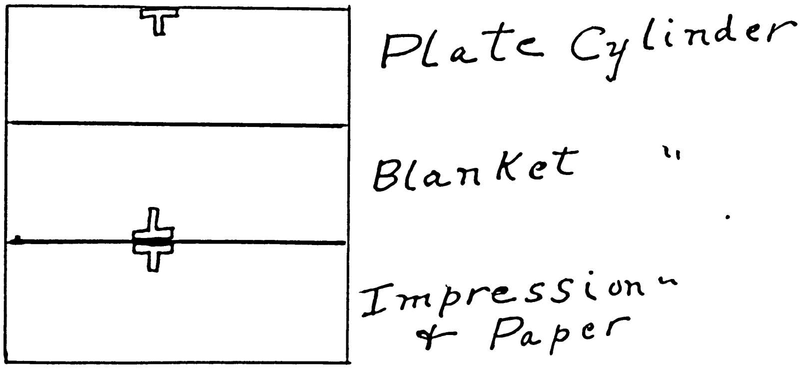
d) Suppose, now, that droplets of ink are formed directly by threading, or that some of the broken threads fall back in such a manner that they lie partly on water-wet areas of the plate, rather than on the inked areas from which they came. The droplets will tend to spread and to disperse on the surface of the water. If they do so, the water will be covered by a rather thin film of ink. If not, the droplets will still exist. The latter case should be the result of a low spreading coefficient. All samples of ink taken from lithographic shops were capable of spreading on the surface of those fountain waters with which they were being used. This does not include any scumming inks, since none of these were being used at any time when the author was in the plant.

When the small section of plate which is in question reaches the blanket, if there are droplets on the surface, they will be picked up by the blanket. If there is, on the other hand, a film, it will be at least partly picked up also. A given sample of blanket has a definite speed of oil absorption under any given set of conditions. If two samples of blanket receive the same amount of ink, in one case in the form of a film, in the other as droplets, the oil will be much more rapidly removed from the film than from the droplets, because the whole surface of the blanket will come into play in the first case and not in the second. The film will become incapable of printing much sooner than will the droplets.

This furnishes an explanation of "tinting", or printing on non-image areas of the paper, particularly as a tint is always easily resoluble with a low-power microscope into numerous small dots.

e) Greasing of the plate, which was also suspected of being a result of the same characteristics of the ink and the water, and sometimes followed the formation of blanket scum, can be explained by an extension of this idea.

When the author was collecting samples of inks and waters in the shops, he saw a piece of work which had come from a two-color press, in which one color was printed but a few seconds after the other. Thus there had been no time for the ink to dry, and that had resulted in trouble in this particular case. A blue field had been printed first, and lettering in red was being printed into the space left for it. Part of the blue ink was coming off the paper onto the blanket of the second section of the press, as each sheet passed through, and a considerable amount of ink was built up on the blanket on the corresponding areas. Presently a red tint was seen to be printing in the blue field on the sheets that came from the second (red) part of the press. The press was stopped, and the red tint was found on the blanket, and also on the plate. But the red tint was found only in the blue field, not in the blank spaces on the paper nor in the portions of the blanket or plate corresponding to them. That is, it corresponded to the design introduced into the red system by the wet blue ink, and this design was introduced via the blanket. The plate was now taking ink in those areas where it had come in contact with the blue ink on the blanket. It was found, on inquiry, that such an occurrence was not unknown in the shop.



This is conclusive evidence to the effect that wet ink on the non-design areas of the blanket can, in some cases, at least, cause the plate to begin to take ink in dots in corresponding portions of the non-printing area.

f) The mechanism of this greasing of the plate due to wet ink on the blanket was not yet explained in any way. At about this time, Professor Reed observed that a new type of blanket, which was being tried out in one of the shops, gave peculiar results. This blanket had a layer of cloth incorporated in it, very close to the surface. The inked areas of the plate were washed free of ink, after a run, and it was noted that the grain of the metal was seriously flattened in certain places, which formed a very regular pattern. This pattern corresponded, in spacing, to the high points of the weave of the cloth (where warp and woof crossed). The flattening of the grain was not visible in the non-inked portions of the plate. Abrasion of the plate by the ink, backed and pushed by the blanket, seemed the only explanation. Some stress in that part of the blanket immediately under the plate at any given time is unavoidable if any pressure is applied. If a lubricating medium is between them, slip will take place. If the lubricating medium contains an abrasive, wear will also take place. The ink-dots accidentally deposited on the blanket fulfil these conditions, though on a small scale. If the non-inked area, or any part of it, suffers wear, the desensitizing coating of dichromated gum will suffer first, and will finally be removed, leaving the bare metal, which is then receptive to grease and inks, which is the effect for which we wish to account.

Some new evidence has been introduced here. It was not brought in before because much of it belongs here chronologically, by discovery, and the rest has been postponed until this point because, on account of its detailed and apparently irrelevant nature, it would hardly have been remembered by the reader now if mentioned in the theoretical part of the thesis.

Further Experimental Work

Attempted Precipitation of Turkey Red Oil

Since calcium and barium soaps are, in general, very insoluble in water, it was thought that it might be possible to precipitate most of the turkey red oil, and so change σ of the solution. Turkey red oil solutions were found to give a precipitate with calcium, zinc, or barium chloride. Barium chloride solution was added to turkey red oil solution, and σ then fell more rapidly than it had fallen in the same turkey red oil solution alone. This was still true when an excess of barium chloride was present. Turkey red oil is a mixture of water-insoluble free sulfonated ricinoleic acid and the water-soluble sodium soap of the same material. It was considered that probably the presence of the water-insoluble material was almost unaffected chemically by the barium chloride, and that the barium soap, no longer able to stabilize an oil in water emulsion, released the free acid from colloidally protected state, so that some of it, at least, came more easily to the surface than when the oil in water type emulsion was being stabilized by the sodium soap.

An ether extraction on a new turkey red oil solution was therefore carried out. A small amount of barium chloride solution was added to the water solution after the ether had been boiled out, and after the solution had been cooled and several readings of σ taken. Perhaps after addition of barium chloride, the lowering of σ becomes slightly slower, but the difference is neither marked nor constant, even when excess barium chloride is used. Calcium chloride and zinc chloride, both giving similar precipitates, give similar results in this respect also.

If the trouble is as diagnosed, the above expedient will not be a remedy.

Grinding of Inks with Buffers

To get an idea of what inks and aqueous solutions of various pHs did to each other when ground together, inks were ground, by means of a glass muller on a glass plate, with buffers, with phosphoric acid solutions, and simply with water. The use of the buffers, of whatever acid pH, caused a good deal of material, rather rich in pigment, and almost pure pigment when the particles were small, to separate from the body of the ink. This was accentuated after one lot of the buffer had been mulled to dryness with the ink, and more so when yet another lot had been mulled in. The solution of phosphoric acid, pH 2.2, gave the same effect, but in less degree, while water alone had almost no effect, except in some cases--when a lake was used--to dissolve part of the dye from the surface of the base on which it had been precipitated. Apparently a high concentration of electrolytes is the most important factor here.

The use of a buffer gave, as well as dispersion of material in the solution, a scattering of ink over the top of the solution. This ink was quite finely divided. After the muller had passed over the surface of the water, this material reticulated very rapidly--in a fraction of a second--into little threads and groups. The size of these aggregates varied with the size of the pigment particles in the ink. The coarsest pigments gave aggregates barely visible to the naked eye under good light conditions. The finest gave aggregates only visible with about ten diameters' magnification.

Rate of Spreading

So far in this thesis, the statement has simply been made that an acid, oil, or ink, spread or did not spread on the surface of a given water or fountain water, and a value near the equilibrium value has sometimes been given for the σ_f produced, but nothing has been said regarding the speed of spreading.

It seemed certain that the rate of spreading of an ink on the surface of a water would increase if its spreading coefficient were increased. It was desired to try this out, for it had a decided bearing on the functioning of the mechanism of scumming proposed in the third hypothesis. An ink was used which had been successfully used on the press, and a series of solutions of calcium nitrate of various concentrations, and another series of magnesium nitrate solutions of the same molality were used as the water phases. The solution was put in a large tray, and the surface repeatedly dusted with talc and swept with strips of paper, to remove any surface film of impurities which might be present. The surface was then dusted with talc, so that the spread of the film might be traced. The ink was picked up on a glass rod, rolled against a glass plate to remove extra ink that would increase the perimeter exposed for spreading, and allowed to stand five seconds to come to equilibrium. Then it was thrust as nearly vertically as possible into a tray containing the solution, and the time of spreading over a circle 8 cm. in radius was observed. The same volume of solution was always used so that the rod would always be thrust in to the same depth, and any action of stripping the acid off the outside of the ink would be constant. The results are expressed in Table XIII and Plate LX as sq. cm. /sec covered. The point on the y-axis in the figure is the minimum surface tension which will cause any spreading of this particular ink, the point at which S is zero, that is. The tray used was much larger than the circle, so that the back pressure from surface impurities not removed would not build up to such a point as seriously to affect the reading.

The figure shows that the rate of spreading is not proportional to the spreading coefficient throughout, for this ink, for d(rate of spreading)/dS is seen to be much greater at high values of S than at low ones. The apparatus was rather crude, and the checks are pretty poor, but they show this trend very decidedly. The rapid rate of increase, with respect to S, of rate of spreading at high values of S made it seem quite possible that if σ of a solution were increased enough by the addition of an inorganic salt to the fountain water, the postulated ink-droplets might thus be allowed to spread and disintegrate in the time available.

Oleic Acid Inks

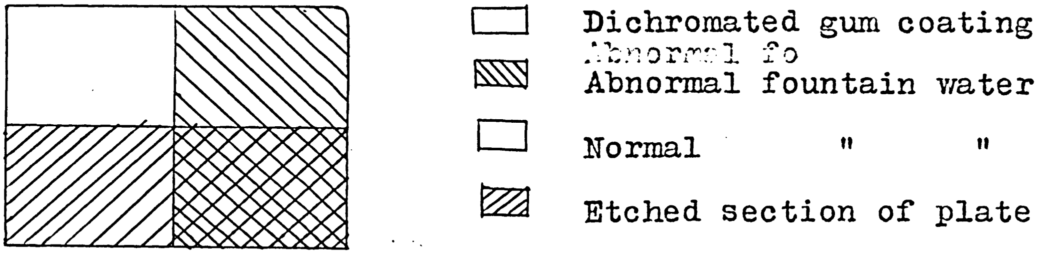
An ink made of 12 parts of oleic acid and 10 parts of carbon black was tried out on water, both as to σ_f produced and as to speed of spreading. Another ink was also made up, containing less pigment and more acid, and tried also. (See Table XII). The speed of spreading varied very little with change in concentration of oleic acid in the ink, but, as can be seen, the produced σ_f behaves differently, showing increasing values as the percentage of oleic acid in the ink decreases. Also, it is interesting that σ_f for the 10 to 12 ink passed through a minimum on standing. The thinner ink showed no such effect. No explanation of this is offered,

It has been found that for ordinary inks made in the lab, the minimum value of σ_f is about 5 dynes above the minimum value for the varnish. This statement does not represent many cases studied.

Press Tests

The whole ink and water systems of the lithographic press in the laboratory were divided into halves, each roller having a ring removed at the center, so that two different inks or two different fountain waters could be used without their mixing.

A plate was made up. The top half was desensitized by dichromated gum, the bottom with etch only. By using one fountain water on one side, one on the other, it was possible to get four divisions of area.



The etched section was included so that, if any further work were done, it would be known whether definite results could be obtained in a much shorter length of time by using an etched plate than by using one which had been desensitized with dichromated gum.

Variation in the fountain waters was tried first. The same ink was used on both sides. A standard fountain water, known to work uniformly well, was used on the left side of the plate, while on the right side was used a fountain water containing the same materials in the same amounts, except that it also contained .0008% of turkey red oil and enough more phosphoric acid to make its pH the same as that of the normal fountain water. There was no trouble during a run of about 2700 impressions, and no difference could be noticed between the two sides of the plate, the blanket, or the print.

The procedure was repeated, using the same plate, but using .013% turkey red oil in the fountain water on the right side of the press. About 3300 more impressions were run off, and still no difference was observed.

The procedure was repeated, using .316% turkey red oil in the fountain water on the right side of the press. The fountain water was now definitely turbid. The press run now showed considerable differences between the two sides. First, the right side of the blanket showed a heavy scum. A visible tint soon began to be noticed in the lower right-hand section of the print. Microscopic examination showed a much lighter tint in the upper right and lower left sections of the print, and practically none in the upper left. The sketch of the arrangement of sections on the plate shows this also. The scum on the right side of the blanket was uniform, top and bottom. A number of microscopic ink dots were seen on the plate. Checking of their position in comparison with that of the ink-spots in the tint on the paper showed correspondence of position in some cases but not in others. The lack of correspondence ran largely in one direction. That is, most of the dots examined on the plate had counterparts on the print, but many of the dots on the print did not correspond to any dot on the plate, and this can be understood from the viewpoint that some of the dots on the paper came direct from the water by way of the blanket. The correspondence noted suggests further comparisons and more work on the subject, but is not such as to warrant any claims.

Emulsification is clearly indicated in this case. The third hypothesis as to formation of blanket scum falls to the ground, for the amounts of droplet-formation on the two sides of the plate should have been at least comparable in magnitude, which should give comparable amounts of ink on the two sides of the blanket, even though it arrived there as a film on one side of the press and as droplets on the other. But the left side of the blanket, where standard fountain water was used, was almost completely clean. Ink on the surface of the water, differing in scumming and non-scumming cases only by being aggregated, and spread in a thin film, respectively, can hardly be the explanation. The idea of emulsification, however, demands that the quantity of loose ink on the side containing the emulsifying agent and showing scumming shall be greater than on the other side, and that is what we find here.

However, the σ_f relationships noted between water and bad inks and bad varnishes are not in agreement with the idea of emulsification, for a high value of σ_i should act as a deterrent to emulsification.

