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UMI

FACTORS WHICH INFLUENCE THE DRYING RATE OF CERTAIN LITHOGRAPHIC INKS

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PREFACE

The rate of drying of lithographic ink depends on the composite effect of several factors on the drying process. Certain factors are connected with the formulation of the ink; namely, pigment, varnish, and drier. Others depend upon conditions under which the ink is used: concentration of drier, relative humidity, nature of the paper surface to be printed, temperature, pH value of the fountain solution, and the amount of moisture in the ink and paper.

On the basis of preliminary studies the most important of the drying factors for a given ink appear to be as follows:

1. Concentration of drier in ink
2. Nature of paper to be printed
3. Relative humidity.

The technical literature contains conflicting data with regard to the drying of ink because previous investigations have been handicapped by lack of a satisfactory method for determining the drying time of ink. Therefore, a device has been constructed which may be used for this purpose. Also a method has been developed by means of which the effect of one variable on drying may be investigated while others are held constant.

Using these methods the relation between drying

rate and the important lithographic variables has been determined for several experimental and commercial inks.

In addition the gain in weight of pigmented and unpigmented varnishes during drying has been investigated in order to learn more about the role of oxidation in the drying of inks and varnishes.

INTRODUCTION

It is well known that the drying of inks is influenced to a large extent by the kind of varnish and pigment in the ink.

Varnishes prepared from different drying oils and by different methods have widely different drying properties. At one time the rate of drying was thought to depend almost entirely upon the degree of unsaturation of the varnish. It is now becoming increasingly clear that the type of unsaturated linkages and the positions of the double bonds in the drying oil molecule also are important factors controlling drying.

The effect of the pigment on drying appears to depend upon two important characteristics: the chemical nature of the pigment and the amount of surface area possessed by the pigment particles.

Krumbhaar[1] has shown that some pigments are able to react with free fatty acids in the varnish forming metallic soaps which may accelerate drying by acting as driers. Also it has been established that certain pigments may act as oxidizing agents by supplying oxygen to the drying oil molecules and thus may take part directly in the drying process.

On the other hand, pigments which possess a very large surface area often are capable of removing driers

from the varnish by adsorption. The drier, in an obscure manner, becomes attached to the pigment surface and its catalytic action usually is reduced or entirely ceases. There is some evidence that adsorption of drier by the pigment accelerates the drying of ink containing alumina[2] but this requires further investigation.

Rhodes and Van Wirt[3] found that pigments adversely affect oxygen absorption by reducing the rate of diffusion of oxygen through the varnish film.

Driers are added to inks to cause drying to occur in a practical length of time. The manner and speed of drying depends on the kind and amount of drier. Certain driers are said to be "surface" driers since they are believed to promote dryihg at the surface of ink films. Others are called "through driers" because they are thought to cause uniform drying throughout the ink film. It is generally agreed that combinations of two or more driers are more effective than a single drier.

The increase in drying rate of ink is not proportional to the amount of drier added but seems to approach a maximum value. The addition of more drier at this point causes little or no increase in drying rate.

The drier concentration necessary for satisfactory drying depends largely upon the conditions connected with the formulation and application of the ink. In the

printing industry there appears to be considerable disagreement as to the proper amount of drier to use in an ink under any given set of conditions.

The application of ink to paper introduces a number of factors which contribute to the complexity of the drying process. Most papers are porous and tend to absorb the varnish from the ink leaving the ink film with a higher concentration of pigment. Absorption combines with oxidation and polymerization to cause more rapid drying than oxidation and polymerization alone.

The extent to which absorption affects drying depends upon the physical characteristics of the paper surface and at present cannot be determined accurately. It is well known, however, that changes in the moisture content of paper cause changes in the physical structure which greatly affect the ink absorptive properties of paper. It is also known that different kinds of paper are not affected to the same extent by changes in moisture content. Since the moisture in paper tends to be in equilibrium with that in the surrounding atmosphere it is evident that relative humidity plays an important part in the drying of lithographic ink.

THEORY

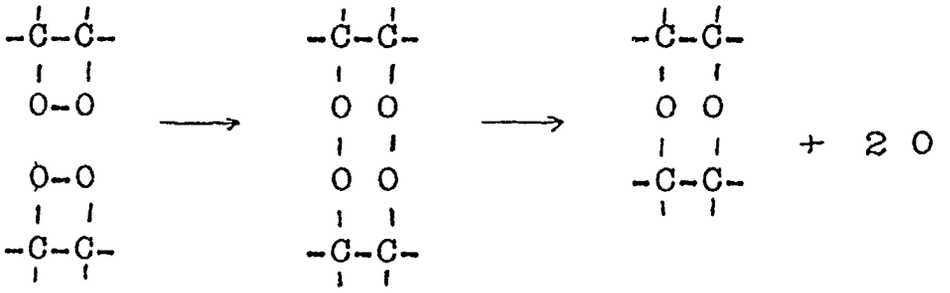
Since lithographic ink is composed of pigment ground in a drying-oil varnish it is evident that the drying of ink consists in the transformation of the varnish from a liquid to a solid state. Although the reactions responsible for this change are not known with certainty a great deal has been learned about the drying process. A detailed discussion of the mechanism of drying is included in the supplement of this thesis, since only a brief review of the reactions involved will be presented here.

The solidification of ink films is the result of two primary processes: oxidation and polymerization.

When ink films are exposed to air oxygen is absorbed at the double bonds in the drying oil molecules. If driers are present the induction period is reduced from several hours to a few minutes. It is generally accepted that driers aid in drying by undergoing reversible valence changes which enable the drier to act as a carrier of oxygen from the atmosphere to the varnish molecules.

The first step in the drying process is the formation of peroxide groups at the double bonds. The existence of peroxides is proved by the release of iodine when a potassium iodide solution is mixed with partially oxidized drying oils. However, attempts to isolate and identify drying oil peroxides have been unsuccessful.

The peroxide groups seem to be able to combine with other peroxidic or unsaturated groups with the release of oxygen. Morrell[4] has proposed the following mechanism:



The oxygen is absorbed at other double bonds and new peroxides are formed which enter into and continue the auto-oxidative process. The reactions between peroxidic groups unite the drying oil molecules and they become increasingly larger in size. Finally when polymerization has reached a certain point coagulation occurs and a gelatinous film is formed.

Ink films on paper dry in a much shorter time than similar films on glass. The decrease in drying time is caused by absorption of the ink vehicle by the paper. Absorption, according to some authorities,[5,6,7] consists in the penetration of varnish between the individual paper fibers and depends upon the physical structure of the surface layer of the paper.

It is not exactly known how absorption affects the drying of ink but it has been suggested that the varnish would be distributed in a thin layer over the surface of the paper fibers and would present a large surface to the air.[8] Oxidation and polymerization might then be expected

to occur rapidly. It is also possible that after the interstices between paper fibers become filled with varnish only a relatively small amount of polymerization results in the formation of a moderately strong gel structure. This might cause the ink film as a whole to appear dry.

The determination of the effect of absorption on drying is very difficult because there is no satisfactory method for evaluating the ink absorptive properties of paper.

It has been shown that during the absorption period the ink vehicle penetrates only a short distance below the paper surface.[9] It is also known that the structure of paper at the surface may be quite different from that in the interior of the sheet because of treatment which the paper receives after the sheet is formed (calendering, coating, etc.). Methods which depend on the measurement of the rate of penetration of air or oil through the paper sheet, therefore, cannot be expected to yield accurate information about surface porosity.

The "ink absorption test" also is used to measure ink penetrability characteristics of paper. However, only relative values are obtained and the method is not very satisfactory.

With an increase in moisture content paper undergoes dimensional changes. The individual paper fibers absorb moisture and swell, the swelling occuring more in the lateral than longitudinal direction. This expansion probably decreases the diameter of the capillary pores and reduces the volume of ink vehicle which the paper can absorb. That is, changes in moisture content cause changes in the absorptive properties of paper.

The effect of moisture on oxidation and polymerization in inks has not been definitely established. Small amounts of moisture have been found to increase the rate of gain in weight of varnish films during drying.[10] Investigations by the Patra group[11] indicate that unpigmented varnishes dry slightly faster in high relative humidities. However, the dried films are somewhat softer than those obtained in lower humidities. A similar investigation by Benemelis has yielded essentially the same results,[12] and the studies are being extended to include inks.

It is difficult by observation to determine which of a number of different kinds of paper possesses the greatest ink absorbency. For example, offset paper which has a comparatively rough and porous surface often is considered to be more absorbent than coated paper which seems to have a hard and impervious surface. Actually, ink drying tests indicate that the opposite is true.

The reason for this is evident from a consideration of the following illustrations.

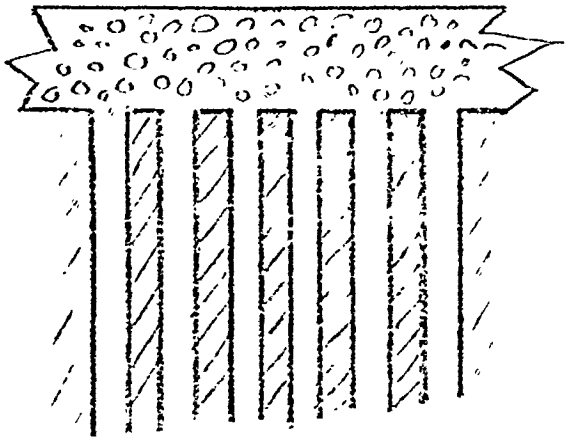


Fig. A

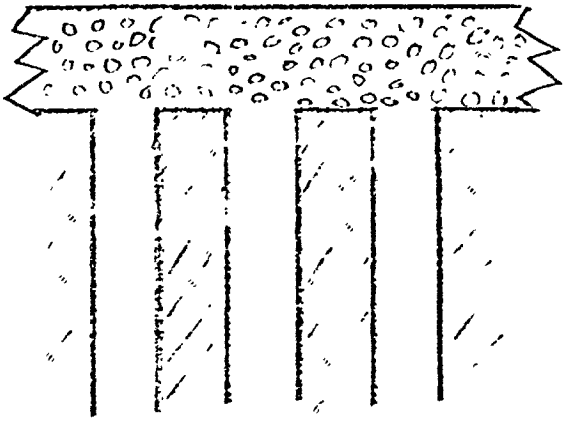


Fig. B

Figures A and B represent cross sections of sheets of coated and offset paper, respectively, to which an ink film has been applied. (It is not meant to infer that the capillary pores in paper are uniformly the same in radius and arrangement. In reality the capillaries run in every direction and are of many different shapes and sizes.

Immediately after printing the force of gravity and surface tension cause the ink vehicle to penetrate the capillary pores of the paper. It can be shown mathematically that in some cases the penetration pressures reach enormous values. The force of gravity is small in proportion to the capillary force and can be neglected. The latter in terms of force units per unit area of capillary

opening is given by the following equation:

$$F = \frac{K}{r}$$

The value of K is constant and depends upon factors connected with the paper and the varnish. Briefly, the equation states that the force tending to cause absorption is inversely proportional to the pore radius. For example, if the pore radius in Figure A is half that in Figure B the penetration force will be twice as great.

The rate of absorption depends on the penetration force, the viscosity of the varnish, the force required to drain part of the varnish from the pigment suspension, the pore capacity of the paper, and perhaps on other factors not known. It follows, therefore, that the greater the penetration force, the more quickly opposing forces will be overcome and the more rapidly absorption will occur. The ink absorptive properties of paper thus depend upon both the relative number and the average radius of the capillary pores.

EXPERIMENTAL PROCEDURE

The work presented here is a continuation of the study of various factors which control the drying rate of lithographic ink.

The results of drying tests previously conducted with a commercial black lithographic ink indicated that it was desirable to learn how the drying of different inks is affected by the following factors:

1. Concentration of drier in the ink
2. Kind of paper printed
3. Relative humidity.

Other factors such as the concentration of acid in the fountain solution and temperature have been shown[8] to affect drying. However, the effect of acids in the fountain solution is negligable when the pH value is above 3.0, as usually is the case in printing. The effect of temperature on drying is better known and usually it is possible to compensate for temperature changes by properly adjusting the drier concentration.

Experimental Method

Several improvements were made in the experimental method previously used in order that more rapid progress could be made in the present investigation.

In earlier work[8] the drying time of ink on paper was determined by drawing the finger across the ink film

and the margin of the paper under moderate pressure. When a smudge of ink could no longer be detected on the margin the ink was considered dry. Since this was a laborious and inaccurate method a "Drying Tester" was designed and constructed by Professor Reed, and was used to determine the drying times of the inks in this work.

The Drying Tester consists essentially of an endless belt propelled at a constant rate over a horizontal platform by a suitable driving mechanism. Above the platform is a device which periodically raises and drops eight plungers to which 100-gram weights are attached.

In practice strips of printed paper are mounted on a glass plate, the glass plate is placed on the platform, and clean strips of paper are suspended slightly above the ink films. The belt carries both the printed strips and the clean strips forward and the plungers periodically force a contact between the clean paper strips and the ink films. The ink film is considered to be dry when the ink no longer transfers to the paper strip. The drying time obtained under these conditions corresponds approximately to that obtained by the "rub test" previously employed.