Our idea of the trouble we are studying is thus split into two parts: The presence of an emulsifying agent causes emulsification with consequent scumming, and as to the troublesome inks, we can return to that half of the third hypothesis which concerns the ink, or we can try to find another reason.

One really striking thing about the oleic acid inks was the fact that the amount of pigment spread on the surface of the water could not be condensed by surface compression to a visible film, as was possible with all other inks tried. There simply was not enough of the pigment spread on the surface. Oleic acid, forming, as it does, a monomolecular rather than a polymolecular film on the surface of water, is required in such small amounts completely to saturate the surface that but little of the pigment is deserted by its liquid vehicle. Also, the speed of spreading is so much greater than that of ordinary inks that, if one wishes to put it this way, the "surface vacuum" on top of the water which is effective at the ink-drop is so much lessened by the frictional resistance of the oleic acid film's dragging across the top of the water, that it is not sufficient to burst and scatter the ink-droplet over the surface of the water. But an ordinary ink which is deficient in fatty acids may not be able to furnish acids at a high enough rate of speed to satisfy this "surface vacuum" sufficiently to forestall the disruption of the particle. If the ink is in the form of a dot surrounded with water, and attached to the plate, its edges are still liable to this sort of disruption. This was the only explanation thought of at the time.

Two inks were made up, one with drier, carbon black, and normal varnishes, the other with drier, carbon black, and C#3 varnish. Great pains were taken to make them of the same consistency, as to length, tack, and mobility. The neutral ink was capable of lowering the surface tension of water to 58 dynes, the other, 53. They were put in opposite sides of the press and run with the same fountain water that had been used as standard before, and with a new plate like the one previously used. No difference in their effects was perceptible in 8,000 impressions.

This largely dashed the idea that the acid content of an ink, or its σ_f on water was alone the criterion of its scumming. Of course, it was possible that under the particular conditions of this run, almost any ink could have been used without causing trouble, but if work had been resumed on this basis, it would have meant much cut and try work, with no guiding hypothesis. Also, the press was needed for other trials, so work was stopped here.

Conclusions

1. Examination of the literature indicates that polymerization of linseed oil through its ethylene linkages is the reaction which most plausibly accounts for the various effects noted in the process of heat-bodying it.

Experiments indicate that the free acids present are directly, rather than indirectly, concerned in the heat-bodying reactions.

2. The lowering of σ by a thick external film of castor oil or of normal #00 varnish or of paraffin oil proceeds according to the equation $d\sigma_f/dt=A(\sigma_f-c)$ until in the case of castor oil and #00 varnish it reaches a point where the thick film reticulates. If linoleic acid be added, this equation only applies after an initial period of 15 minutes. Addition of linoleic acid to these film-forming materials lowers the value of the constant c.

3. A varnish added to an aqueous solution of turkey red oil or Nekal may have a clarifying effect on it by dissolving the water-insoluble material from the solution. Oleic acid and raw linseed oil behave in the same way in dilute solutions, but tend to be emulsified in more concentrated ones.

4. σ-lowering ability of turkey red oil solutions cannot be much decreased by precipitation of insoluble soaps by addition of barium, zinc, or calcium chloride, either with or without a previous ether extraction.

5. In one case, that of oleic acid on Nekal solutions, $\sigma_f - \sigma \rightarrow \sigma_i$ as $\sigma_i \longrightarrow$ zero. This indicates that in this case, the film has become polymolecular or that most of the deviation of σ_f from $(\sigma + \sigma_i)$ is due largely to conditions at the interface rather than at the surface. This conclusion is not general.

6. A varnish film on water will reticulate if σ of the water be decreased much below σ_f of the film.

7. Rate of spread of a representative ink on water increased much more rapidly than in proportion to the spreading coefficient. It has not been proved that this applies to inks in general, but it is believed that it does.

8. Emulsification is at least one of the troubles of lithography. It causes ink to be deposited on the blanket, from which it can print onto the paper and may sometimes deposit itself on the plate.

Summary.

The ring method of determining σ was used in all cases. It was noticed by Professor Reed that coated papers, and especially those whose aqueous extracts foam, were apt to give blanket scum and sometimes tinting and greasing of the plate, which seem to be related troubles. The σ of these extracts was found to be lower than the average. There seemed to be trouble of the same sort with inks which were unable to lower σ of water very far by spreading on it.

It was found that σ_f could be decreased by the addition to the film-forming material of a more active σ-lowerer. The σ_f-concentration curve was deeply concave upward, as would be expected. Of course σ_f decreased with time. After trying several type equations it was found that the equation $\log(\sigma_f - c) = At + B$, where $t =$ age of the film, fitted the curves very well, except that when fresh acid was added to the material, the curves only applied after about 15 minutes. Comparison of the values of c for castor oil and normal #00 varnish, both with the same amount of linoleic acid added, showed approximately the same effect, indicating that the acids in heat-bodied linseed oil are directly, rather than indirectly, affected by the heat-bodying.

A table was compiled, from experimental work, of the σ of turkey red oil solutions of different concentrations and pHs, and of Nekal and saponine and sodium oleate solutions.

Some imterfacial tensions were also noted, and it was found that for oleic acid on Nekal solutions, $(\sigma+\sigma_i-\sigma_f)$ reaches a very low value when σ_i also reaches a low value, in one case. As σ remained practically constant, the difference must have been decreased via σ_i or σ_f or both, unless a polymolecular film was formed. No case was found in which a water-insoluble film would spread if σ_f was not less than σ_{soln}.

Long standing of a variety of materials in solutions of turkey red oil and Nekal was tried. It was found that oleic acid and raw linseed oil tended to emulsify on standing in some concentrated solutions, expecially of Nekal, and that varnishes had a clarifying effect in all cases, and that raw linseed oil and oleic acid also had a clarifying effect in dilute solutions. It was also discovered that a varnish would continue to dissolve Nekal from the solution after the water-insoluble part had been removed and clarification was apparently complete.

Varnish was spread on the surface of water, and a solution of σ-lowerer added to the water "sub-cutaneously". Reticulation of the varnish took place in all cases when there was enough σ-lowerer to lower the σ of the water phase below the σ_f maintained by the varnish.

Three hypotheses were drawn up. The firse supposed that blanket scum, tinting, and greasing of the plate were caused by emulsification of the ink. Another, that they were due to reticulation of ink on the surface of the water, caused by changing σ of the water. The last, that it was due to non-spreading of ink droplets on the surface of the water.

Turkey red oil could be precipitated from solution, in large part at least, by addition of barium, calcium, or zinc chloride, but σ of the solution is not thus increased.

Some study was given the relation of speed of spreading to S, the spreading coefficient, especially at high values of S, and d(rate of spreading)/dS was found to increase as S increased.

Press tests were carried out, and when .316% of turkey red oil was used in an otherwise standard fountain water, a heavy blanket scum was formed and some tinting occurred during a run of 3000 impressions. This, it was clear, was due to emulsification. It is interesting, though perhaps not significant, that this is the lowest concentration of turkey red oil in solution that was able to cause visible spontaneous emulsification of oleic acid within 10 hours. in another press test, it was found that an ink made with C#3 varnish, one of a brand which was supposed to give this trouble of blanket scum, behaved quite as well as an ink of similar consistency, which was made of standard ingredients.

Acknowledgement.

The help of Professor R.F.Reed, who suggested the problem, is gratefully acknowledged. Several of the ideas in this paper are his, and he placed the lithographic press in the laboratory at the disposal of the author at a time when such action meant considerable inconvenience to him. Paul Dorst of the Lithographic Research Laboratory gave of his time to help in the press tests at some sacrifice to himself.

The author also thanks Doctor George, likewise of the department, for the suggestions and encouragement that he has given,

The U.S.Playing Card Co. and the Hennegan Lithographigg Co., of Cincinnati, as well as the Nivison-Weiskopf Co., of Reading, Ohio, have contributed samples of troublesome inks, and have opened their shops to the author, who wishes to express his appreciation of these aids.

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Table III.

Varnish	η, poises.	% acids, computed as oleic acid	σ_f on water.
Raw linseed o oil, normal	1.24	2.14	41.95
Boiled "	1.75	3.12	50.0
#0000, normal	4.94	5.29	50.8
#00 "	14.12	----	52.3
#7 "	1440.	13.48	53.2
C#3	46.	.88	56.8

Table IV. (28)

Linseed oil, heat-bodied at 293°C

Time of heating	Mol. wt.	Acid no.	Iodine no.	A_0	A (packed)	F	$\frac{A_0}{A}$	L	$\frac{\text{Mol. wt}}{A_0}$
0 hours	795	2.16	183	121	94	11.0	1.29	11.9	65.7
.75 "	933	3.6	1.54.3	141	118	10.2	1.19	11.8	65.3
2.25 "	1235	3.4	141.3	178	142	10.0	1.25	12.8	69.5
3.0 "	1441	3.6	---	206	166	10.2	1.24	11.8	69.8
4.5 "	1903	4.3	111.5	287	226	10.0	1.27	11.3	66.3
5.5 "	2370	4.7	---	335	277	9.7	1.21	11.9	70.8

Column 11

Time of heating in hours	0	.75	2.25	3.0	4.5	5.5
M/A	84.5	79.0	87.0	87.0	84.0	85.5

F is stated in dynes/cm., A_0 and A in square Ångstrom units, and L, the length of the molecule, in Ångstrom units. A_0 is the area per molecule at zero compression, A the area at the crumpling point, and F the surface pressure at the crumpling point.

Table V. (28)

Material	Mol. wt.	Ao	L	A	F
Stearic ~~Oleic~~ acid	284.3	22.5	21.9	18	60
Oleic acid	282.3	52	10.2	28	28
Mixed acids (of linseed oil)	280	67	8.2	28	28
Oleic monoglyc'de.	356	47	12.8	25	29
" di "	625	86	12.7	63	16.7
" tri "	885	127	12.3	100	12.3
Mixed mono "	354	61	10.3	35	25
" di "	617	103	10.3	73	15
" tri "	879	143	10.7	110	12
Linseed oil, raw	795	121	11.9	94	11.0
", boiled .75 hour	933	141	11.8	118	10.2
" " 5.5 "	2370	335	11.9	277	9.7
Ethylene glycol mixed diester	586	98	10.9	72	14
Diethylene glycol mixed diester	630	110	10.2	73	18.4
Mannitol diester	706	105	11.5	75	15
" tetra "	1230	176	12.1	147	8.2

Table VI.

Part of a table given by J.F.Carriere (31)

Surface	Value, dynes/cm.	Author.
Water whose surface is saturated with oleic acid, σ_f	43	(32) Miss Pockels
Oleic acid, σ.	32.27	Harkins (36)
Water-oleic acid interface	16.05	" (36)

Table VII.

Surface tension of turkey red oil solutions.

	Concentration of turkey red oil	solution alone max. readg.	min. readg.	Oleic acid added.
1.	1.60%	36.9	36.5	36.5
2.	.316%	41.2	40.7	40.3
3.	.066%	44.1	42.9	42.5
4.	.013%	48.5	48.5	43.5 ?
5.	.0026%	54.9	50.8	43.8 ?
6.	.00049%	70.5	67.4	42.7
7.	.00021%	72.7	72.6	42.7

Oleic acid will spread on Solution #3 and those below it in the table, but C#3 varnish will only spread on the Solution #6 and those below.

Concentration, in %.	pH	surface tension in dynes/cm.
.632%	---	38.1
	4.4	41.3
	2.7	40.6
	2.0	40.2
	1.7	40.1
.126	6.9	40.9
	2.8	41.5
	2.0	41.3
.0253	7.4	44.4
	2.8	43.8
	2.0	43.7
.00505	8.0	47.3
	2.6	43.9

Table VIII.

Nekal solutions.

20% solution	surface tension	35.6
5% "	" "	37.7

Oleic acid spread, giving γ_f of 34.8

4% solution	C#3	normal #2	normal #1
γ of "	38.3	38.4	38.3
γ with varnish present	38.2	38.4	38.3
γ_i " "	2.8	1.5	.9
γ of "	37.3	37.0	37.7

No spreading took place.

1% solution	C#3	normal #1	oleic acid
lines same as	39.2	39.2	38.8
corresponding ones above	39.2	38.6	35.1
	3.90	.95	.62
	37.5	37.6	34.7

.2% solution	normal #1 varnish	C#3
γ of "	50.1	51.2
γ with varnish present	46.8	49.5

.04% solution	normal #1 varnish	C#3
γ of solution	58.3	62.0
γ with varnish present	50.7	55.4

.008% solution	normal #1 varnish
same headings	67.8
	52.7

Table IX.
Saponine solutions.

1% solution

Age of film in minutes	surface tension
1	42.9
5	41.0
15	40.1

.2% solution

1	46.8
5	42.5
10	40.1

.0

SAponine solutions

Age of film in minutes	surface tension
.04% solution	
1	61.5
10	55.8
20	55.1
30	54.9
40	54.3
50	53.8
60	53.4
oleic acid was added	
10	47.1
30	43.6
.008% solution	
¾	71.6
11½	66.7
22	61.8
188	59.7
oleic acid was added	
½	55.4
1 2/3	53.9
3	51.5
4 1/6	47.7
6	46.2
7 1/2	44.1
11	43.7
16	43.6

Table X.

Sodium oleate solutions.

.01% solution	
1½	43.5
2½	42.3
3½	41.4
5½	41.7
6½	41.5
8 1/6	41.1
13	40.4
17	40.4
20	40.1
oleic acid was added	
1½	40.8
2½	40.6
7	40.6
20 hours	

Sodium oleate solution Age of film in minutes	surface tension
.001% solution	
1 1/2	64.9
2 2/3	63.3
3 2/3	61.7
4 2/3	60.5
6	59.0
6 3/4	58.3
9	57.6
13	57.3
24	55.2
53	51.6
59	51.0
65	50.5
oleic acid was added	
30	42.4
40	42.2

Table XI.

Raw linseed oil on water	σ_f
5 seconds	49.0
4 1/2 minutes	43.76
6 1/3 "	43.2
10 "	42.6
45 "	41.9
Boiled linseed oil on water	
2 minutes	51.5
3 2/3 "	51.2
5 3/4 "	50.9
9 2/3 "	50.8
105 "	50.0
#0000 varnish on water	
4 1/2 minutes	51.4
9 "	51.3
27 "	51.1
33 "	50.9
45 "	50.8
#00 varnish on water	
1/2 minute	53.6
2 1/2 "	52.9
4 "	52.5
28 "	52.3
46 "	52.3
54 "	52.26

Age of film	σ_f
#7 varnish	
1 1/6 minutes	53.8
2 5/6 "	53.6
3 5/6 "	53.4
9 "	53.2
15 "	53.1
C#3 varnish	
1 minute	59.0
2 3/4 "	58.2
3 3/4 "	57.8
8 "	57.1
16 "	56.8

Table XII.
Oleic acid inks

Ink 1: 12 gm. oleic acid, 10 gm. carbon black.

5 minutes	43.8
7 "	43.3
10 "	43.5
37 "	45.9
55 "	46.2
4 hours	44.3
16 "	42.3

Ink 2: 3.6 gm. oleic acid, 2.3 gm. carbon black.

1 minute	44.3
2 "	43.2
4 "	42.9
10 "	42.7
6 hours.	42.6

Speed of spreading of Ink 1--13.7 sq. cm. /sec.
" " " " " 2--20 " " "

Table XIII.

A). Calcium nitrate solutions

Surface tension of the solution	mean speed of spread	maximum deviation from mean.
73.9	3.24	5%
76.6	6.83	5%
79.6	12.3	9%
86.1	21.21	5%
71.8 (water)	2.42	

B). Magnesium nitrate solutions

74.9	3.94	
77.6	6.64	.9%
79.7	8.24	6%
84.6	11.84	6%
73.0	2.75	1.3%

Table XIV

f-concentration of linoleic acid in #00 varnish.

% acid added	approximately equilibrium value of σ_f.
0	52.3
.5	50.4
1.0	49.1
2.0	47.8
5.0	45.4
100.0	40.9

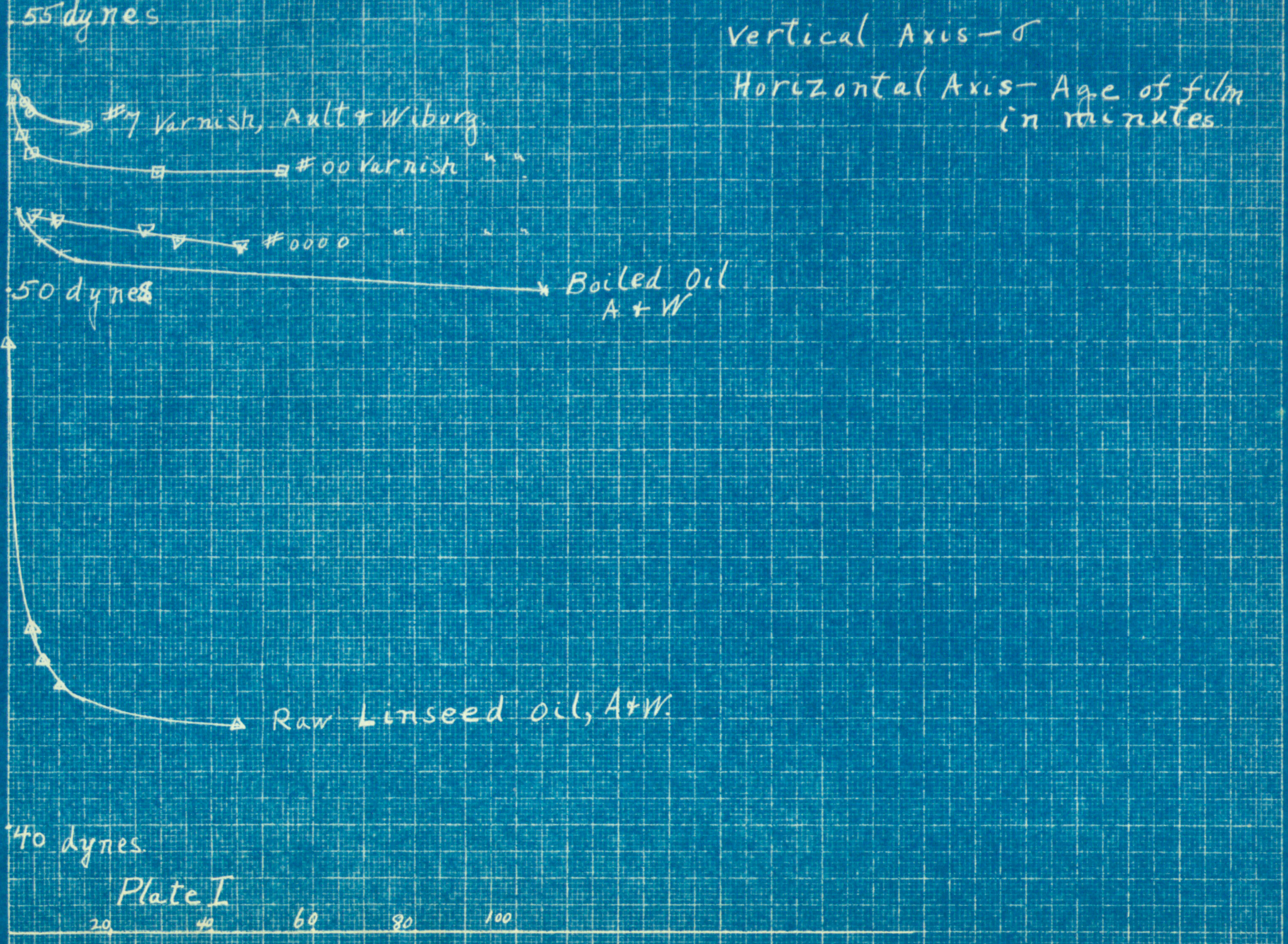


Plate I

55 dynes
50 dynes
40 dynes
Vertical Axis – σ
Horizontal Axis – Age of film in minutes
#7 Varnish, Ault + Wiborg.
#00 Varnish " "
#0000 " "
Boiled Oil A + W
Raw Linseed oil, A+W.
20
40
60
80
100

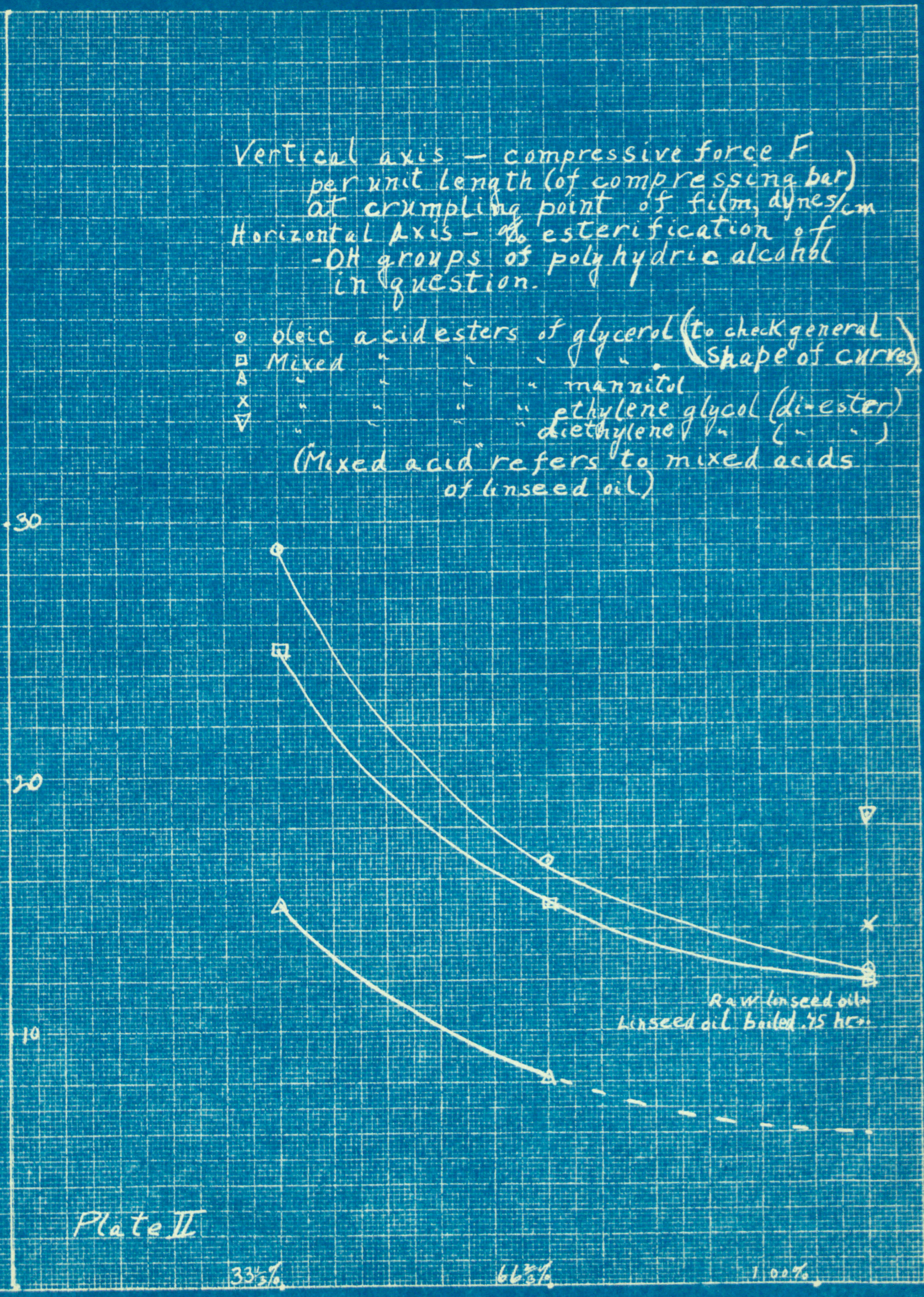

Vertical axis – compressive force F per unit length (of compressing bar) at crumpling point of film, dynes/cm
Horizontal Axis – % esterification of -OH groups of polyhydric alcohol in question.
○ oleic acid esters of glycerol (to check general shape of curves)
□ Mixed " " " " .
△ " " " " mannitol
× " " " " ethylene glycol (di-ester)
▽ " " " " diethylene " (" ")
("Mixed acid" refers to mixed acids of linseed oil.)
30
20
10
Raw linseed oil →
Linseed oil boiled .75 hrs →
33⅓%
66⅔%
100%

Plate II

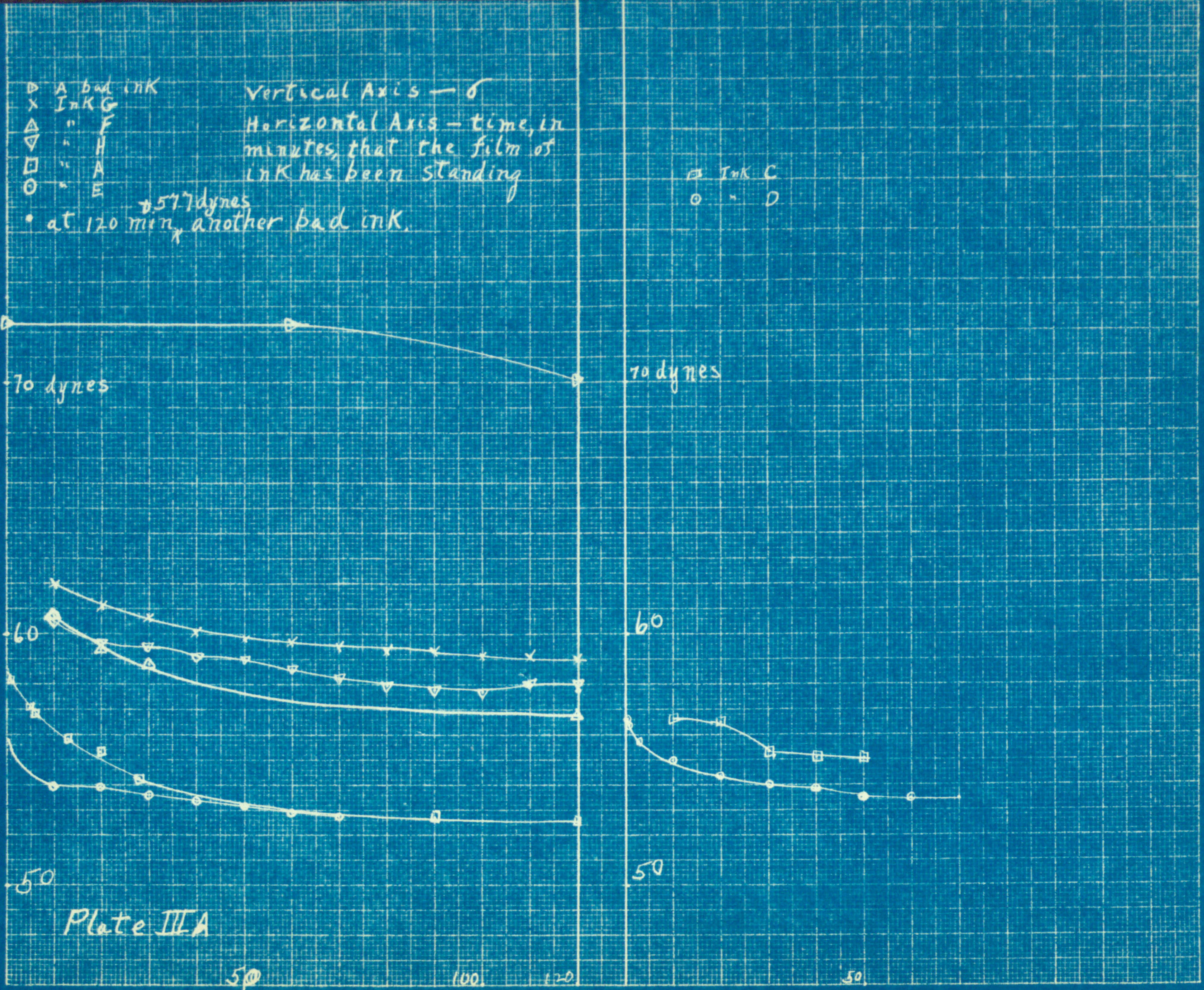


Plate IIIA

▷ A bad ink
× Ink G
△ " F
▽ " H
□ " A
⊙ " E
• at 120 min. another bad ink. 57.7 dynes
Vertical Axis — σ
Horizontal Axis — time, in minutes, that the film of ink has been standing
□ Ink C
⊙ " D
70 dynes
60
50
50
100
120
70 dynes
60
50
50