Humidity Control

A small cabinet was constructed to fit over the Drying-Time Tester. A means was provided for raising and

lowering the cabinet to make the machine easily accessible. The seams of the cabinet were sealed with beeswax and the lower edges were fitted with a sponge-rubber gasket. Glycerine was used to seal the gasket to the table top on which the Drying Tester was placed. Circulation of air in the cabinet was effected by a fan driven by an electric motor mounted outside. The desired relative humidities were maintained by placing trays containing suitable aqueous solutions in the cabinet. The solutions used to obtain different relative humidities were as follows:

Solution	Relative Humidity (Calculated from wet and dry bulb temperatures inside cabinet) Dry bulb temperature = 83° F.
1. Potassium acetate (sat. soln.)	29 %
2. Potassium carbonate (sat. soln.)	44 %
3. Glycerine (20° Bé soln.)	69 %
4. Ammonium sulfate (sat. soln.)	81 %
5. Water	92-95 %

Usually the relative humidity became approximately constant in about 30 minutes.

Temperature Control

During the early part of the work the temperature was maintained at approximately 83° F. by heat from two 60-watt bulbs in series with a bimetallic thermostat. Later

it was found necessary to make certain changes which provided more accurate te perature control. The bulbs were replaced by several feet of Chromel A metal ribbon which was fastened around the inside of the cabinet. A mercury thermoregulator was installed which acted through a relay to control the current through the heating element. In this way temperature variations were reduced from a few degrees to a fraction of a degree.

Inks Tested

Both experimental and commercial inks were used in this work. However, the drying characteristics of commercial and experimental inks containing the same pigment often were quite different and more emphasis was placed on the study of the drying of commercial ink.

The commercial inks were furnished by the Sinclair and Valentine Company. The experimental inks were prepared by grinding different pigments with #00 varnish on a three-roll laboratory mill.

Driers Used in Inks

Three kinds of driers were used in the inks. In most cases the kind of drier was the same as that used in the ink in commercial practice so that the results would be of practical as well as theoretical value. The drier compounds were quantitatively analyzed to determine the concentration of drier metals present, and analytical data on

their composition is given in the following table:

	Drier	Drier Metal Content
1.	Lead-manganese naphthenate	13.1% Pb, 2.6% Mn
2.	Lead-manganese commercial paste	20.1% Pb, 0.75% Mn
3.	Cobalt naphthenate	6.0 % Co.

Paper Used in Drying Tests

Four different kinds of commercial lithographic papers were used for the drying tests: offset, bond, super calendered, and coated. The ink was applied to the felt side of the first three papers.

Method Used to Obtain Prints

A known volume of ink was rolled out with an ink roller on a stencil having a rectangular opening 8 x 11 inches beneath which was placed a smooth aluminum plate. The plate was transferred to the bed of a small offset proving press, covered with strips of paper to be printed, and rolled several times with the blanket roller. This procedure gave uniform results and eliminated a source of error which was noted in drying time measurements when the offset printing method was employed; namely, absorption of varnish from the ink by the blanket.

Determination of Drying Time

The printed strips were removed from the plate, cut into narrower strips if desired, and placed in the Drying-

Time Tester. For most of the work two-inch strips of four different kinds of paper were printed simultaneously. This procedure yielded eight one-inch strips and made it possible to run duplicate tests on each kind of paper.

After the printed strips were mounted in the machine and the starting positions marked on the transfer strips the cabinet was lowered into place. The driving motor was started and the fan was connected and placed in operation. At the end of the run the fan was disconnected, the cabinet was raised, the final position of the strips was marked, and the driving motor was stopped.

The drying time was taken as the time elapsed when complete set-off dots could no longer be detected on the transfer strips. This was determined as follows: the total distance traveled by the strips divided by the time of travel gave the speed. The speed divided into the distance from the starting point to the "dry" point gave the time required for the inks to dry after the test was started. This time plus the time elapsed between printing and starting the test gave the drying time of the ink.

Thickness of Ink Films

In actual practice ink films printed by the offset lithographic method probably range in thickness from two to five microns. In this investigation the thickness of the ink films was approximately 4.0 microns except in cases

where the effect of film thickness on drying time was being studied.

The method used to obtain ink films having a desired film thickness was as follows:

A known volume of ink was rolled out on the plate and stencil. A sheet of paper was weighed, printed, and re-weighed to determine the weight of ink transferred to the paper. The weight of ink divided by the density gave the volume of ink, and this quantity divided by the area of the ink film gave the film thickness.

Knowing the film thickness obtained with the original volume of ink it was possible to calculate by direct proportionality the approximate volume of ink required to give any desired film thickness.

The printing process was then repeated using the newly calculated volume of ink and the film thickness was again determined. If this value failed to fall within the desired range a second approximation was made as before using the ratio of the new volume of ink and the corresponding film thickness to determine the volume necessary for the desired film thickness. Usually two approximations were necessary to arrive at the proper volume of ink to use.

PRELIMINARY WORK

Because the Drying-Time Tester had not been used previously in this laboratory it was essential to investigate its characteristics to provide a firm basis for further work. For this investigation four experimental inks were prepared by grinding each of the following pigments with #00 varnish on a three-roll mill: Milori Blue, Medium Chrome Yellow, Alumina Hydrate, and Lithol Rubine B Toner.

The composition of the experimental inks was as follows:

Milori Blue Ink	
#00 Varnish	52.5%
Milori Blue	47.5%
	100.0

Medium Chrome Yellow	
#00 Varnish	22.0%
Med. Chrome Yellow	78.0%
	100.0

Lithol Rubine B Toner	
#00 Varnish	42.8%
Lithol Rubine B	57.2%
	100.0

Alumina Hydrate	
#00 Varnish	50.0%
Alumina Hydrate	50.0%
	100.0

The Alumina Hydrate ink was so transparent it was difficult to judge the end point in the drying tests. On the basis of work reported in the supplement of this thesis, where it is shown that a small addition of Toluidine Red pigment does not noticeably affect the drying of #00 varnish, it was considered permissable to add to the ink 2.0 per cent of Toluidine Red ink. With this change the set-off

track on the transfer strips became very distinct.

The Alumina Hydrate ink tested then had the following composition:

#00 Varnish	50.2%
Alumina Hydrate	49.0%
Toluidine Red Pigment	0.8%
	100.0

Inks of different drier concentrations were prepared by thoroughly mixing weighed amounts of drier with weighed amounts of ink. A mixture of lead and manganese naphthenates (13.1% Pb, 2.6% Mn) was used as the drier. The inks were printed on the felt side of offset paper.

The drying times of the four experimental inks, each containing different amounts of the drier mixture, were determined with the Drying Tester. The temperature during most of the time was about 83° F. and the relative humidity was approximately 44 per cent. The results are given in Table 1 and Figure 1.

Certain irregularities were noted in some of the drying time curves which appear to result from variations in conditions under which drying tests were being conducted. For example, in Figure 1 it is seen that Milori Blue ink containing 0.5 per cent of drier requires more than 12 hours to dry, while the same ink with no drier and with 1.0 per cent of drier dries in about 8.5 hours.

After considerable investigation it was discovered

that temperature variations during the tests were responsible for at least part of the discrepancies in drying times.

The method of temperature control was improved as previously described and the precision of drying time determinations was then found to improve.

Determination of Accuracy of Drying Time Determinations

Before proceeding with further studies it was considered advisable to determine the accuracy with which the drying time of an ink could be determined with the Drying Tester. For this work experimental Lithol Rubine B Toner ink containing 6.0 per cent of the lead-manganese naphthenate mixture was used. The drying time of the ink on offset paper was determined on ten different occasions. The relative humidity was 44 per cent and the temperature was 84° F. Every effort was made to control printing and drying conditions so that the only variations in drying times would be those resulting from experimental error in the drying time determination.

The results and the statistical analysis of the results are given in Table 2.

Several other factors which possibly might affect the accuracy of drying time determinations also were investigated.

The temperature and relative humidity were the same as in the previous experiment. Likewise, the same ink and paper were used.

Effect of Thickness of Ink Films on Drying Time

Ink films ranging in thickness from 3.1 to 5.7 microns were printed and the drying times of the ink were determined. The results are given in Table 3.

Variations in Drying Found on Consecutive Sheets of Same Kind of Paper

Four consecutive sheets of paper were selected from the paper pile, cut into two-inch strips, and the strips were then printed from the same inked plate. The drying times of the ink on the different paper strips are given in Table 4.

Effect of Differences in Moisture Content of Paper at Time of Printing on Drying

A sheet of paper was cut into three strips. One strip was suspended over water in a closed jar, another was placed in a desiccator containing calcium chloride, and the third was suspended before an electric fan in the laboratory. After two hours the three strips were printed from the same plate and the drying times of the ink were determined. The results are given in Table 5.

The remainder of the time was devoted to determining the effect of relative humidity on the drying of inks containing different amounts of drier.

The inks included in this study and the driers

used in the inks were as follows:

	Ink	Drier Used in Ink
1.	Experimental Lithol Rubine B Toner	Pb-Mn Naphthenate
2.	Commercial Chrome Yellow	Pb-Mn Naphthenate
3.	Commercial Chrome Yellow	Pb-Mn Commercial Paste
4.	Commercial Milori Blue	Pb-Mn Naphthenate
5.	Commercial Black	Co Naphthenate
6.	Commercial Conc. Violet Toner (phosphotungstic lake of methyl violet)	Co Naphthenate

The results are given in Tables 6, 7, 8, 9, 10, and 11, and in Figures 2, 3, 4, 5, 6, and 7.

DISCUSSION

The Drying Tester appears to provide a satisfactory means for determining the drying time of lithographic ink.

Although the maximum deviation from the probable drying time was about 24.1 per cent, the average deviation was only about 9.0 per cent. The reason for the high maximum deviation is not evident. It may have been caused by variation in some factor which was not taken into account and which therefore was not rigidly controlled.

The mean deviation of the average of ten independent determinations was only 3.0 per cent. Hence, it is apparent that to accurately determine the drying time of an ink several independent drying tests must be run and the results averaged.

During the present work there was not sufficient time to determine the exact drying time of each ink drier combination on different papers at different relative humidities. In order that this investigation could be extended to include as many inks as possible the following procedure was adopted:

Drying time determinations were made for each ink varying the amount of drier, the type of paper, and the relative humidity. In cases where the results of a particular determination were not consistent with the bulk of the

collected data an additional test was run in order to obtain a more representative value. In this way the maximum deviation probably was reduced to about 10 per cent. The differences in measured drying times caused by experimental errors in the drying time determination were found to be very small in proportion to the differences caused by differences in relative humidity and drier concentration.

Observations A, D, and G in Table 2 differ considerably from the average and probably may be discarded. If this is done the maximum deviation is reduced to less than 6.0 per cent. It is believed that this value indicates the precision which probably could be achieved by further improvements in the control of printing and drying conditions.

Ink films ranging in thickness from 3.1 to 5.7 microns were found to dry in very nearly the same length of time. Since ink films in commercial practice probably come within this range, it is probable that only slight variations in drying time are caused by differences in film thickness.

Likewise variations in the drying time of ink on different sheets of the same kind of paper appear to be negligable.

The results in Table 5 show that the moisture contents of the three papers at the time of printing had little effect on drying when the papers were allowed to come to

equilibrium with the same atmosphere soon after printing. It may be concluded, therefore, that the drying of the inks was not appreciably affected by the relative humidity in the laboratory during the short time the ink films were being prepared for the drying tests.

Relative humidity exerted a great influence on the drying time of the lithographic inks tested. In general an increase in relative humidity caused an increase in the drying time but there were several exceptions to this depending upon the nature of the ink, the drier concentration, and the kind of paper printed. For example, the drying rate of Chrome Yellow ink with commercial paste drier on each kind of paper increased with relative humidity up to 80 per cent. On bond and coated paper the rate continued to increase with relative humidity, but on super-calendered and offset paper the increase in drying rate was observed only when the ink contained more than 2.0 per cent of drier. With less drier the drying rate sharply decreased.

It is seen that the drying curves for Chrome Yellow ink containing naphthenate driers are quite different from the curves for the same ink with paste drier. Naphthenate driers contain a large proportion of hydrocarbon solvent which dilutes the ink vehicle and reduces the viscosity of the varnish. This results in a change in the rate of absorption of varnish by the paper and consequently affects the drying time of the ink.

The drying of the Black and Milori Blue inks was greatly retarded at high humidities. It is evident that above 80 per cent relative humidity satisfactory drying could not be obtained merely by increasing the drier concentration. Under such conditions in practice it would appear advisable to postpone printing of these inks until the relative humidity falls below 70 per cent.

It will be noted in Table 1 that the experimental Milori Blue ink without drier required less than ten hours to dry while in Table 9 it is seen that commercial Milori Blue containing 3.0 per cent of drier did not dry in 24 hours. The difference in drying times probably is caused by the presence in the commercial ink of non-drying materials such as grease and wax which are added to improve the working qualities of the ink.

The minimum drier concentrations required for satisfactory drying of the inks on different kinds of paper and in different relative humidities are given in Table 12. It is evident that the amount of drier depends upon the kind of ink and drier and upon the conditions under which the ink is to be used. For practical reasons, therefore, it would be worthwhile to investigate the drying of all inks of importance in commercial printing.