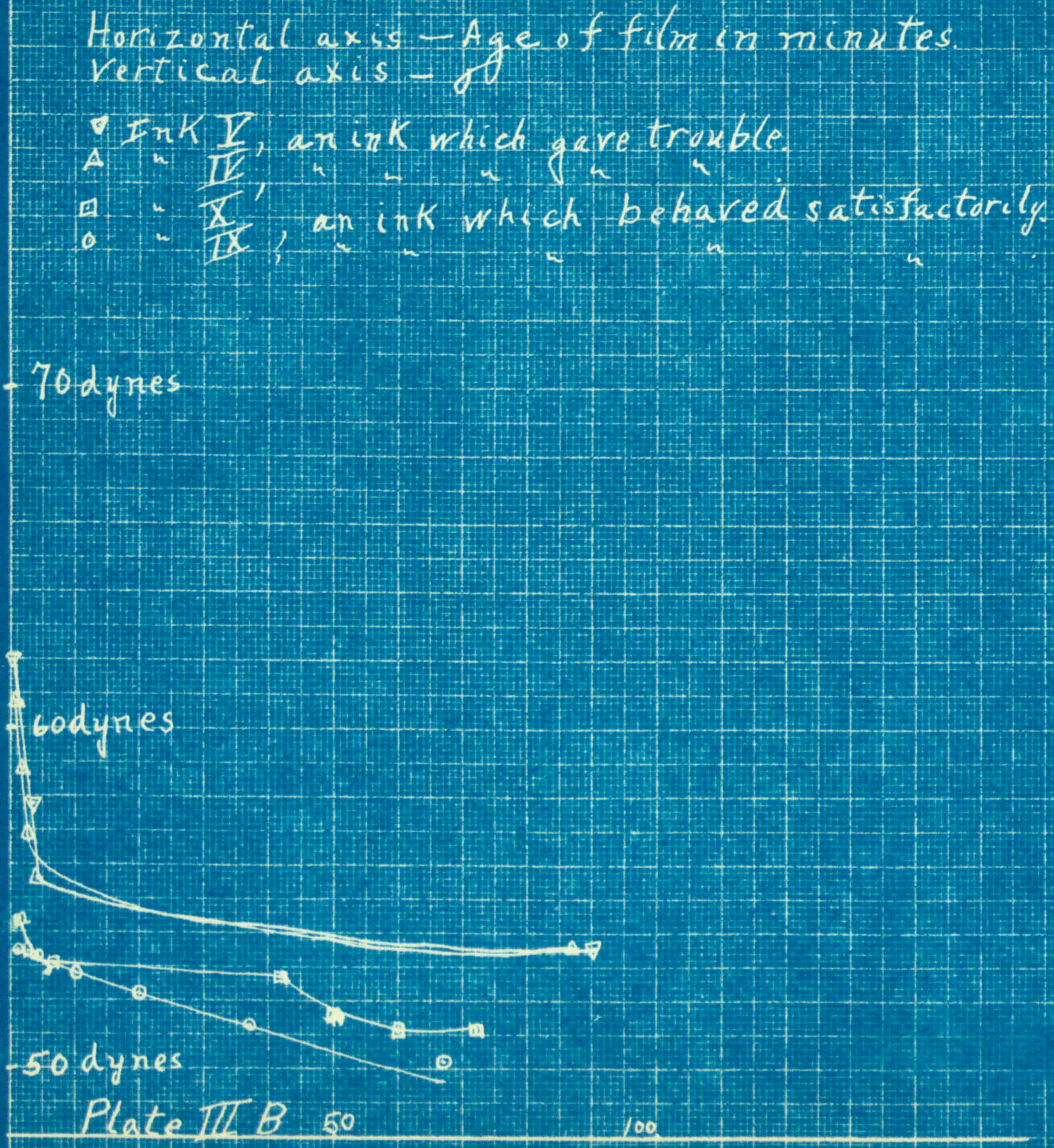
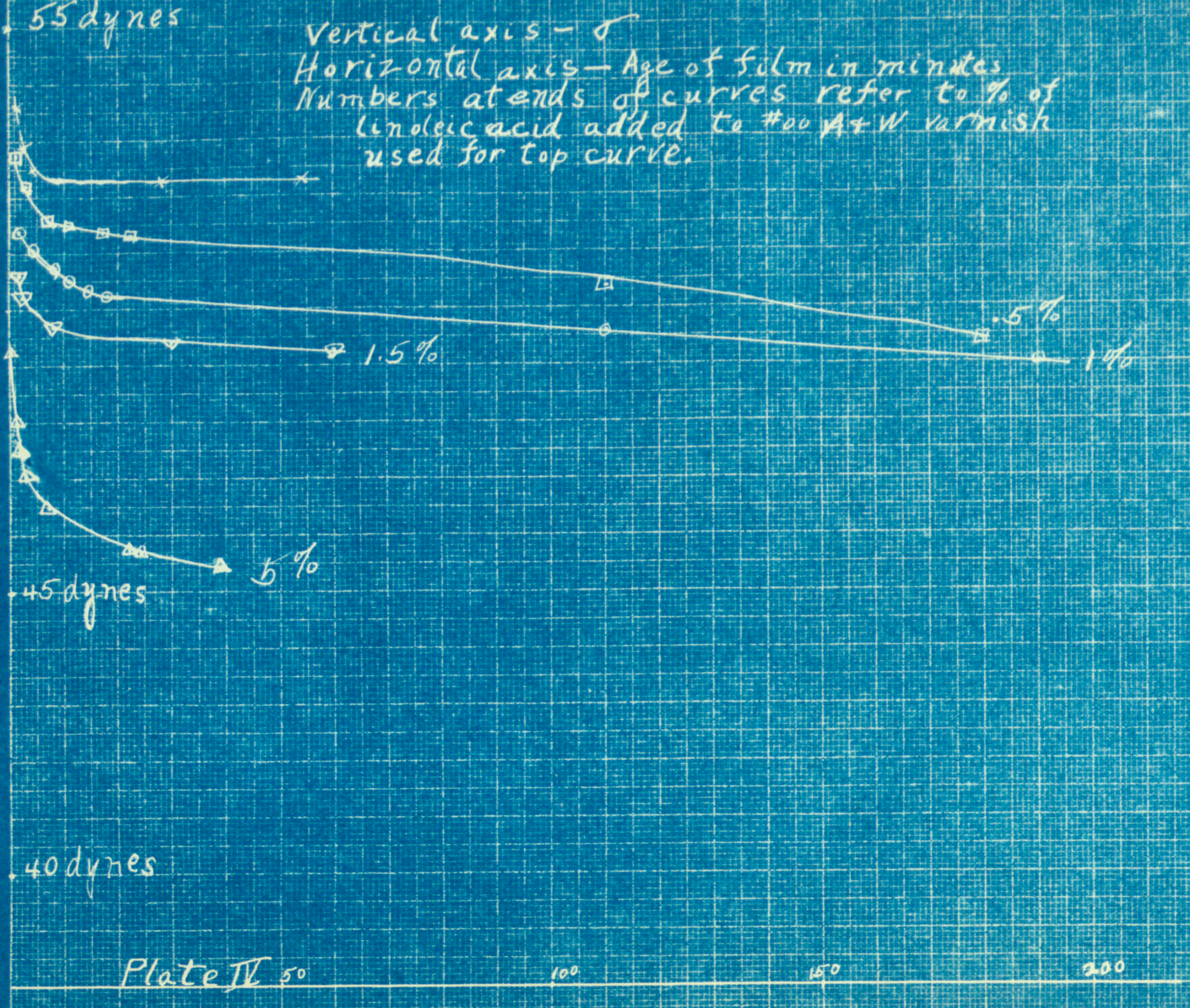
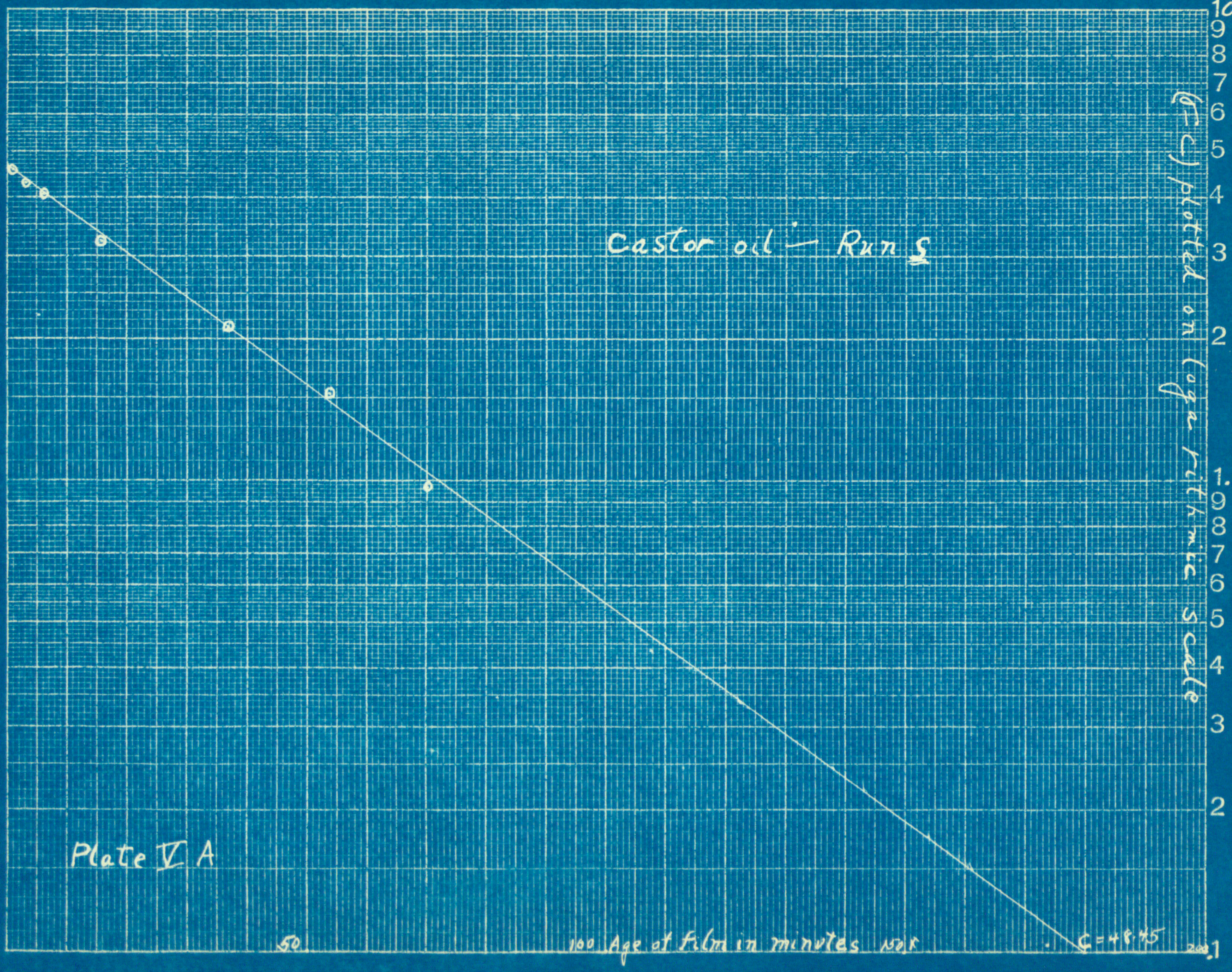

Horizontal axis – Age of film in minutes.
Vertical axis – γ
▼ Ink V, an ink which gave trouble.
△ " IV, " " " " "
⊡ " X, an ink which behaved satisfactorily.
○ " IX, " " " " "
70 dynes
60 dynes
50 dynes
50
100

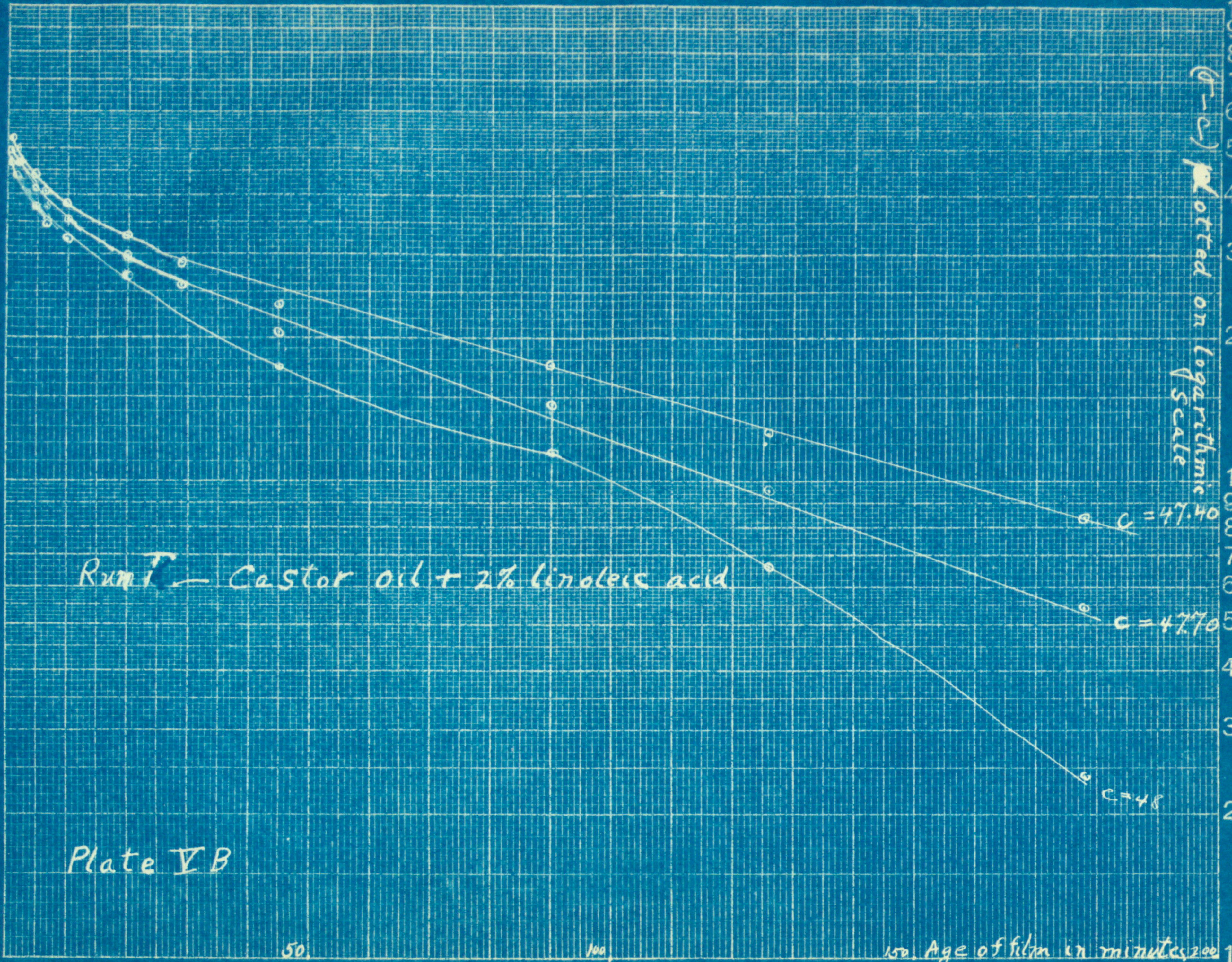
Plate III B



Vertical axis – σ
Horizontal axis – Age of film in minutes
Numbers at ends of curves refer to % of
linoleic acid added to #00 A+W varnish
used for top curve.

Plate IV


Castor oil – Run 5
Plate V A
(σ−C) plotted on logarithmic scale
10
9
8
7
6
5
4
3
2
1.
9
8
7
6
5
4
3
2
.1
50
100
Age of film in minutes
150
C = 48.45
200



Run I — Castor oil + 2% linoleic acid

Plate V B

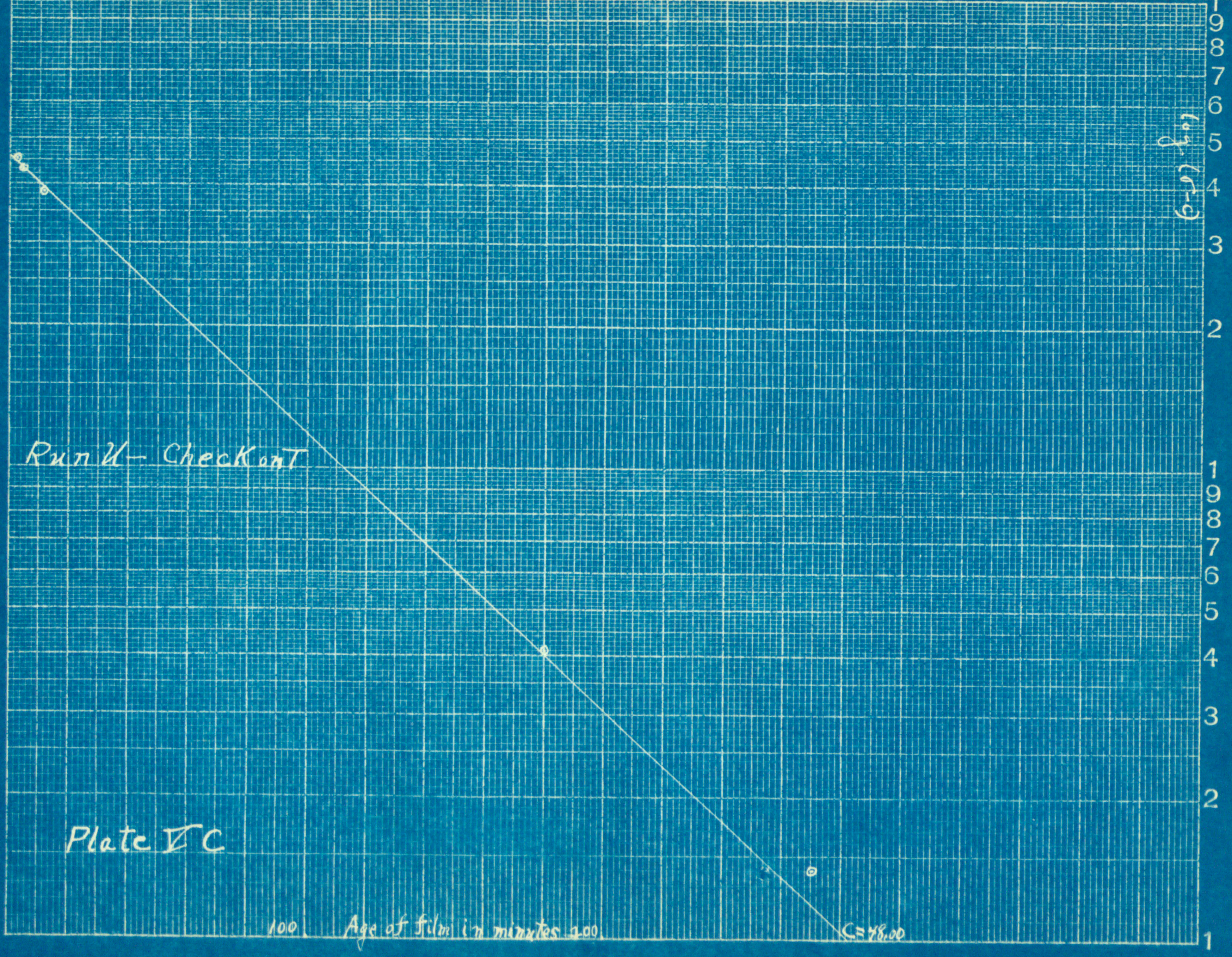

log (σ-c)
1
9
8
7
6
5
4
3
2
1
9
8
7
6
5
4
3
2
1
Run U - Check on T
100
Age of film in minutes 200
C=78.00

Plate VI C

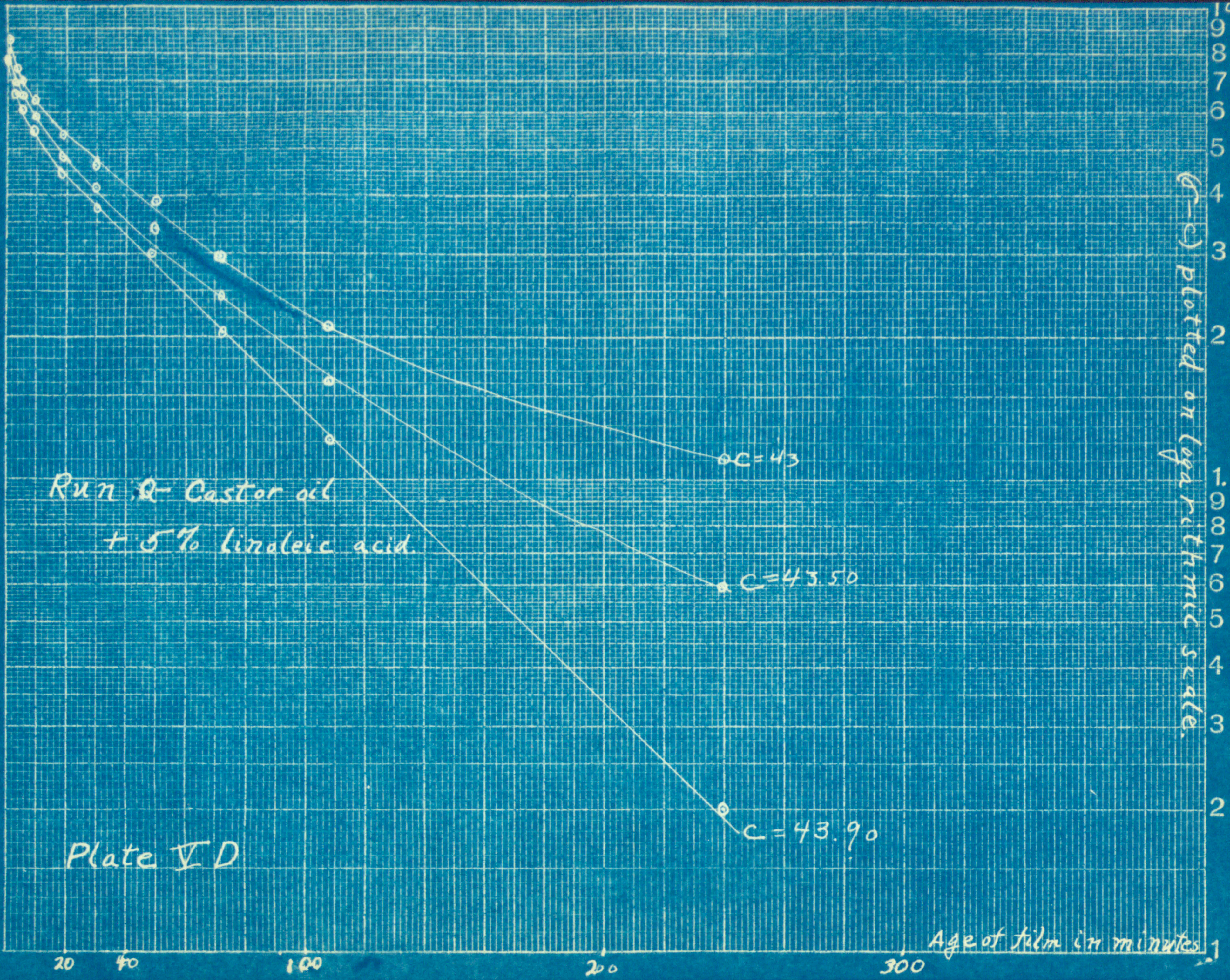

(σ–c) plotted on logarithmic scale.
C=43
C=43.50
C=43.90
Run Q- Castor oil
+ 5% linoleic acid.
Age of film in minutes
20
40
100
200
300
1
2
3
4
5
6
7
8
9
1.
2
3
4
5
6
7
8
9
10

Plate V D

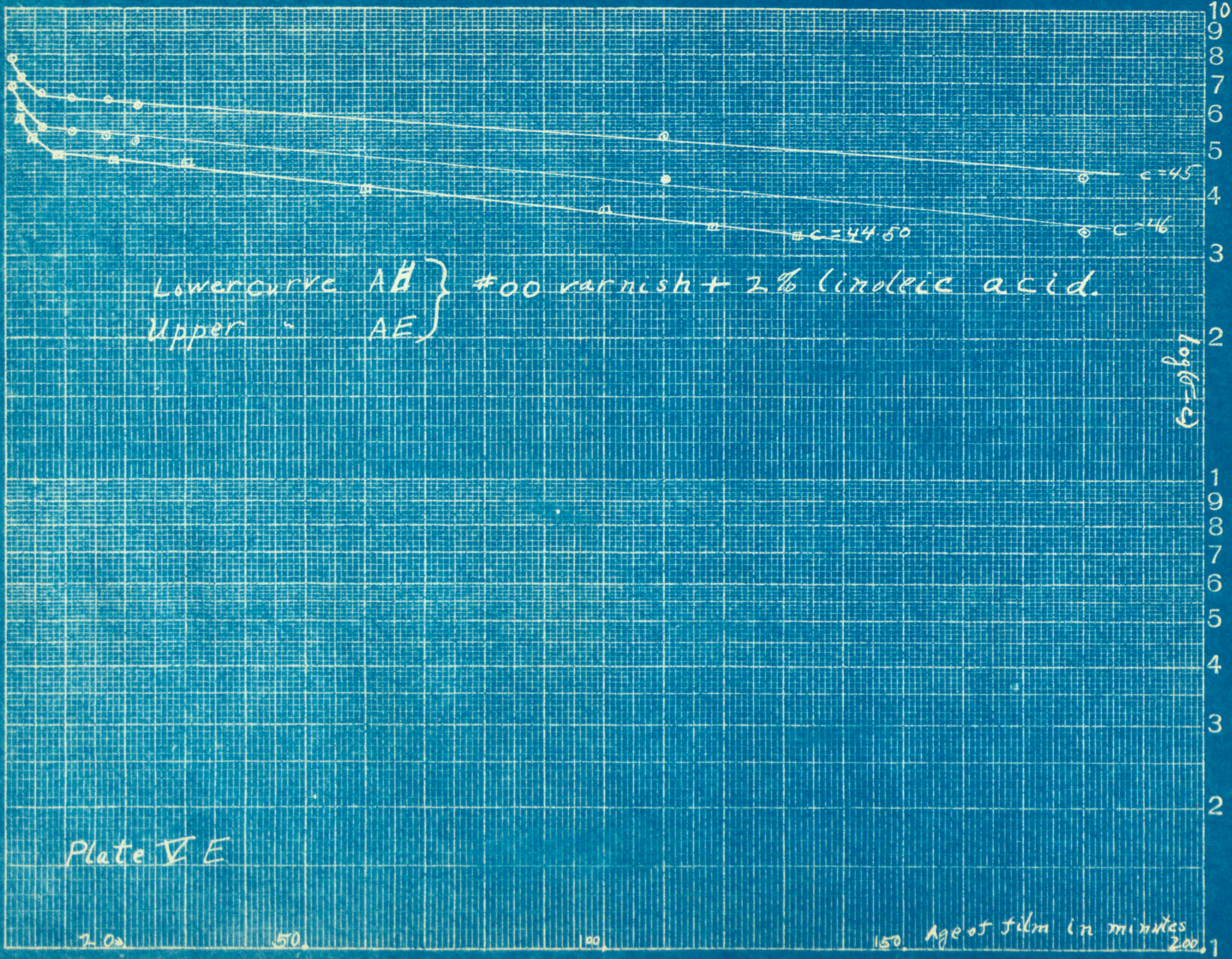

10
9
8
7
6
5
4
3
2
1
9
8
7
6
5
4
3
2
1
Log(σ−c)
c=45
c=46
c=44.50
Lowercurve AH
Upper " AE
#00 varnish + 2% linoleic acid.
20
50
100
150
200
Age of film in minutes