It will be observed that although the drying rate of each ink was different for different papers, in each case the order in which drying occurred with respect to

paper was: coated, bond, offset, super-calendered. While the drying rate of ink on coated papers has been found to depend upon the pH value and the porosity of the coating, little is known about the factors which control the drying rate on uncoated paper except that this quantity is closely connected with the degree of surface porosity of the paper. It is conceivable that the drying of ink also may be affected by materials present in paper. This might explain why drying was more rapid on the bond than on the offset paper in these tests, since bond is generally considered to be relatively less porous than offset paper.

Attempts to devise a method to evaluate the surface porosity characteristics of paper so far have not been successful and it has been shown that porosity values as determined for the entire thickness of the sheet are not directly related to the drying rate of ink on the paper surface. During drying the ink vehicle is known to penetrate only a short distance into the paper, and since the porosity of paper near the surface also is known to be quite different from that in the interior of the sheet it is evident that close correlation between "through" porosity and rate of drying of ink cannot be expected.

The results of this investigation indicate the extent to which several operating factors affect the drying of lithographic ink. However, the manner in which these factors influence the chemical and colloidal processes of

drying still is not fully understood.

It is well known that penetration of the ink vehicle is slower at high relative humidities and therefore it would seem logical to expect that drying also would be slower. This was found to be true for all inks tested except Chrome Yellow, in which case the drying rate was found to increase with relative humidity up to 80 per cent on all papers and up to 95 per cent on bond and coated papers, the increase being more pronounced when the drier concentration was below 2.0 per cent. These results cannot yet be explained satisfactorily. It would appear that oxidation and polymerization drying of Chrome Yellow ink is accelerated with an increase in relative humidity, the extent of acceleration being more than sufficient to overcome the adverse effect of an increase in relative humidity on penetration drying. On the other hand the drying rate of Black ink is so reduced above 80 per cent relative humidity that oxidation and polymerization as well as absorption must be considered to be greatly retarded.

Obviously in order to gain a clear understanding of the mechanism of the drying of inks as affected by changes in relative humidity it will be necessary to distinguish between the effect of this variable upon oxidation and polymerization and upon absorption in relation to drying. Therefore experiments are being undertaken to determine the effect of relative humidity on the drying of films of

various inks on glass where absorption will not be a factor. From a comparison of these results and the results of drying tests on paper it should be possible to arrive at more definite conclusions with regard to the effect of relative humidity on the primary drying processes.

The relation between absorption and the reactions of oxidation and polymerization also require clarification. It is generally believed that the drying of ink is accelerated by the increase in pigment concentration which results when the ink vehicle is absorbed by the paper. The pigment particles become closely packed together and it is thought that only a relatively small amount of oxidation and polymerization is required to cause gelation of the ink film. Therefore, it is evident that the effect of pigment concentration on the drying of inks should be investigated.

It is possible that with pigments which promote drying the effect of increasing the concentration of pigment is to accelerate drying; while with pigments which tend to inhibit drying the effect is to retard drying.

CONCLUSIONS

From the results of this work the following conclusions may be drawn with respect to the applications of the Drying Tester:

1. The drying time of lithographic ink can be determined conveniently by means of the Drying Tester. With the methods used to control printing and drying conditions in this investigation, the average deviation of a single observation from the probable drying time was about 9 per cent. The maximum deviation was about 24 per cent and the mean deviation was approximately 3 per cent. In view of the high maximum deviation it is probable that opportunity remains for improvement in the accuracy of drying time determinations.

2. Ink films ranging in thickness from 3.1 to 5.7 microns appear to dry in approximately the same time.

3. The relative humidity of the atmosphere in which the test papers are printed has no appreciable effect on the drying time as determined in the controlled atmosphere of the testing instrument.

With regard to the drying characteristics of the inks studied in connection with this work, the following

conclusions can be drawn:

4. The nature of the paper is a very important factor and relatively large differences in drying rate can be expected on different papers even of the same type. In the case of coated papers the differences have been related to pH value and porosity of the coating. In the case of uncoated papers, however, there is as yet no satisfactory explanation for the differences found.

5. The concentration of drier, as was expected, is of primary importance. In each case except one (Chrome Yellow ink with naphthenate drier) the drying rate increases with increase in drier concentration to a maximum value. The rate of increase in the drying rate, however, is different for different inks and also depends upon the paper, the relative humidity, and the nature of the drier.

6. Relative humidity had a very pronounced effect on drying of the inks. Different inks were affected differently by changes in relative humidity and the same ink may be affected differently in this respect when applied to different types of paper.

The following specific conclusions can be drawn with regard to the particular inks studied:

Experimental Ink from Lithol Rubine B Toner

7. The drying rate of the experimental ink made with Lithol Rubine B Toner was not appreciably affected by relative humidity below 80 per cent, but above this value the drying was retarded when the drier concentration was below 3.0 per cent, the effect being more pronounced on offset and super-calendered papers.

8. The drying rate of the experimental ink made with Lithol Rubine B Toner increased with the concentration of lead-manganese naphthenate drier up to 6.0 per cent, where it appeared to approach a maximum.

Commercial Chrome Yellow Ink

9. The drying rate of commercial Chrome Yellow ink approached a maximum when the concentration of commercial lead-manganese paste drier was about 4.0 per cent.

10. The drying rate of Chrome Yellow ink containing commercial paste drier increased slightly with relative humidity up to 80 per cent. On bond and coated papers the rate continued to increase with relative humidities above 80 per cent, but on offset and super-calendered papers the increase occurred only when the drier concentration exceeded 2.0 per cent. With less drier the rate sharply decreased.

11. The drying of Chrome Yellow ink containing lead-manganese naphthenate drier was quite different from the drying of the same ink containing commercial lead-man-

ganese paste drier. On coated and bond paper the rate of drying of Chrome Yellow ink containing naphthenate drier decreased with increasing drier concentration. On super-calendered and offset papers the drying rate also decreased at low humidities but increased at high humidities. The reason for the reversal in drying rate in the latter case is not known.

Naphthenate driers contain an appreciable amount of non-drying materials (high boiling solvents), and since Chrome Yellow inks contain relatively small proportions of varnish, the addition of naphthenate driers tends to reduce the varnish viscosity and thus to promote excessive absorption of the varnish by the paper. Also, the non-drying materials seem to retard oxidation and polymerization of the ink vehicle, or to so plasticize the oxidized and polymerized film that it never attains the condition of complete dryness.

Commercial Milori Blue Ink

12. The drying rate of Milori Blue ink appeared to approach a maximum when the concentration of lead-manganese naphthenate drier was about 6.0 per cent. When the drier concentration was below 3.0 per cent, satisfactory drying could not be obtained even at 43 per cent relative humidity.

13. The drying of Milori Blue ink was adversely affected by relative humidities exceeding 60 per cent. In

the neighborhood of 90 per cent relative humidity satisfactory drying was achieved only on coated paper and it is probable that this is true only for certain types of coated paper.

Commercial Offset Black Ink

14. The maximum drying rate of the Black ink occurred when the concentration of cobalt naphthenate was about 8.0 per cent.

15. Drying of the Black ink was greatly retarded by high relative humidity. On coated paper the extent of retardation became appreciable only when the drier concentration was below 5.0 per cent, but on offset, bond, and super-calendered papers the drying rate sharply decreased with an increase in relative humidity, regardless of drier concentration.

Commercial Concentrated Violet Toner

16. The drying rate of concentrated Violet Toner ink approached a maximum when the concentration of cobalt naphthenate reached about 6.0 per cent.

17. The drying rate of concentrated Violet Toner ink containing 6.0 per cent of cobalt naphthenate did not change appreciably until the relative humidity exceeded 80 per cent; then it decreased rapidly. When the drier concentration was below 6.0 per cent, the drying rate decreased continuously with increase in relative humidity, and above

80 per cent satisfactory drying could not be obtained.

It has been pointed out that the present investigation permits only a few general conclusions with regard to the factors governing the drying of lithographic ink. It has been shown that rate of drying depends upon the concentration of drier, the paper, and the relative humidity of the atmosphere in which drying takes place, and it is likely to be widely different for inks containing different pigments. Therefore, to obtain a satisfactory understanding of the drying of inks in general and its relation to ink composition and other variables in the art of printing, it will be necessary to investigate the drying characteristics which are imparted to inks by each of the lithographic pigments used.

Suggestions for Future Work

It has been shown that the drying rate of ink depends largely upon the nature of the paper to which the ink is applied. Benemelis[12] has found wide differences in the drying of ink on different kinds of coated paper and it is probable that similar differences exist in the drying of ink on different kinds of offset, bond, and super-calendered papers. It, therefore, would be worthwhile to determine further the drying characteristics of inks on different papers of the same type.

It is well known that certain combinations of

drier metals are more effective than single drier metals. Practical experience has shown that combinations of lead and manganese cause faster drying than either alone and preliminary studies indicate that a definite ratio exists for lead and manganese which for any given total metal concentration produces the fastest drying in inks and varnishes. Undoubtedly this also is true for other combinations of drier metals. Hence the most effective drier metal ratios should be determined for various drier combinations: lead-manganese, lead-cobalt, manganese-cobalt, and cobalt-manganese-lead.

A wide variety of different drier compounds is used in inks: tungates, linoleates, resinates, stearates, borates, naphthenates, etc. Investigations in the field of paints and varnishes have been undertaken to determine the relative efficiencies of each of the drier metals with respect to different organic radicals[13], and the results indicate that the naphthenate driers are the most effective with lead and manganese and the resinates with cobalt. The linoleates and resinates are claimed to have the same drying time with lead and manganese while cobalt is said to be slowest with the naphthenate.

Since ink contains a greater proportion of pigment than paint, and very little, if any, solvent, and also since the drying of ink occurs partly by absorption, it is

doubtful if the results with paints and varnishes apply directly to inks. It has already been shown that lead-manganese naphthenate drier is far less effective as drier for Chrome Yellow ink than commercial paste drier containing lead linoleate and manganese resinate. It is apparent, therefore, that the relative efficiencies of driers with regard to the drying of inks should be further investigated.

In practice inks seldom are used exactly as they are received from the manufacturer. Usually they are modified immediately before use by the addition of extenders and modifiers. Extenders are mixtures of different white pigments (alumina hydrate, zinc oxide, magnesia, titanium dioxide) and drying oil varnishes which are added to reduce the color strength of the ink. Modifiers consist of non-drying oils, waxes, greases, drying oils, drying oil varnishes, etc., which are used singly or together to change ink consistency in order to impart desired working properties to the ink.

Undoubtedly the addition of extenders and modifiers affects the drying of ink. Since their use in inks is so common their effect on drying should be studied.

TABLE 1

EFFECT OF DRIER CONCENTRATION

ON DRYING OF EXPERIMENTAL INKS

Naphthenate Drier Mixture (13.1% Pb, 2.6% Mn)
Temperature - 83° F.
Relative Humidity - 44 per cent

Kind of Ink \ Per Cent Drier in Ink	0.0	0.2	0.5	1.0	2.0	4.0	6.0	9.0
	Drying Time in Hours							
Medium Chrome Yellow	30	2.6 2.9	2.9	---	3.0	---	10.4	---
Lithol Rubine B Toner	>42	---	16.5	---	7.3 6.7	7.3	7.5 8.5 6.7 7.1	7.2 8.2
Milori Blue	8.3	---	12.4	8.5	8.8	---	5.4 5.7	6.4
Alumina Hydrate	>42	---	>18	---	>22	2.7	2.8 2.8	4.9

TABLE 2

DETERMINATION OF ACCURACY

OF DRYING-TIME TESTER

Ink - Lithol Rubine B
Drier Conc. - 6.0 per cent Naphthenate Drier Mixture Which Contains 13.1% Pb and 2.6% Mn
Paper - Offset
Temperature - 84° F.
Relative Humidity - 44 per cent

Drying Tests Conducted on Different Occasions	A	B	C	D	E	F	G	H	I	J
Drying Time (Average of Several Determinations)	6.4	5.3	5.8	4.1	5.5	5.5	4.4	5.8	5.7	5.8

Average Drying Time - 5.4 hours
Average Deviation - 0.51 hours
Per Cent Average Deviation - 9.44%

Maximum Deviation - 1.3 hours
Per Cent Maximum Deviation - 24.1%

Mean Deviation - .16 hours
Per Cent Mean Deviation - 2.98%

If observations A, D, and G are discarded:

Average Drying Time - 5.6 hours
Average Deviation - .23 hours
Per Cent Average Deviation - 4.12%
Maximum Deviation - .30 hours
Per Cent Maximum Deviation - 5.36%

TABLE 3

EFFECT OF FILM THICKNESS

ON DRYING OF INK

Ink - Lithol Rubine B Toner
Drier Conc. - 6.0 per cent Naphthenate Drier Mixture Which Contains 13.1% Pb and 2.6% Mn
Paper - Offset
Temperature - 83° F.
Relative Humidity - 44 per cent

Calculated Film Thickness (microns)	3.1	4.2	5.1	5.7
Drying Time (hours)	5.2 5.4	5.6 5.6	5.5 5.5	5.0 5.1

TABLE 4

VARIATIONS IN DRYING OF INK

ON DIFFERENT SHEETS OF SAME KIND OF PAPER

Ink - Lithol Rubine B Toner
Drier Conc. - 6.0 per cent Npahthenate Drier Mixture Which Contains 13.6% Pb and 2.6% Mn
Paper - Offset
Temperature - 83° F.
Relative Humidity - 44 per cent

Consecutive Sheets of Paper in Paper Pile	A	B	C	D
Drying Time (hours)	7.0 7.0	7.1 7.1	7.3 7.1	7.1 7.3

TABLE 5

EFFECT OF DIFFERENCES IN MOISTURE CONTENT OF PAPER AT TIME OF PRINTING ON DRYING OF INK AT 44 PER CENT RELATIVE HUMIDITY

Ink - Lithol Rubine B Toner
Drier Conc. - 6.0 per cent Naphthenate Drier Mixture Which Contains 13.1% Pb and 2.6% Mn
Temperature - 83° F.
Paper - Offset

# Relative Humidity of Paper (per cent)	* 0-5	** 50	*** 95-100
Drying Time (hours)	5.4 5.3	5.0 4.9 4.9	4.9 4.7

By relative humidity of paper is meant the relative humidity of the atmosphere with which the paper was in equilibrium.