Plate V E

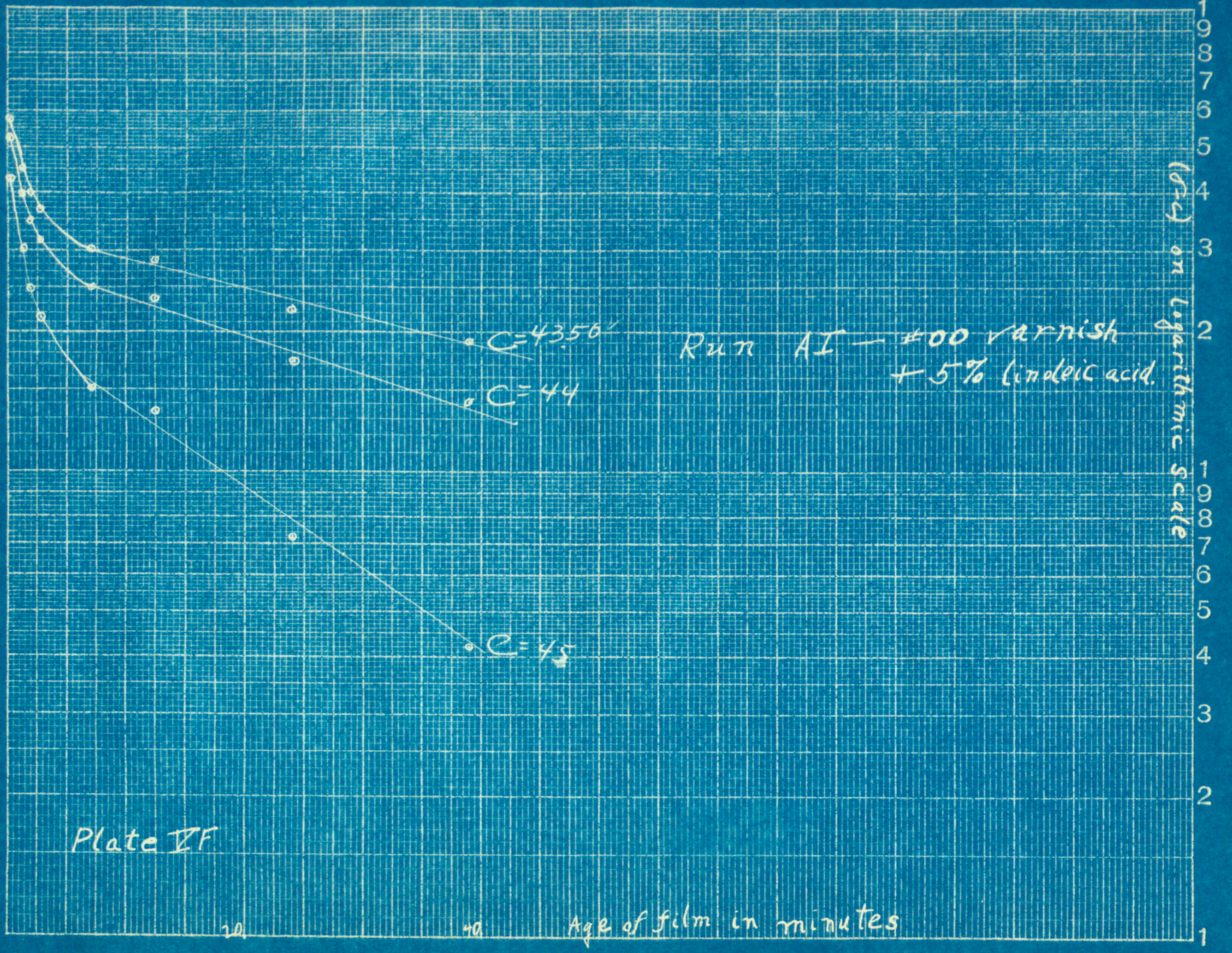

Run AI — #00 varnish
+ 5% linoleic acid.
C=4356'
C=44
C=45
(δ-c) on logarithmic scale
Age of film in minutes
20
40
1
9
8
7
6
5
4
3
2
1
9
8
7
6
5
4
3
2
1

Plate V F

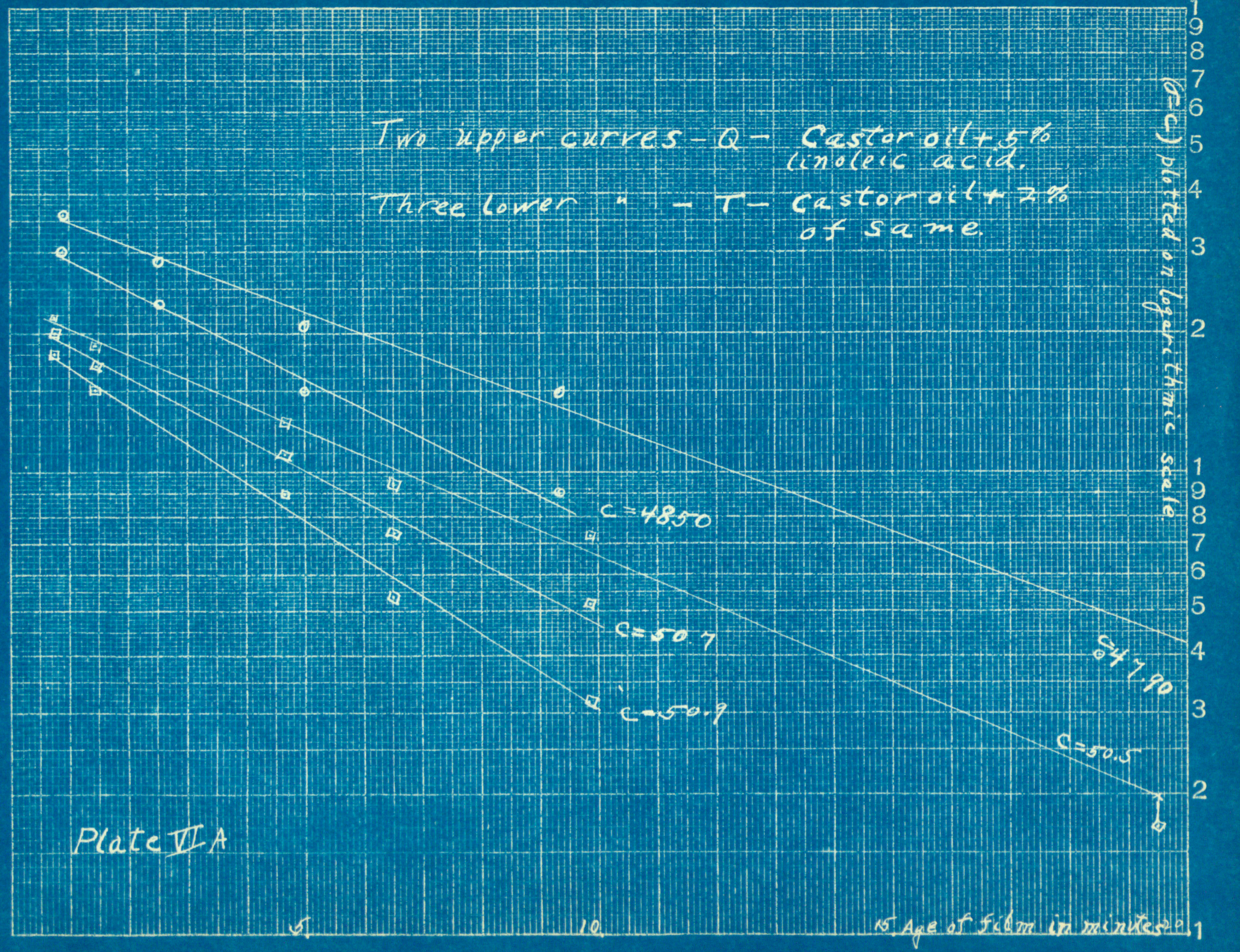

Two upper curves - Q - Castor oil + 5% linoleic acid.
Three lower " - T - Castor oil + 2% of same.
(σ−C) plotted on logarithmic scale
Age of film in minutes
5
10
15
20
1
2
3
4
5
6
7
8
9
C=48.50
C=50.7
C=50.9
C=47.90
C=50.5

Plate VI A

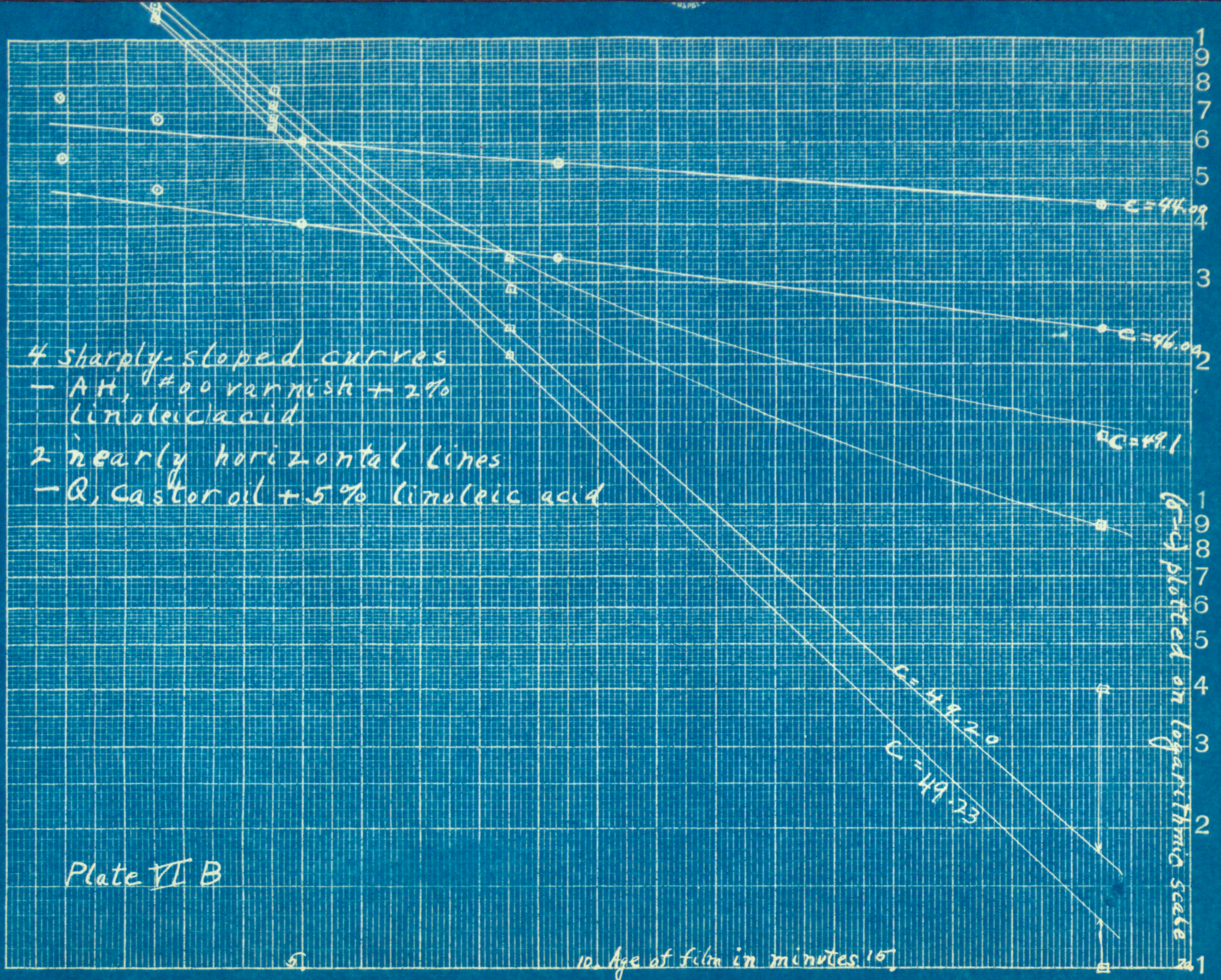

c = 44.09
c = 46.09
c = 49.1
c = 49.20
c = 49.23
4 sharply-sloped curves
— AH, #00 varnish + 2% linoleic acid.
2 nearly horizontal lines
— Q, Castor oil + 5% linoleic acid.
(σ-c) plotted on logarithmic scale
1
9
8
7
6
5
4
3
2
1
9
8
7
6
5
4
3
2
1
5
10
Age of film in minutes
15
20