* Paper placed in desiccator containing calcium chloride before printing.

** Paper in equilibrium with laboratory atmosphere.

***Paper suspended over water in closed container before printing.

TABLE 6

DRYING OF EXPERIMENTAL LITHOL RUBINE B INK CONTAINING LEAD-MANGANESE NAPHTHENATE DRIER

(Drier Contains 13.1% Pb and 2.6% Mn)
Temperature - 84° F.

Per Cent Relative Humidity	Per Cent Drier in Ink	DRYING TIME (hours)			
		Offset Paper	Bond Paper	Super-Calendered Paper	Coated Paper
29	6.0%	5.4	4.7	5.6	4.4
44		5.8	5.3	6.7	4.8
69		6.4	6.6	6.5	4.7
81		5.7	6.4	5.8	4.5
95		6.7	6.9	8.4	5.5
29	3.0%	6.0	5.0	6.3	4.4
44		5.8	4.8	6.3	3.9
69		6.0	5.0	6.9	3.9
81		7.2	6.1	8.8	4.2
95		7.7	7.2	9.5	5.5
29	1.0%	10.0	8.9	10.8	7.9
44		8.9	8.3	10.3	6.7
69		8.4	7.5	10.2	5.8
81		9.1	6.5	10.9	5.2
95		16.2	11.2	18.2	7.6
29	0.5%	14.1	13.1	14.9	11.9
44		14.6	13.2	16.3	11.9
69		13.9	12.0	15.8	10.7
81		17.6	13.4	> 20.5	12.2
95		> 24.0	18.4	> 24.0	13.6
44	0.0%	> 24.0	> 24.0	> 24.0	> 24.0

TABLE 7

DRYING OF COMMERCIAL CHROME YELLOW INK

CONTAINING LEAD-MANGANESE NAPHTHENATE DRIER

(Drier Contains 13.1% Pb and 2.6% Mn)
Temperature - 82° F.

Per Cent Relative Humidity	Per Cent Drier in Ink	DRYING TIME (hours)			
		Offset Paper	Bond Paper	Super-Calendered Paper	Coated Paper
--	4.0%	---	---	---	---
44		17.1	17.3	16.8	> 24.0
--		---	---	---	---
81		9.6	16.1	9.4	> 24.0
95		3.7	7.1	3.9	17.0
--	2.0%	---	---	---	---
44		7.6	7.6	12.2	13.8
--		---	---	---	---
81		8.3	9.7	8.6	12.8
95		3.5	5.5	> 20.0	17.1
--	1.0%	---	---	---	---
44		6.1	6.8	8.3	9.6
--		---	---	---	---
81		6.1	6.3	8.9	7.4
95		>24.0	5.8	>24.0	10.5
--	0.5%	---	---	---	---
44		4.9	3.7	3.9	3.3
--		---	---	---	---
81		6.0	3.9	19.5	3.5
95		>24.0	4.0	>24.0	4.3

TABLE 8

DRYING OF COMMERCIAL CHROME YELLOW INK

CONTAINING COMMERCIAL LEAD-MANGANESE PASTE DRIER

(Drier Contains 20.1% Pb and 0.75% Mn)
Temperature - 82° F.

Per Cent Relative Humidity	Per Cent Drier in Ink	DRYING TIME (hours)			
		Offset Paper	Bond Paper	Super-Calendered Paper	Coated Paper
25	4.0%	4.4	4.0	4.0	1.7
44		4.6	3.6	3.7	2.0
--		---	---	---	---
81		4.1	3.1	3.6	2.2
95		3.1	2.9	3.4	2.1
25	2.0%	4.6	4.9	4.7	2.5
44		4.0	4.7	4.7	2.2
--		---	---	---	---
81		4.4	3.8	5.7	2.6
95		2.7	2.9	3.0	1.9
25	1.0%	10.7	8.6	12.6	5.5
44		9.0	7.8	11.4	5.5
--		---	---	---	---
81		6.7	5.2	9.0	3.1
95		> 24.0	4.8	> 24.0	3.9
25	0.5%	18.0	13.8	> 24.0	10.1
44		13.8	10.7	20.0	7.8
--		---	---	---	---
81		11.1	7.2	16.5	6.7
95		> 24.0	4.8	> 24.0	3.6

TABLE 9

DRYING OF COMMERCIAL MILORI BLUE INK

CONTAINING LEAD-MANGANESE NAPHTHENATE DRIER

(Drier Contains 13.1% Pb and 2.6% Mn)
Temperature - 83° F.

Per Cent Relative Humidity	Per Cent Drier in Ink	DRYING TIME (hours)			
		Offset Paper	Bond Paper	Super-Calendered Paper	Coated Paper
29	6.0%	---	---	---	---
44		7.2	7.4	11.1	4.9
69		10.7	10.1	12.4	8.1
81		11.7	10.9	18.1	8.3
95		>24.0	22.0	>24.0	7.5
29	4.0%	---	---	---	---
44		9.6	7.3	14.4	5.2
69		18.3	15.9	22.0	15.4
81		---	---	---	---
95		---	---	---	---
29	3.0%	---	---	---	---
44		>24.0	>24.0	>24.0	>24.0
69		---	---	---	---
81		---	---	---	---
95		---	---	---	---
44	1.0%	>24.0	>24.0	24.0	>24.0
44	0.5%	>24.0	>24.0	>24.0	>24.0
95		>24.0	>24.0	>24.0	>24.0

TABLE 10

DRYING OF COMMERCIAL BLACK INK

CONTAINING COBALT NAPHTHENATE DRIER

(Drier Contains 6.0% Co)
Temperature - 83° F.

Per Cent Relative Humidity	Per Cent Drier in Ink	DRYING TIME (hours)			
		Offset Paper	Bond Paper	Super-Calendered Paper	Coated Paper
29	8.0%	4.0	5.1	3.6	1.8
44		6.0	6.9	6.1	2.3
--		---	---	---	---
81		8.3	7.7	9.8	---
95		>24.0	11.1	>24.0	2.5
29	5.0%	4.3	5.4	4.8	2.0
44		6.0	7.2	6.4	2.6
--		---	---	---	---
81		12.5	9.6	19.6	---
95		>24.0	>24.0	>24.0	3.8
29	3.0%	9.6	11.1	11.5	3.0
44		9.5	10.9	12.0	3.8
--		---	---	---	---
81		>24.0	16.9	>24.0	9.4
--		---	---	---	---
29	2.0%	17.7	16.7	21.9	15.4
44		>24.0	19.6	>24.0	19.6
--		---	---	---	---
81		>24.0	>24.0	>24.0	>24.0
--		---	---	---	---

TABLE 11

DRYING OF COMMERCIAL VIOLET TONER

(PHOSPHOTUNGSTIC LAKE OF METHYL VIOLET)

CONTAINING COBALT NAPHTHENATE DRIER

(Drier Contains 6.0% Co)
Temperature - 83° F.

Per Cent Relative Humidity	Per Cent Drier in Ink	DRYING TIME (hours)			
		Offset Paper	Bond Paper	Super-Calendered Paper	Coated Paper
29	6.0%	2.9	3.3	3.4	1.7
44		3.5	3.7	4.6	1.9
--		---	---	---	---
81		3.9	5.0	6.5	2.9
95		13.0	4.7	19.3	7.2
29	3.0%	3.3	3.3	4.0	1.8
44		3.5	3.5	5.5	2.1
--		---	---	---	---
81		6.8	6.3	12.8	3.5
95		>24.0	13.0	>24.0	>24.0
29	1.0%	6.9	7.1	16.1	3.2
44		10.1	9.0	>24.0	4.5
--		---	---	---	---
81		>24.0	14.4	>24.0	>24.0
95		>24.0	>24.0	>24.0	>24.0
29	0.5%	>24.0	16.2	>24.0	9.3
44		>24.0	21.0	>24.0	18.5
--		---	---	---	---
81		>24.0	>24.0	>24.0	>24.0
--		---	---	---	---

TABLE 12

DRIER CONCENTRATION NECESSARY TO CAUSE INK TO DRY IN LESS THAN 12 HOURS AT DIFFERENT RELATIVE HUMIDITIES

INK AND DRIER	PAPER	DRIER CONCENTRATION (per cent)				
		30% R.H.	50% R.H.	70% R.H.	80% R.H.	90% R.H.
Chrome Yellow Pb-Mn Paste Drier (20.1% Pb, 0.75% Mn)	Offset	1.0	1.0	1.0	1.0	2.0
	Bond	1.0	1.0	0.5	0.5	0.5
	Super-Calendered	2.0	2.0	2.0	2.0	2.0
	Coated	0.5	0.5	0.5	0.5	0.5
Milori Blue Pb-Mn Naph. Drier (13.1% Pb, 2.6% Mn)	Offset	4.0	4.0	6.0	6.0	*
	Bond	4.0	4.0	6.0	6.0	*
	Super-Calendered	6.0	6.0	6.0	*	*
	Coated	4.0	4.0	6.0	6.0	6.0
Black Co Naph. Drier 6.0% Co	Offset	3.0	3.0	5.0	8.0	**
	Bond	3.0	3.0	5.0	5.0	8.0
	Super-Calendered	3.0	5.0	8.0	8.0	**
	Coated	3.0	3.0	3.0	3.0	5.0
Lithol Rubine Pb-Mn Naph. Drier (13.1% Pb, 2.6% Mn)	Offset	1.0	1.0	1.0	1.0	3.0
	Bond	1.0	1.0	1.0	1.0	3.0
	Super-Calendered	1.0	1.0	1.0	1.0	3.0
	Coated	1.0	1.0	1.0	1.0	1.0
Conc. Violet Toner Co Naph.Drier 6.0% Co	Offset	1.0	1.0	3.0	3.0	6.0
	Bond	1.0	1.0	3.0	3.0	6.0
	Super-Calendered	3.0	3.0	3.0	6.0	*
	Coated	0.5	1.0	3.0	3.0	6.0

* Ink did not dry in 12 hours with 6.0% of this drier.

** Ink did not dry in 12 hours with 8.0% of this drier.

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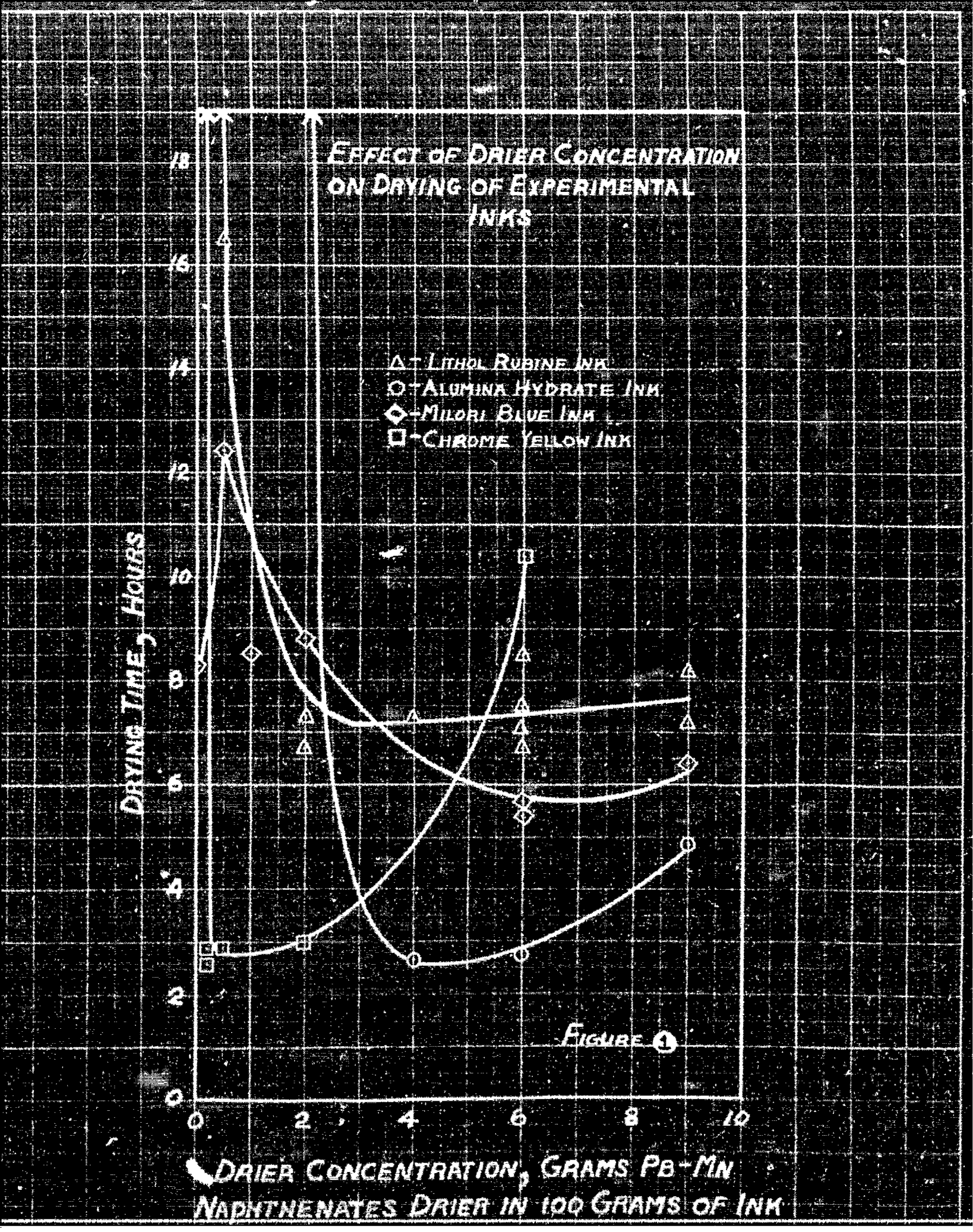