Plate VI B

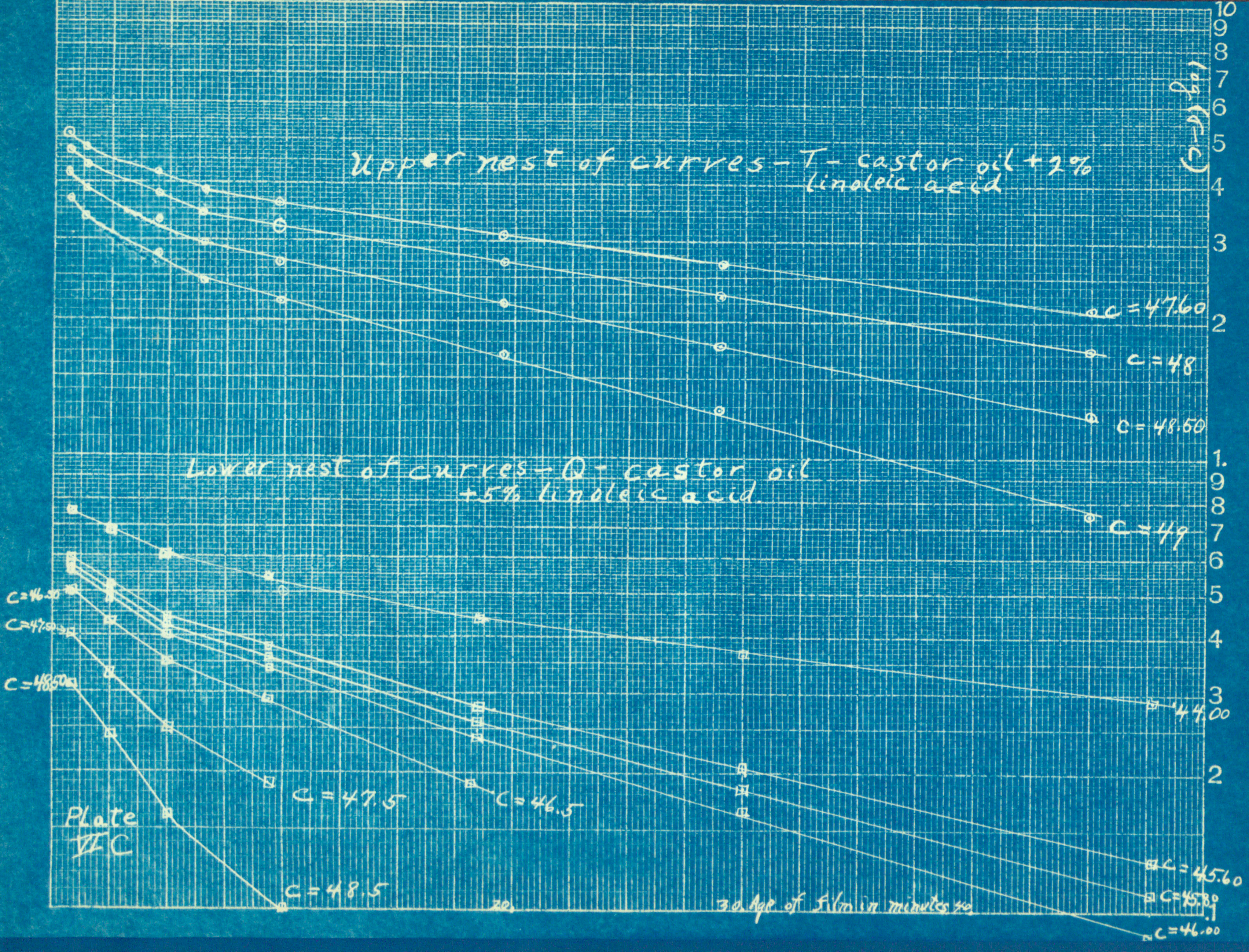
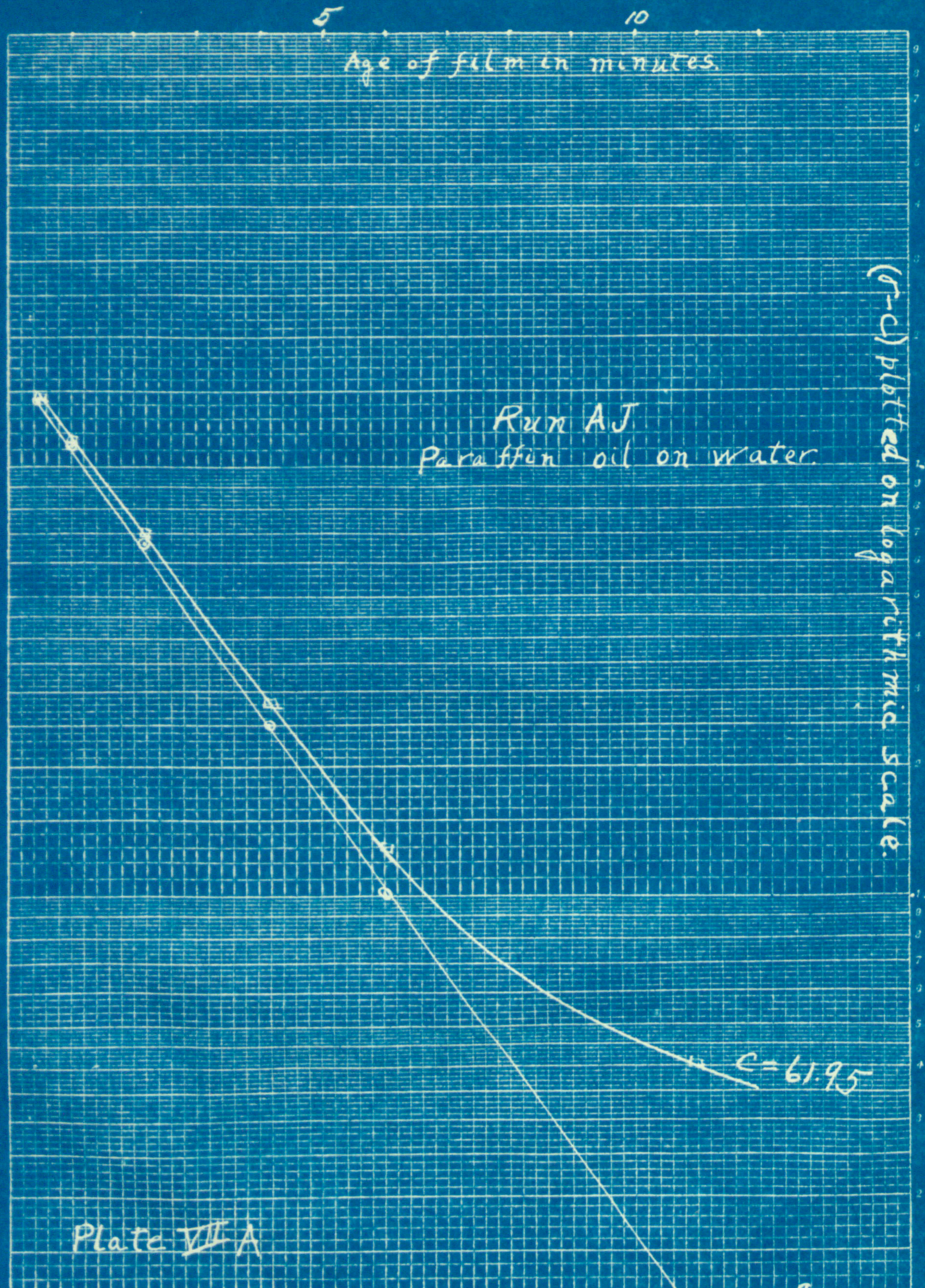


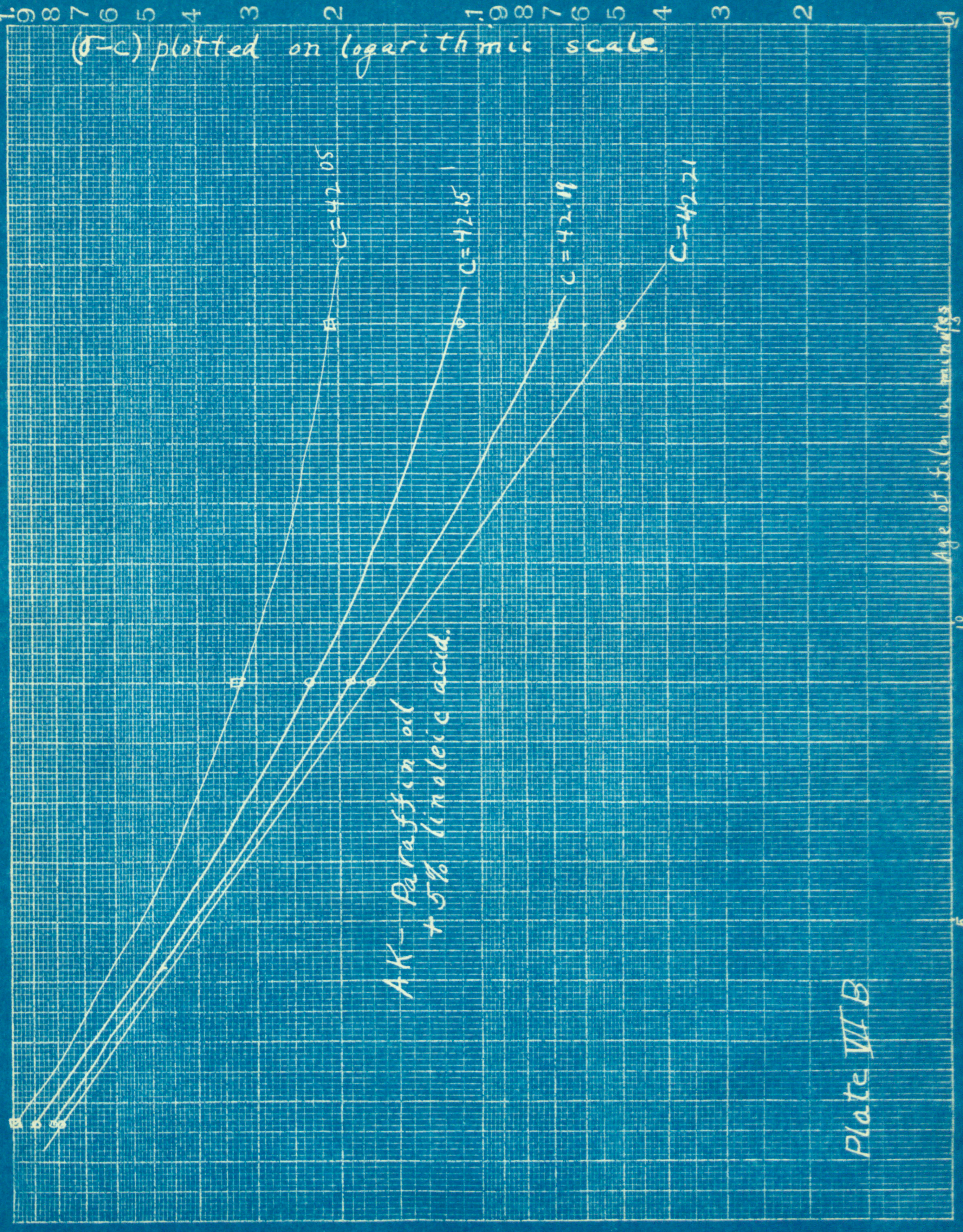
Plate VI C

log (σ−C)
10
9
8
7
6
5
4
3
2
1.
9
8
7
6
5
4
3
2
.1
Upper nest of curves – T – castor oil + 2% linoleic acid
C = 47.60
C = 48
C = 48.60
C = 49
Lower nest of curves – Q – castor oil + 5% linoleic acid
C = 46.50
C = 47.50
C = 48.50
44.00
C = 47.5
C = 46.5
C = 48.5
C = 45.60
C = 45.80
C = 46.00
20.
30. Age of film in minutes 40.



Run AJ
Paraffin oil on water.

Plate VII A



(σ-c) plotted on logarithmic scale.

Plate VII B

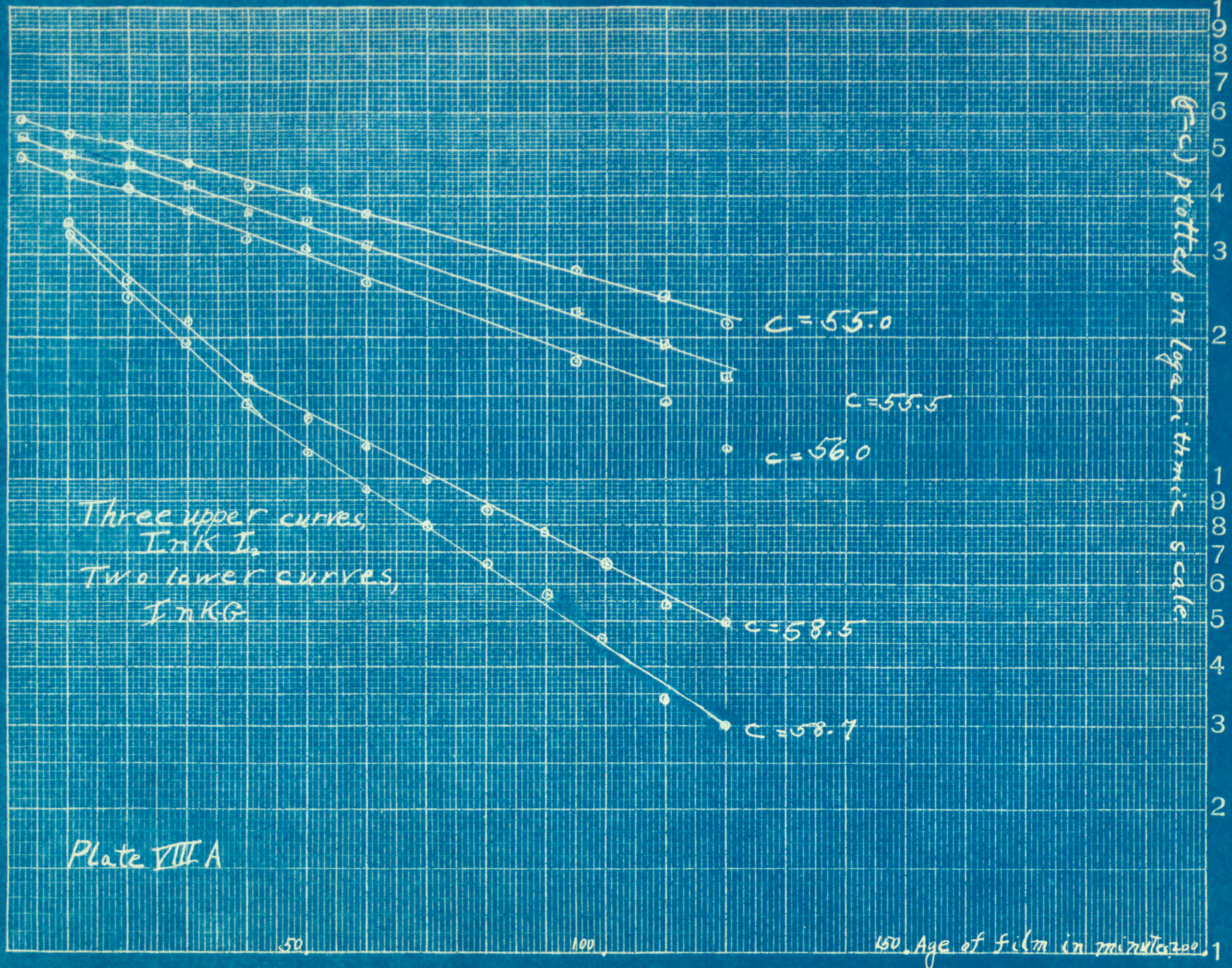

(σ-c) plotted on logarithmic scale.
1
9
8
7
6
5
4
3
2
1
9
8
7
6
5
4
3
2
1
C = 55.0
C = 55.5
C = 56.0
C = 58.5
C = 58.7
Three upper curves, Ink I.
Two lower curves, Ink G.
50
100
150
Age of film in minutes
200