FIGURE 1

DRYING OF EXPERIMENTAL LITHOL RUBINE B INK ON DIFFERENT KINDS OF PAPER

DRIER – PB AND MN NAPHTHENATES
TEMPERATURE – 84°F

LEGEND
6.0% DRIER
3.0% "
1.0% "
0.5% "

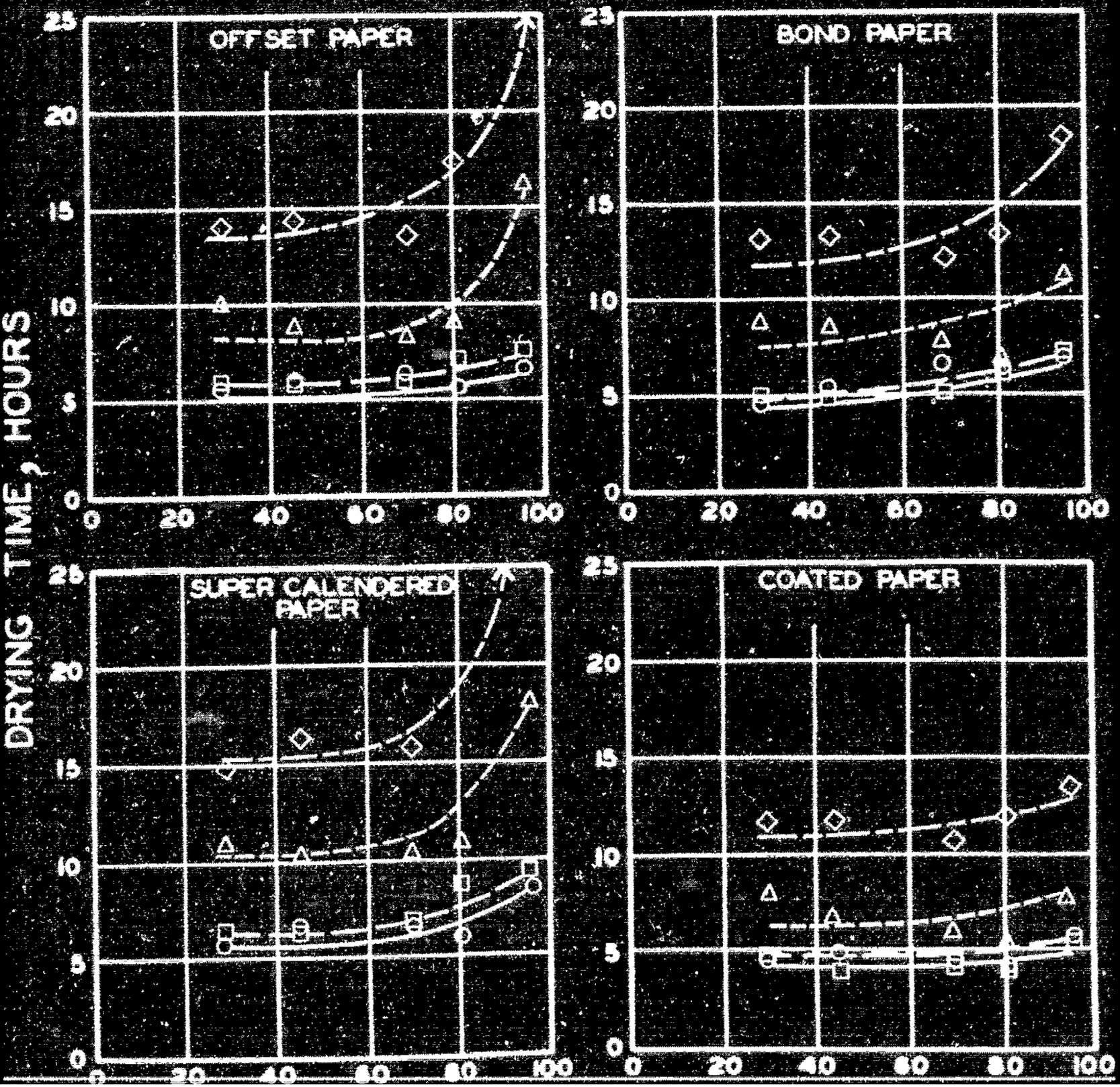


Fig. 3

DRYING OF COMMERCIAL CHROME YELLOW INK ON DIFFERENT KINDS OF PAPER

DRIER - PB AND MN NAPHTHENATES
TEMPERATURE - 82°F

LEGEND: —○— 4.0% DRIER
—□— 2.0% "
-△- 1.0% "
—◇— 0.5% "

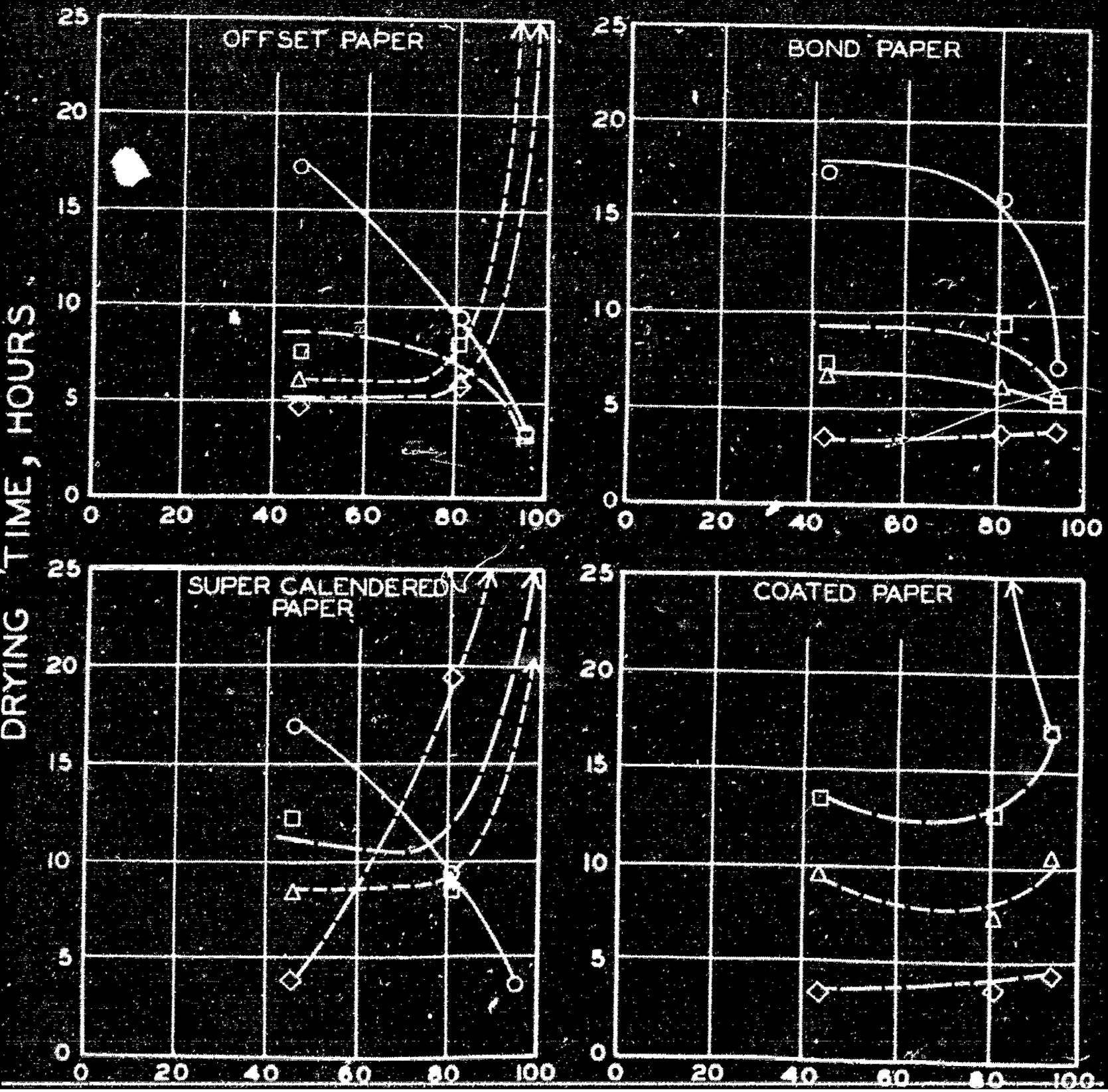


Fig 1

DRYING OF COMMERCIAL CHROME YELLOW INK ON DIFFERENT KINDS OF PAPER

DRIER – COMMERCIAL PB AND MN PASTE
TEMPERATURE – 83° F

LEGEND: 4.0% DRIER, 2.0% DRIER, 1.0% DRIER, 0.5% DRIER

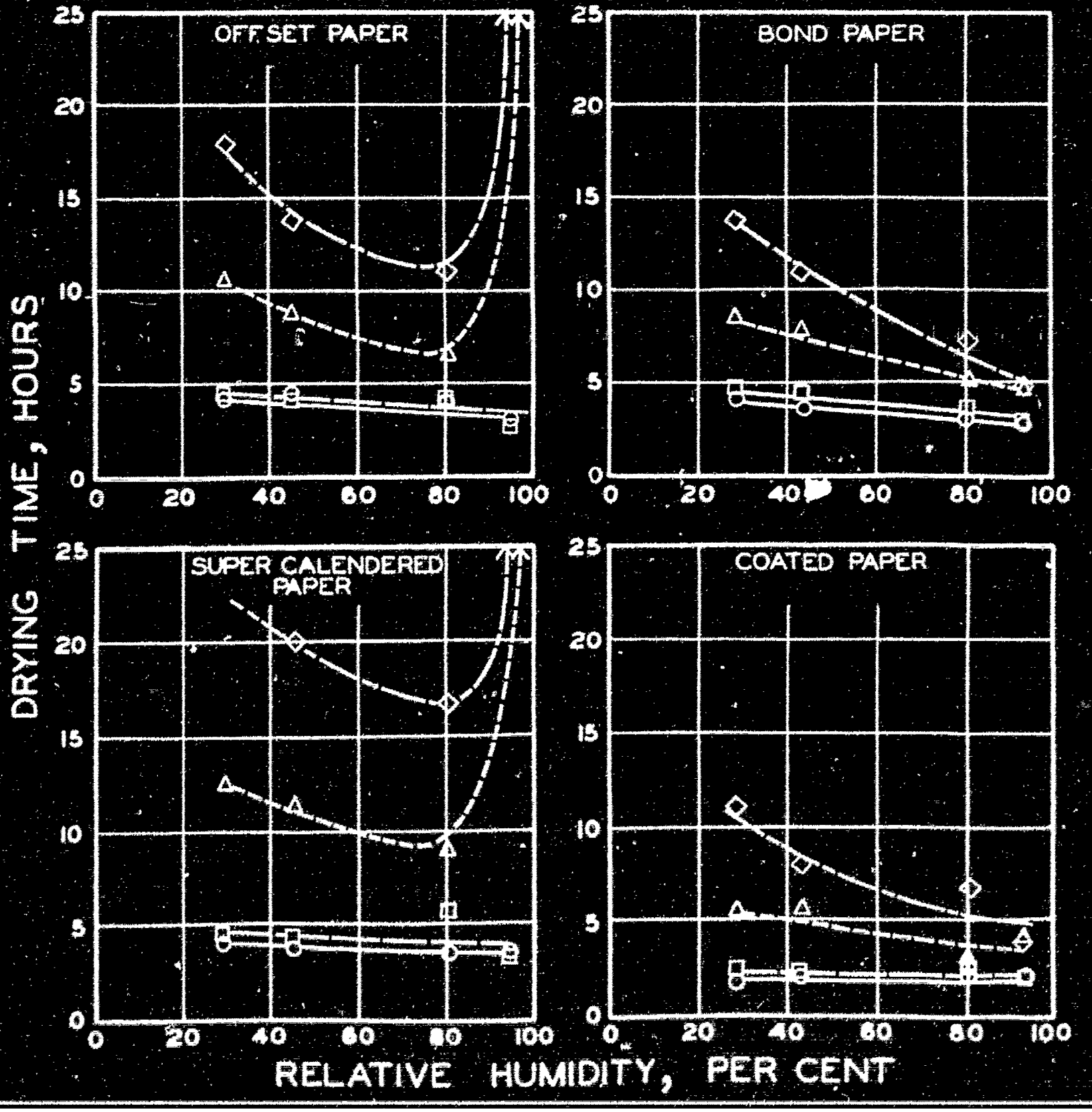


Fig. 5

DRYING OF COMMERCIAL MILORI BLUE INK ON DIFFERENT KINDS OF PAPER

DRIER – PB AND MN NAPHTHENATES
TEMPERATURE – 83° F

LEGEND: —○— 6.0% DRIER
—□— 4.0% "