Plate VIII A

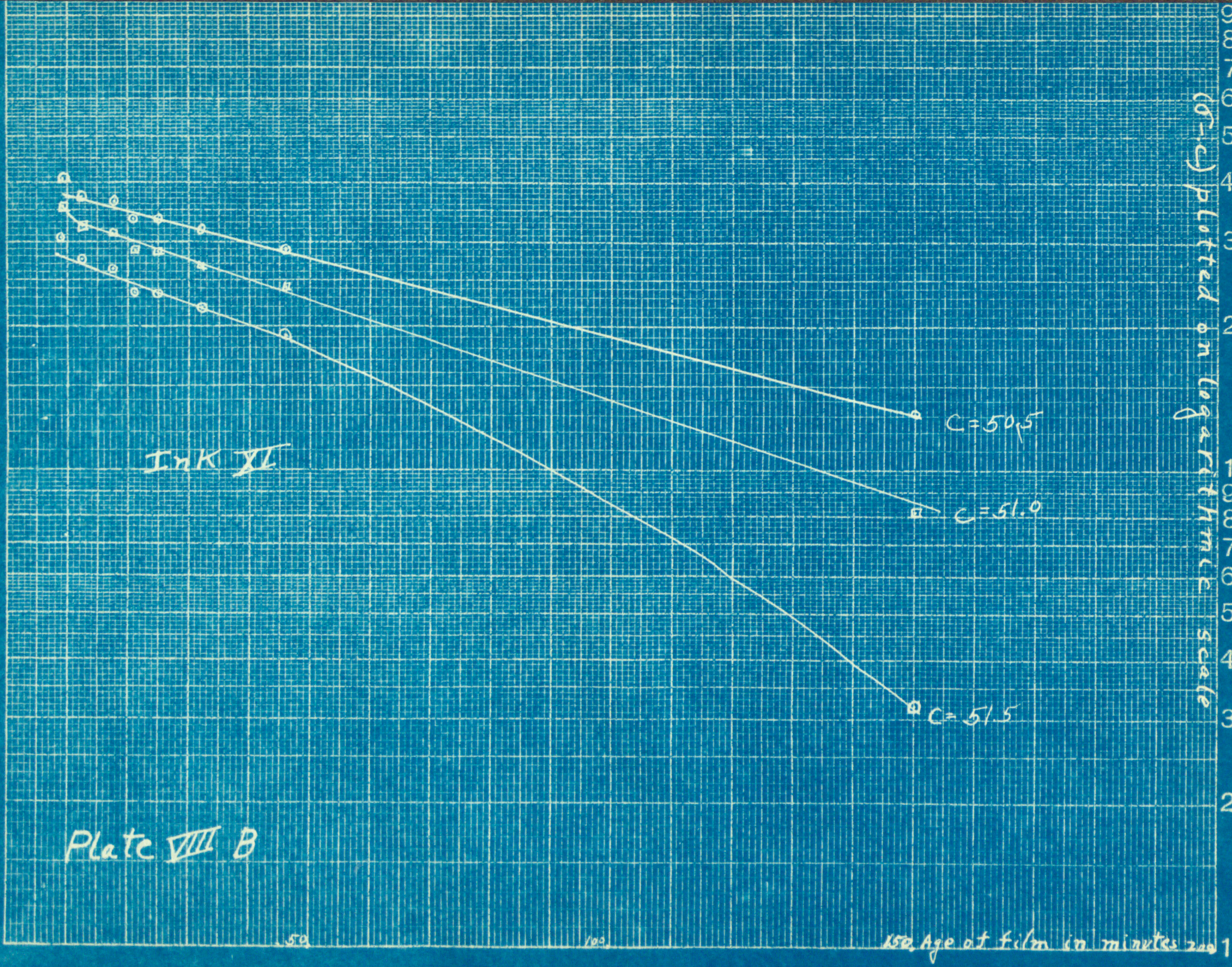
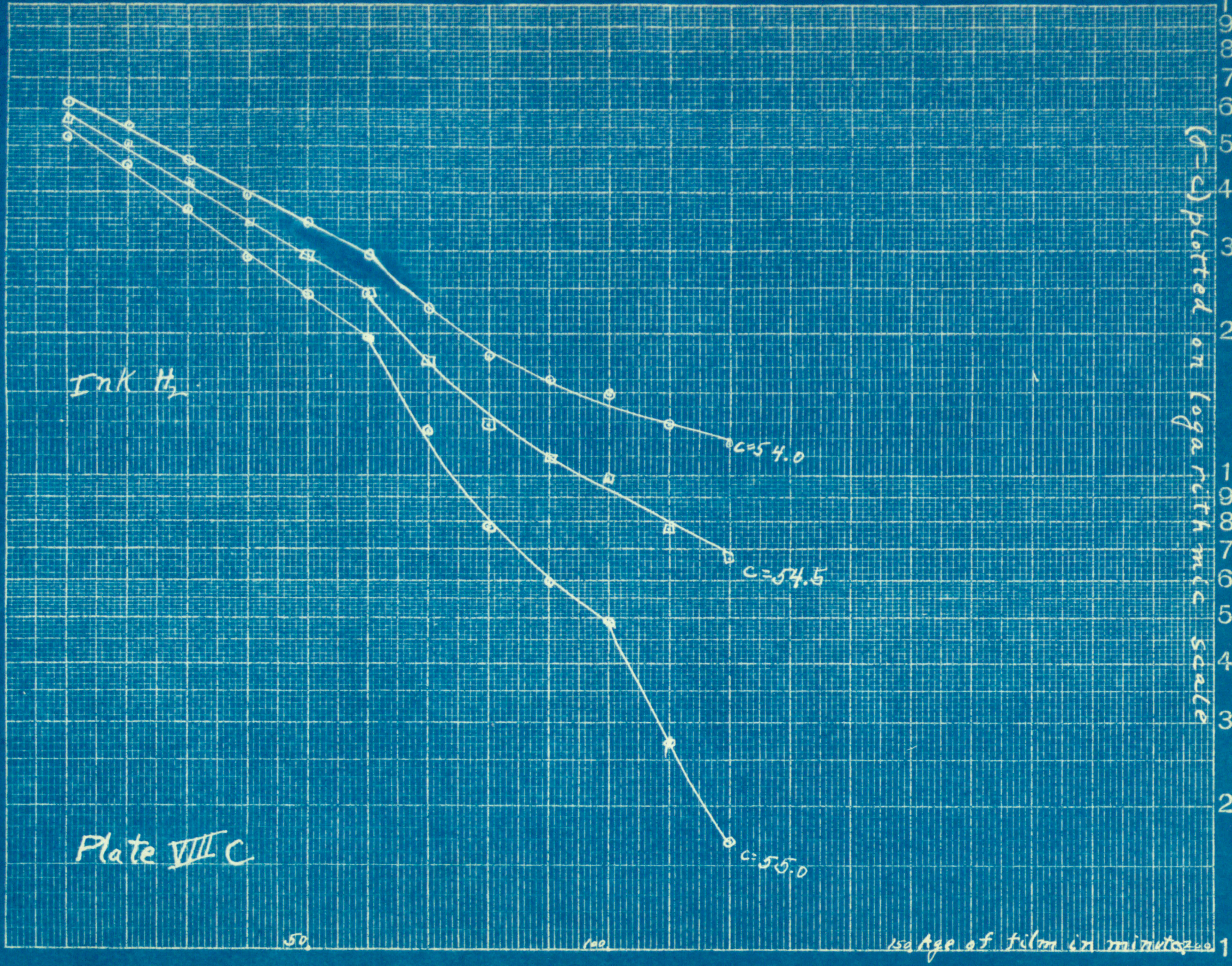

(σ-c) plotted on logarithmic scale
9
8
7
6
5
4
3
2
1
9
8
7
6
5
4
3
2
1
C=50.5
C=51.0
C=51.5
Ink VI
50
100
150
Age of film in minutes
200

Plate VIII B


(δ-c) plotted on logarithmic scale
Ink H_2
c=54.0
c=54.5
c:55.0
Plate VIII C
50.
100.
150 Age of film in minutes 200
1
9
8
7
6
5
4
3
2
1
9
8
7
6
5
4
3
2
1

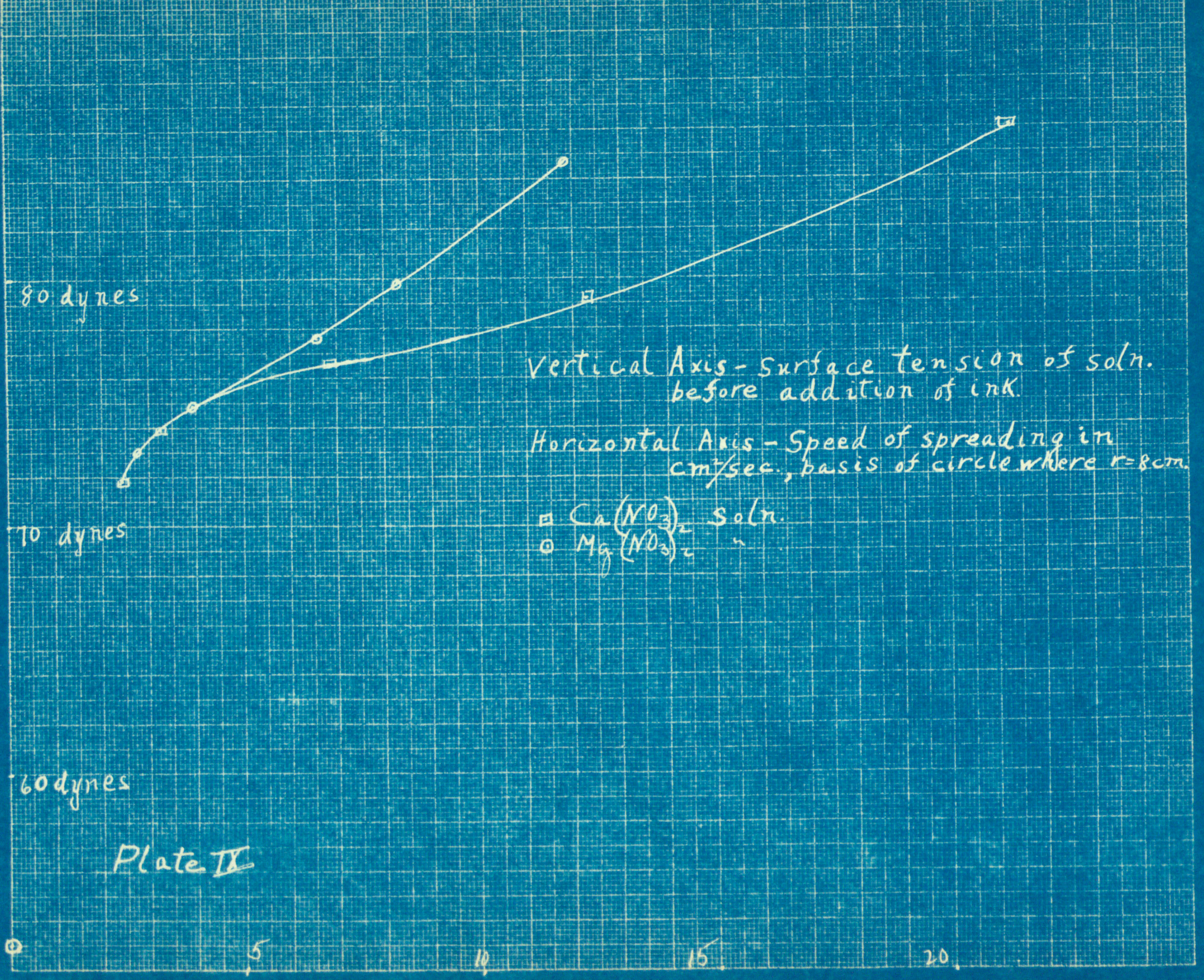

80 dynes
70 dynes
60 dynes
Vertical Axis - Surface tension of soln. before addition of ink.
Horizontal Axis - Speed of spreading in cm/sec., basis of circle where r=8cm.
□ Ca(NO3)2 soln.
○ Mg(NO3)2 "
0
5
10
15
20

Plate IX