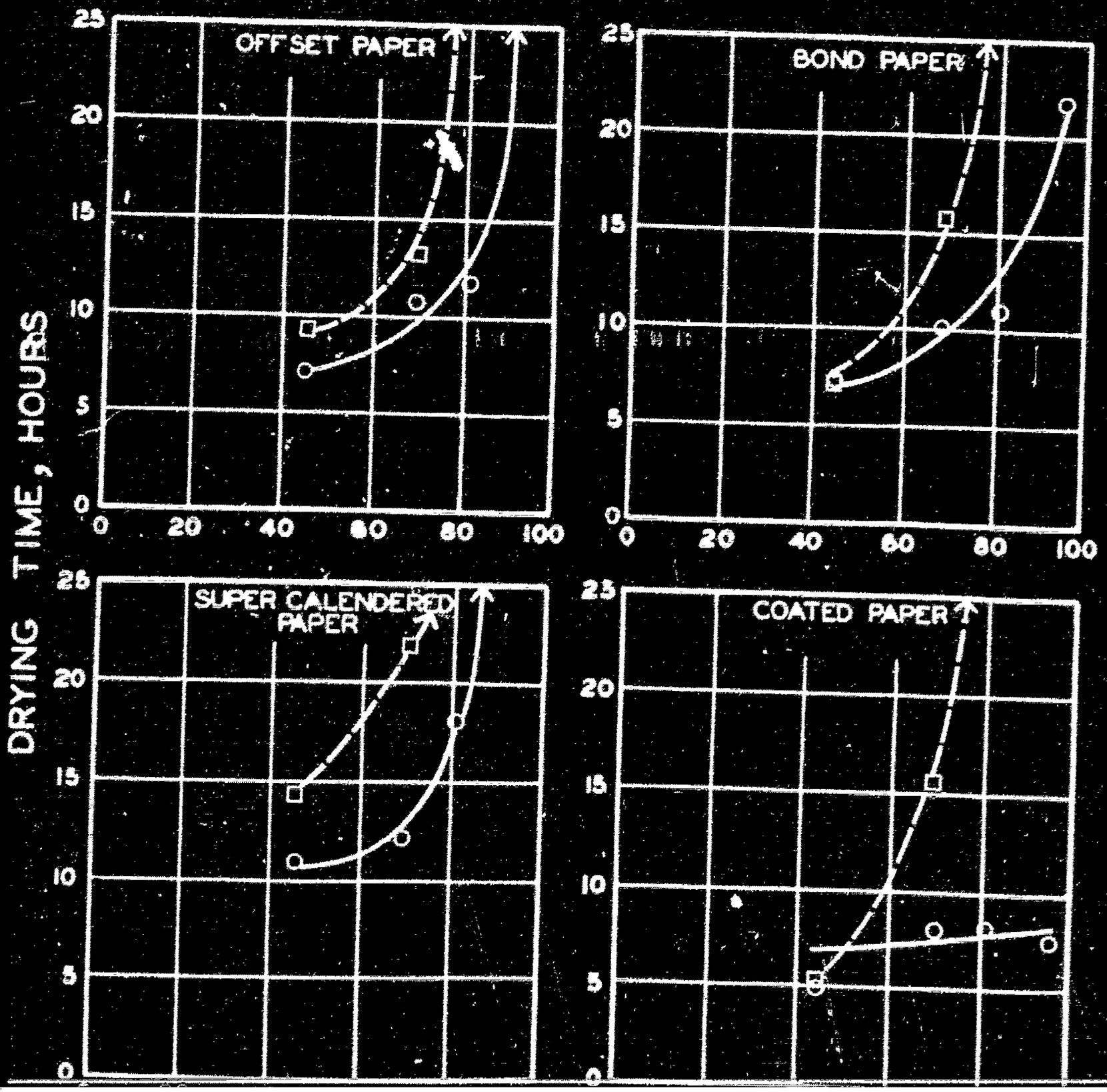


Fig. 6

DRYING OF COMMERCIAL BLACK INK ON DIFFERENT KINDS OF PAPER

DRIER – CO NAPHTHENATE
TEMPERATURE – 83°F

LEGEND: —○— 8.0 % DRIER
—□— 5.0 % "
---△--- 3.0 % "
—◇— 2.0 % "

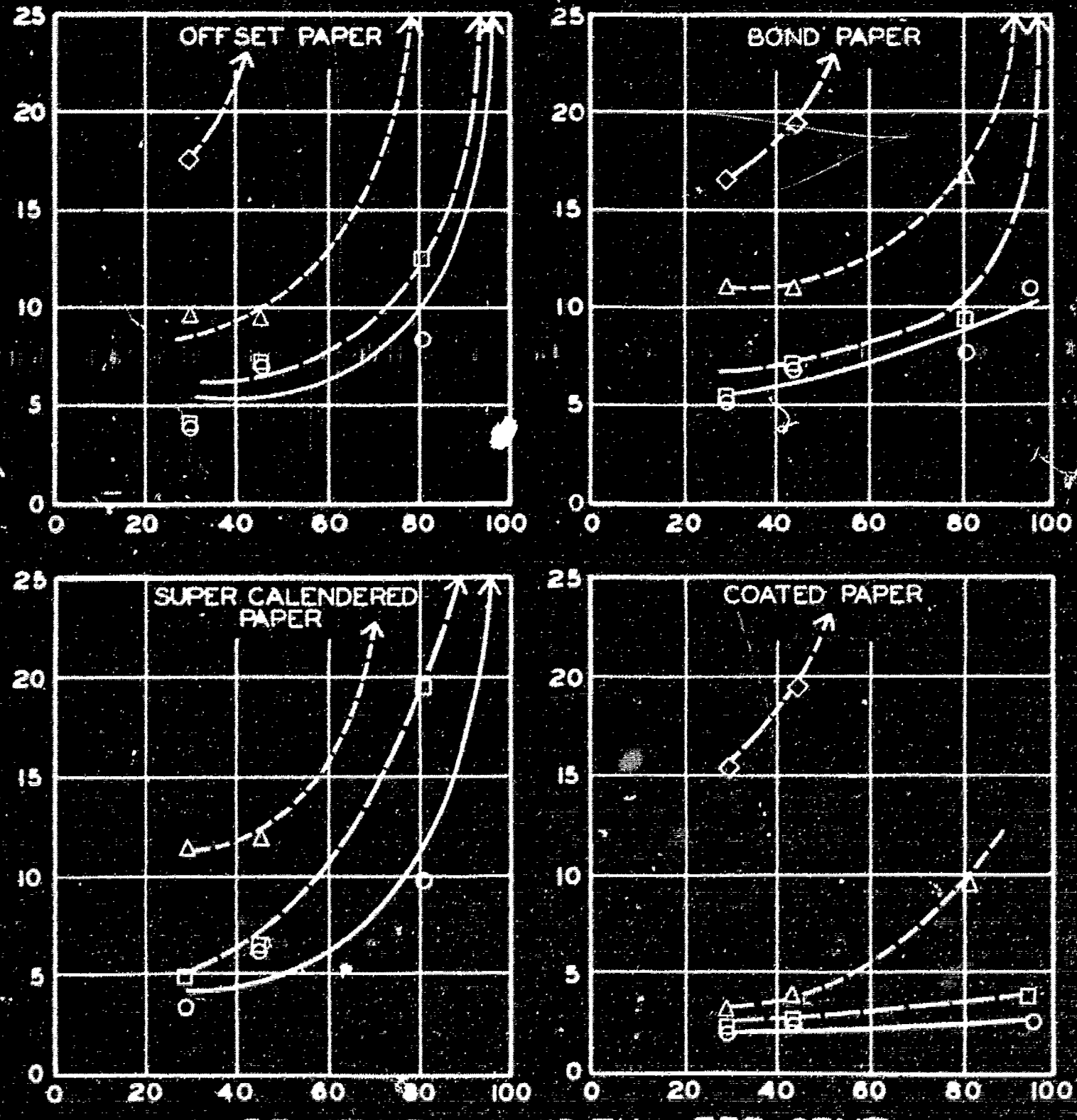
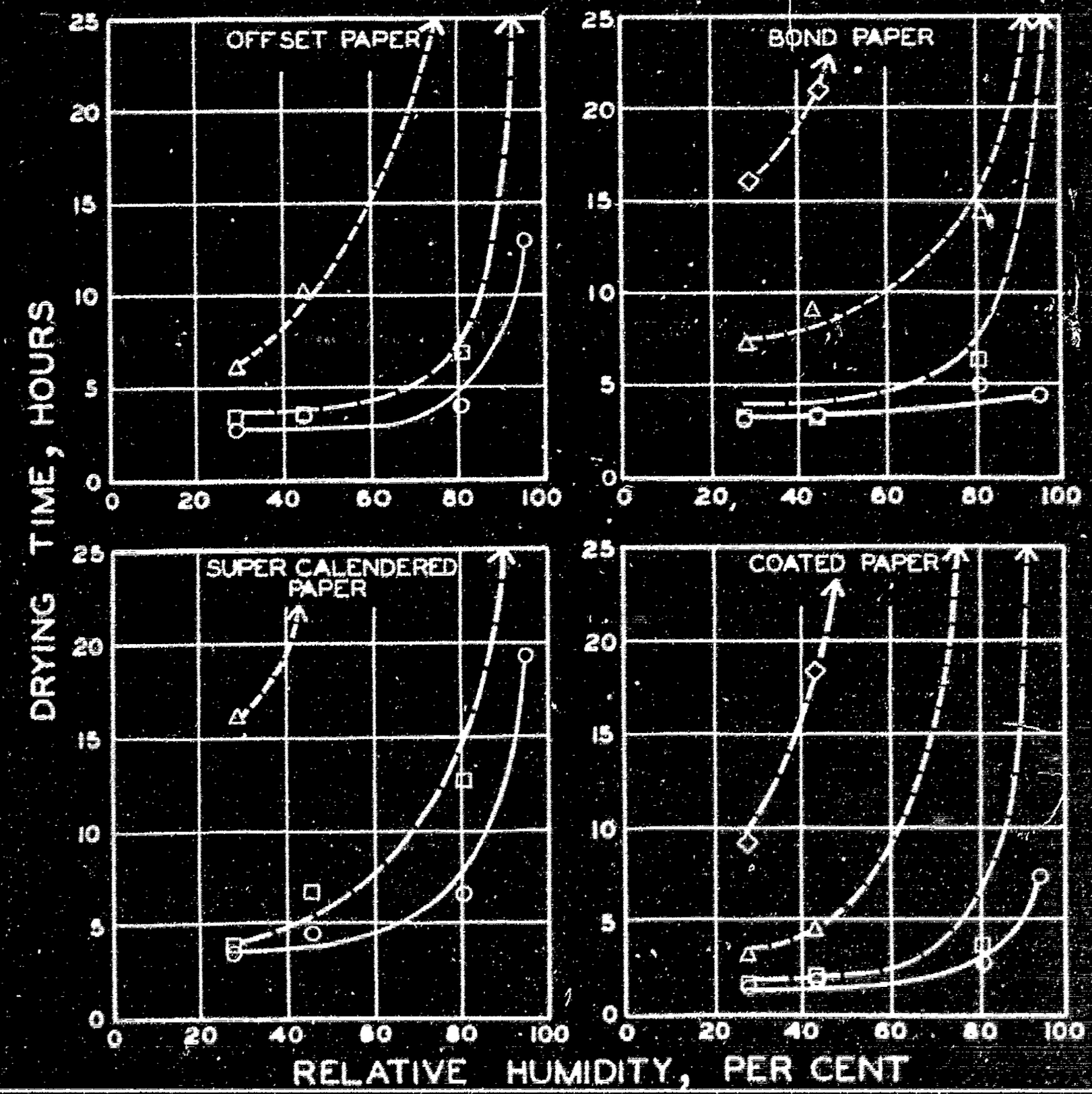


Fig. 7

DRYING OF COMMERCIAL VIOLET TONER (PHOSPHOTUNGSTIC LAKE OF METHYL VIOLET) ON DIFFERENT KINDS OF PAPER

DRIER – CO NAPHTHENATE
TEMPERATURE – 83° F.

LEGEND:
- 6.0% DRIER
- 3.0% "
- 1.0% "
- 0.5% "



THESIS SUPPLEMENT A

DRYING OF LINSEED OIL

The reactions which occur in linseed oil during drying have been investigated by chemists for many years. In spite of the large amount of information which has been collected the exact mechanism of drying is not known.

Linseed oil is expressed or extracted from flax seed. It has a variable composition depending upon its source. The analyses of two typical linseed oils are given below:

Saturated acids and unsaponifiable matter	8.1[1-A]	10.0[1-A]
Glyceryl radical	4.3	4.6
Oleic acid radical	5.0	5.0
Linolic acid radical	48.5	48.3
Linolenic acid radical	34.1	32.1
	100.0	100.0

The saturated fatty acids definitely identified are stearic, palmitic, myristic, and arachidic. The unsaponifiable matter consists of albuminoids and carbohydrate materials.

A desirable set of specifications for linseed oil is given by Wolfe:[2-A]

Specific gravity	.932-.934
Acid number	3-6
Saponification number	196-200
Iodine number	168-180

Since the acid number is low it is evident that only a small amount of free acids are present. The remainder exist as glycerides.

Since glycerol is a trihydroxy alcohol it might be expected that besides mixed glycerides, simple mono-, di-, and triglycerides also would be present. Actually mono- and diglycerides never have been detected in natural fats or oils and only one simple triglyceride has been reported. Linseed oil, therefore, contains mixed triglycerides.

The study of the chemistry of mixed glycerides is complicated by the problem of space relationships of acid radicals attached to the glycerol. Thus, it is possible for glycerides to have the same empirical formulas, yield the same products on hydrolysis, and yet have different physical properties because of differences in space configurations of the acid radicals. Furthermore, the acid radicals may have identical empirical formulas, but if they contain unsaturated linkages they may confer widely different properties to the glyceride molecules by existing in different steriometric forms (cis-trans isomerism).

These facts, together with the fact that glycerides always occur as mixtures from which they are exceedingly difficult to separate, indicate the difficulties involved in the study of the chemistry of linseed oil.

Oleic acid has the structure:

$CH_3-(CH_2)_7-CH=CH-(CH_2)_7-COOH$

Two sterioisomers obviously are possible. The other form is elaidic acid and is not found in nature.

Linolic acid probably has the structure:

$CH_3-(CH_2)_4-CH=CH-CH_3-CH=CH-(CH_2)_7COOH$

Four sterioisomers are possible and there is evidence[3-A] that derivatives of all four have been prepared. A review of the literature, however, indicates that there are probably only two linolic acids in linseed oil.

The following structure has been proposed for linolenic acid:

$CH_3-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH=CH-CH_2-(CH_2)_6COOH$

Eight sterioisomers theoretically are possible but Erdman[4-A] and Cocchinaras[5-A] have concluded that only two are present in linseed oil, an α and a β form whose space configurations are not yet known.

When a thin film of linseed oil is exposed to air it slowly changes from a liquid to a gelatinous state and, upon further exposure, to a flexible, tough mass. During drying the weight of the film increases as the iodine number decreases indicating that oxygen is absorbed at the unsaturated linkages. The absorbed oxygen forms peroxides and promotes chemical changes whereby (a) a part of the oxygen is transferred to other molecules or (b) further oxidation occurs with subsequent breaking of the carbon-carbon linkages at certain points in the molecule. The reaction (b) occurs to an appreciable extent for it has been

shown that the volatile oxidation products contain water, carbon dioxide, acetic, formic, and acrylic acids[6-A] together with small amounts of butyric acid[7-A] and acrolein[8-A] As (a) and (b) proceed the viscosity increases rapidly indicating that polymerization or association of the reaction products is taking place. Finally coagulation of the system occurs with the formation of a gelatinous film.

The oxidation process is generally considered to be autocatalytic because in the early stages of drying there is a period of induction during which little oxygen is absorbed; but after which the absorption of oxygen occurs rapidly for some time and then gradually decreases. It is thought that during the induction period peroxides are formed very slowly at first, but at an increasing rate as the initial peroxides catalyse the oxidation reaction. It has also been claimed that antioxidants naturally present in the oil are responsible for the induction period. Cohen[9-A] has detected cephaline in an aqueous extract from linseed oil and there is some indication that phosphotides and carotinoids also may be present. However, it is probable that these do not exist in sufficient quantities to appreciably affect drying.

The induction period can be reduced greatly by the addition of oil-soluble soaps of certain metals, the most effective of which are lead, manganese, and cobalt. The drier metals are believed to act catalytically to facili-

tate the transfer of oxygen from the atmosphere to the drying oil molecules. To a lesser extent, driers also appear to exert an orienting influence and to act as coagulating nuclei in polymerization. However, the action of driers is not yet fully understood.

Drying is accelerated by benzoyl peroxide, oxidized turpentine, and partially oxidized linseed oil. Conversely, drying is inhibited by amines, polyphenols, and certain other similar compounds.

Raw linseed oil is not used to a great extent in lithographic inks. Usually it first is subjected to a heat treatment which increases the viscosity and improves the working and drying properties. In the "bodying process", which consists of maintaining the oil at a temperature of about 250° C. for a few hours, a number of changes occur which resemble in effect the changes which occur in drying at ordinary temperatures.

In the early stages of processing the viscosity increases almost in proportion to the decrease in iodine number. The later value appears to approach asymptotically a value between 100 and 120, while the viscosity continues to increase and, if heating continues, gelation results.

During the heat treatment a considerable quantity of decomposition products is evolved. Also there is an increase in acid value which according to Long and McCarter[10-A] results through rupture of the molecules at

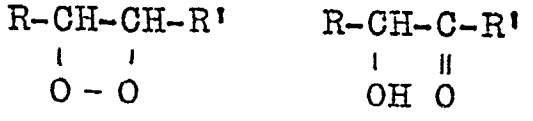
the double bonds, since insufficient water is present for hydrolysis of the ester linkages. This reaction would be expected if oxygen were present to oxidize the broken molecular chains to acids. However, Mattiello and Work[11-A] have shown that for the same processing temperature and viscosity the acid value is higher for oils processed in carbon dioxide than in air. This apparent anomaly has not yet been explained satisfactorily.

When drying oils are stored for long periods there is a noticeable increase in viscosity. Hence, it may be concluded that while polymerization proceeds rapidly at elevated temperatures it occurs also to an appreciable extent without oxygen even at ordinary temperatures.

As polymerization continues the average molecular weight of the drying oil molecule progressively increases. Caldwell and Mattiello[12-A] have established molecular weight values of 800-900 for the initial bodying stage and indicate that for varnishes of higher viscosity the molecular weight may exceed 1600. Long, Egge, and Welterau[13-A] found that the gel resulting from the oxidation of linolenic monoglyceride has an average molecular weight of 1700-1800. Chataway[14-A] extracted dried linseed oil with acetone and found a molecular weight of about 1200 for the soluble fraction. The molecular weight of the insoluble fraction could not be determined but undoubtedly is several times larger. Chataway estimates this value may be from 10,000 to 20,000.

Very little appears to be known about the drying oil polymer or association complex. The final product, linoxyn, is a very complex mixture of unchanged saturated glycerides and olein, together with the condensation products of the primary oxidation products. All attempts to resolve the polymer into its several constituents so far have been unsuccessful.

Several mechanisms have been proposed to explain the drying of linseed oil. It is generally agreed that the primary process consists in the oxidation of drying oil molecules to peroxides, but there is considerable disagreement concerning subsequent reactions. Fahrion[15-A] has proposed that the peroxides may undergo intramolecular changes with the formation of one or more ketoxy groups according to the number of unsaturated linkages which are oxidized:



The ketoxy compounds might then condense to form linoxyn. Long, Rheineck, and Ball[16-A] studied the effect of different solvents on dried linseed oil films and concluded on the basis that "like dissolves like" that the polar groups C=O and OH are present. The yellowing of oil films is attributed by Elin to the formation of keto-derivatives.

Salway[8-A] believes that the carbon-carbon linkage in the peroxide group is split yielding aldehydes which polymerize.

According to the most generally accepted theory polymerization occurs directly through the unsaturated linkages containing peroxide groups. What happens to the peroxidic oxygen is not exactly known. Part of it is released to other oil molecules and the remainder apparently remains in other linkages between polymerized oil molecules.

Although polymerization is conceded to play an important part in the drying process there is considerable uncertainty whether gelation is caused by polymerization or by association; that is, whether gelation is brought about by chemical reactions or by molecular forces of attraction between drying oil polymers.

The fact that considerable quantities of soluble material can be extracted from dried films by solvents is claimed to support the association theory.

Mofrell[17-A] observed that aggregates or gelled portions may be formed in linseed oil during heating or oxidation without an appreciable disappearance of double bonds and he indicates that this phenomenon favors the association concept.

Recently attempts have been made to explain the mechanism of drying according to modern theories of polymerization.

The ability to polymerize depends on substances containing at least two functional or combining groups. If only two groups are present linear polymers are formed,

which in some cases may be of extreme length. The final products are crystalline or semi-crystalline and usually dispersible in solvents. For gelation of the system to occur it is necessary that one of the components possess three or more functional groups. Polymerization then occurs in three dimensions and tends to form insoluble and infusible products. Theoretically it might be expected that this type of polymerization would continue until all the initial molecules were joined together. This condition probably never is achieved because the reduced mobility of large polymers does not permit reactive groups to approach near enough each other to react.

Bradley[18-A] observed the behavior of thin films of the following materials when exposed to air over a period of 15 months: linseed and tung (a) fatty acids, (b) ethyl esters, (c) monoglycerol esters, (d) diglycerol esters. With the exception of the tung diglycerol ester films, he found the films had increased slightly in viscosity but were still fusible and soluble in acetone. The tung diglycerol ester films slowly dried, probably, Bradley states, because of triglyceride impurities.

Several investigators have shown that thermal polymerization of ethyl esters of tung and linseed acids fails to yield polymers of higher molecular complexity than dimers. On the basis of these observations Bradley concluded that drying oil acids (excluding the acid group)

generally are monofunctional.

If the number of functional groups is known and molecular weights are determined at various stages of polymerization, it is possible mathematically to calculate the corresponding iodine number and to compare this with experimentally determined iodine values. At present the application of this method is limited by lack of sufficient data on the polymerization of drying oils and their pure components.

Bradley considered the data of Caldwell and Mattiello[12-A] which shows the relation between indine number and molecular weight during polymerization of linseed oil. Assuming that linseed oil can be approximately represented in average degree of unsaturation and molecular weight by linolic triglyceride, he showed[20-A] that heat bodied linseed oil corresponds closely to a hexafunctional system which loses an addition function at each step in the polymerization process. For example, two glyceride molecules each with a functionality of six combine to form a dimer having ten active groups, two groups being used in the addition process. To satisfy experimental data it must be assumed that an additional function is lost for each step in polymerization. Hence the potential functionality of the dimer is nine.

The loss in functionality is considered to result from reactions between double bonds in the same molecule. These intramolecular additions do not result in polymerization but serve rather to restrict the growth functions and to modify the structure of the polymer.

It is significant that in drying oil acids and simple esters the combination of unsaturated linkages is unifunctional, while in triglycerides it is at least bifunctional. It is evident that all double bonds do not possess the same degree of reactivity. The extent to which they enter into addition reactions, therefore, must depend upon factors connected with the structure and perhaps the degree of orientation of the drying oil molecule. Morrell and Davis[21-A] have shown that there is a difference in reactivity of double bonds in unsaturated fatty acids depending upon their positions in the molecule. Double bonds farthest from the polar end appear to take part more readily in polymerization reactions.

The amount of oxygen required for the drying of unsaturated oils or varnishes at normal temperatures depends upon the nature of the oil or varnish. Tung oil dries with the absorption of considerably less oxygen than linseed oil, and synthetic resins (triethylene maleate, etc.) have been prepared[22-A] which take up very little oxygen in drying. In the latter case it appears that oxygen acts merely as a catalyst for polymerization.

On the other hand, much evidence indicates that in linseed oil drying polymerization between double bonds always is preceded by peroxide formation. Rhodes and Van Wirt[23-A] found that linseed oil films absorb more than 30 per cent of their weight of oxygen. Assuming an average molecular weight of 880 and an average degree of unsaturation of six double bonds per mole, the amount of oxygen absorbed represents about 16 atoms per mole of triglyceride. Bradley and Pfann[24-A] analyzed the insoluble phase of a gelled mixture of oiticica and sardine oil and found that an average molecule could be represented statistically as being composed of eight triglyceride molecules united intermolecularly with intramolecular linkages at two additional points. It is probable that linseed oil gel is similar in structure, in which case it can be calculated that less than four of the six original double bonds participate in polymerization during drying. If peroxides are formed at the four reacting linkages, eight atoms of oxygen are used up leaving an equal number for further oxidation, which in the case of linseed oil appears to be appreciable since more than 20 per cent by weight of the film is lost in volatile decomposition products.

A number of attempts have been made to establish a stoichiometric relationship between the rate of oxygen absorption and the rate of drying without success. Accord-

ing to modern concepts of polymerization a simple relationship cannot be expected.

It has been pointed out that during drying addition reactions may occur between unsaturated groups in different molecules or between groups in the same molecule. Both reactions require oxygen but only the former results in polymerization and drying. Little exact knowledge exists concerning the nature of intermolecular and intramolecular reactions, but it is quite probable that the relative rates of each depend to different extents upon the temperature, amount of moisture present, drier concentration, and the chemical composition of the linseed oil. Under such conditions a simple quantitative relation between rate of oxygen uptake and rate of drying could not be expected. Nevertheless, it is generally agreed that the rate of oxygen absorption is an approximate measure of the drying rate of the oil.

Gain in weight experiments have an advantage over oxygen absorption determinations in that elaborate equipment is not required. Results by both methods are in relatively good agreement but not identical because some oxygen is used in side reactions which yield volatile products. The gain in weight then represents the difference between the gain of absorbed oxygen and the loss of volatile matter. However, in the case of heat-bodied lithographic varnishes it is believed that the decomposition products released

during drying represents only a small fraction of the total weight of the varnish.

Nicholson and Holley[25-A] investigated the gain in weight of linseed oil containing different amounts of various driers. They found that when the gain in weight of the varnish film per unit of time was plotted against time a curve was obtained having a definite maximum point. This point gave the time at which the rate of gain in weight was a maximum, its value being determined by the kind of oil and kind and amount of drier.

It was suggested by one of the research advisors that a similar investigation conducted with lithographic inks and varnishes might yield curves with a well-defined characteristic which could be used as an end point for drying tests. Also since this type of investigation has not been conducted with lithographic varnish it was felt that such a study might shed further light on the nature of the drying mechanism.

EXPERIMENTAL METHOD AND PROCEDURE

The experimental method employed was similar to that of Nicholson and Holley. Approximately 0.1 gram of varnish was applied with a brush to a weighed glass plate $3\frac{1}{4}$ x 4 inches. A uniform film about 15 microns thick was obtained. The plate was weighed to determine the initial amount of varnish and then at intervals as the film dried to determine the gain in weight. For weighing a Christian Becker Chainomatic balance was used. Air maintained at 25° C. and dried by passing through two glass tubes six feet long by one inch in diameter filled with sodium hydroxide and one three feet long by one inch in diameter containing phosphorous pentoxide, was allowed to flow into the balance. The back of the balance case was fitted with a cabinet containing shelves on which several glass plates could be placed. The glass front of the balance case was replaced with a celluloid front containing openings covered with hinged celluloid flaps. Through these openings forceps could be inserted to move the glass plates between the shelves and the balance or to change the weights. The air line contained a valve so that the air could be shut off during weighing. Otherwise air was passed into the balance case continuously at a sufficient rate to prevent diffusion of moist air into the case when either of the flaps was opened to manipulate samples or weights.

The general procedure was as follows: a clean glass plate was placed in the balance, allowed to remain 20 minutes to come to equilibrium with the dry air, weighed, removed from the balance, and coated with varnish. The plate was then placed on one of the shelves in the balance case for 20 minutes more, reweighed and then replaced on the shelf. Usually several films were prepared in the same manner. At frequent intervals the glass plates were transferred to the balance, weighed, and then returned to the shelf. The difference between the weight of the glass plate plus the varnish film and the weight of the clean glass plate gave the weight of the varnish film. The difference between subsequent weights of the glass plus varnish and the original weight gave the gain in weight of the varnish film to that time.

#00 varnish having the following characteristics was used in this work:

Viscosity at 25° C.	12 poises
Specific gravity at 25° C.	.9532
Acid number	9.39
Refractive index	1.4872
Iodine number (Wijs, 2 hr.)	119.8

Cobalt naphthenate containing 6.0 per cent of cobalt was used as drier. This was mixed with #00 varnish to form a drier compound and varnishes of desired drier

concentration were made by adding weighed amounts of this to weighed amounts of #00 varnish. The drier compound was analyzed gravimetrically for cobalt by the α nitroso β naphthol method and found to contain 1.55 per cent of cobalt.

No satisfactory method could be found for producing films of uniform thicknesses. However, after some practice, it was possible to judge very nearly the amount of varnish required, and in cases where considerable time elapsed before gain in weight occurred the films could be weighed several times, adding or subtracting varnish after each weighing as necessary until the correct thickness was reached.

When varnish films applied in ordinary atmosphere and containing less than 0.05 per cent cobalt as cobalt naphthenate were placed in the balance case it was noticed that the varnish slowly contracted into ridges and droplets leaving areas which contained little or no varnish. This caused considerable variation in film thickness and gain in weight determinations were inconsistent. No satisfactory explanation could be found for this "creeping" effect but it was found that it could be eliminated by applying the varnish to the plate in an atmosphere of dry air. This procedure was used in the remainder of the work.

Table 1 and Figure 1 show the effects of traces of moisture on the gain in weight of #00 varnish.

Table 2 and Figure 2 show the effect of film thickness on the gain in weight of #00 varnish.

The results in Table 3 and Figure 3 show the effect of drier concentration on the gain in weight of #00 varnish during drying.

The results in Table 4 and Figure 4 show the effect of adding 5.0 and 20.0 per cent of Toluidine Red pigment to #00 varnish containing 0.2069 per cent of cobalt.

The results in Table 5 and Figure 5 show the effect of adding 5.0 per cent of Peerless carbon black to #00 varnish containing 0.2069 per cent of cobalt.

When 20 per cent of Peerless carbon black was added to #00 varnish containing 0.2069 per cent of cobalt no gain in weight occurred in seven hours but the paint was dry the next morning (about 24 hours).

The maximum gain in weight of the varnishes was about 11.5 per cent. This was reached in four or five days and did not appear to depend on the concentration of drier.

Figure 6 and Table 6 show the gain in weight during 15 minute intervals of #00 varnish containing different amounts of drier.

DISCUSSION

Small amounts of moisture present on the surface of glass plates used in this work (about four or five milligrams of water under ordinary conditions) are able to accelerate drying. Apparently the chemical reactions involved in the oxidation of linseed varnishes, like certain other chemical reactions, are catalyzed by traces of water.

Table 2 shows that the rate of gain in weight of linseed varnish films increased with a decrease in film thickness. The effect of film thickness was not extensively studied but it is conceivable that the per cent gain in weight at a given time approaches a maximum value as the film thickness decreases. Evidence in favor of this is given in the main body of the thesis where it was shown that the drying times of the experimental inks were only slightly dependent on film thickness. Unfortunately it was impossible to obtain gain in weight curves for ink films because a balance having the precision necessary to weigh thin films accurately could not be obtained.

The length of the induction period depends on the concentration of drier in the varnish, the addition of 0.0026 per cent of cobalt as cobalt naphthenate being sufficient to reduce the induction period from several days to about 40 minutes. In Figure 3 the slope of the curve is proportional to the drier concentration and probably ap-

proaches a maximum value when the concentration of cobalt is about 0.2 per cent or slightly higher.

Figure 4 shows that the addition of 5.0 per cent of Toluidine Red pigment has little effect on the drying of #00 varnish. The addition of 20.0 per cent, however, causes a decrease in the slope of the curve, especially during the latter stages of drying. With inks the effect would be even more pronounced because they contain higher concentrations of pigments.

The addition of 5.0 per cent of carbon black pigment likewise only slightly affects the gain in weight of #00 varnish but 20.0 per cent extends the induction period from 20 minutes to more than seven hours and undoubtedly modifies the curve although this was not determined.

In Figure 6 the gain in weight for 15 minute intervals is seen to pass through a maximum point which is proportional to the drier concentration. The time at this point is not well defined and in cases where the drier concentration is low the rate of gain in weight continues at a maximum value for an hour or longer. It is evident, therefore, that this method does not provide a satisfactory end point for testing the drying of varnish films.

CONCLUSIONS

1. Small amounts of moisture accelerate the drying of #00 varnish containing drier.

2. The rate of gain in weight of #00 varnish increases with the concentration of drier.

3. The rate of gain in weight varies with time and passes through a maximum value which is not well defined and which increases with the concentration of drier.

4. The addition of 5.0 per cent of Toluidine Red pigment does not appreciably affect the rate of gain in weight of #00 varnish containing drier, but the effect of this pigment becomes appreciable when its concentration exceeds 5.0 per cent.

5. The addition of 5.0 per cent of carbon black pigment only slightly affects the gain in weight of #00 varnish containing drier, but the addition of 20.0 per cent greatly extends the induction period.

6. Gain in weight determinations do not appear to provide a means for evaluating the drying times of lithographic varnishes or lithographic varnish-pigment mixtures.

TABLE 1

EFFECT OF TRACES OF MOISTURE ON GAIN IN WEIGHT OF #00 VARNISH CONTAINING 0.2069 PERCENT COBALT AS COBALT NAPHTHENATE

A Varnish Applied to Glass Plates in Dry Atmosphere				B Varnish Applied to Glass Plates in Ordinary Atmosphere			
Film Thickness				Film Thickness			
△ 22.9 Microns		□ 24.0 Microns		○ 12.0 Microns		◇ 21.8 Microns	
Time (min.)	% Gain in Weight	Time (min.)	% Gain in Weight	Time (min.)	% Gain in Weight	Time (min.)	% Gain in Weight
20	0	25	0	20	0	15	0
30	0	30	0	45	2.0	40	1.9
50	1.0	60	1.5	75	3.6	65	3.3
67	1.9	75	2.6	110	4.7	100	4.7
80	3.0	95	3.3	190	6.4	130	5.7
100	3.8	120	4.4	240	6.7	170	6.2
125	4.8	155	5.4	295	7.2	225	6.8
160	5.7	180	5.9			285	7.2
185	6.1	250	7.0				
260	7.1	295	7.4				
300	7.6	380	8.2				
365	8.1	445	8.9				
390	8.5						
450	8.9						

TABLE 2

EFFECT OF FILM THICKNESS ON GAIN IN WEIGHT OF #00 VARNISH CONTAINING 0.2069 PERCENT COBALT AS COBALT NAPHTHENATE

Film Thickness							
○ 25.8 Microns		◇ 24.3 Microns		□ 15.2 Microns		△ 14.2 Microns	
Time (min.)	% Gain in Weight	Time (min.)	% Gain in Weight	Time (min.)	% Gain in Weight	Time (min.)	% Gain in Weight
25	0	30	0	20	0	25	0
35	0.1	45	0.2	35	0.3	45	0.3
60	0.8	65	1.0	70	1.7	75	1.9
85	1.8	90	2.0	95	3.0	100	3.2
150	4.2	140	4.0	115	4.0	120	4.1
160	4.7	155	4.6	135	4.8	140	4.8
180	5.2	205	5.7	175	6.0	180	6.0
235	6.3	230	6.2	205	6.7	210	7.1
285	7.1	290	7.1	250	7.4	240	7.2
325	7.6	330	7.6	310	8.2	300	7.8
370	7.9	365	7.8	375	8.7	390	8.5
480	8.6	400	8.2	485	9.4		
		485	8.6				

TABLE 3

EFFECT OF DRIER CONCENTRATION ON GAIN IN WEIGHT OF #00 VARNISH

A 0.2069 % Cobalt		B 0.0770 % Cobalt		C 0.0259 % Cobalt				D 0.0077 % Cobalt				E 0.0026 % Cobalt			
Film Thickness in Microns															
○ 14.5 μ		□ 13.5 μ		○ 15.1 μ		□ 14.1 μ		○ 20.3 μ		□ 22.5 μ		○ 15.7 μ		□ 17.3 μ		○ 15.1 μ		□ 17.6 μ	
T	G	T	G	T	G	T	G	T	G	T	G	T	G	T	G	T	G	T	G
20	0	25	0	20	0	25	0	35	0	30	0	35	0	40	0	35	0	45	0
40	1.1	50	1.7	35	0.3	45	0.3	65	0.8	55	0.8	55	0.3	65	0.4	120	0.5	115	0.3
58	2.1	68	3.3	70	1.7	75	1.9	85	1.6	75	1.5	72	0.6	100	1.1	150	0.9	155	1.0
73	3.6	93	4.4	95	3.0	100	3.2	155	3.3	95	2.2	105	1.2	120	1.5	240	1.8	230	2.0
98	4.6	118	5.5	115	4.1	120	4.1	180	3.8	145	3.3	125	1.6	185	2.6	280	2.3	270	2.3
125	5.8	130	6.2	135	4.8	140	4.8	185	4.1	170	4.1	180	2.5	210	3.1	320	2.8	315	2.9
145	5.9	195	7.1	175	6.0	180	6.0	220	4.8	195	4.5	195	2.8	245	3.5	395	3.3	380	3.3
180	6.8	290	8.2	205	6.7	210	7.1	260	5.4	235	5.2	237	3.8	270	3.9	445	4.0	440	3.9
215	7.4	325	8.4	250	7.4	240	7.2	320	6.2	270	5.8	260	4.0	325	4.7				
295	8.3	385	8.6	310	8.2	300	7.8	385	7.1	330	6.5	280	4.2	370	5.3				
375	8.6	430	8.8	375	8.7	390	8.5			395	7.2	320	4.7	400	5.6				
450	9.0			485	9.4							360	5.3						
												405	5.6						

T - - Time in Minutes

G - - Per Cent Gain in Weight

TABLE 4

EFFECT OF PIGMENTATION WITH TOLUIDINE RED PIGMENT ON THE GAIN IN WEIGHT OF #00 VARNISH CONTAINING 0.2069 PER CENT COBALT AS COBALT NAPHTHENATE

A				B				C	
Film Thickness in Microns									
22.9 μ		24.0 μ		○ 23.4 μ		□ 24.5 μ		△ 27.1 μ	
T	G	T	G	T	G	T	G	T	G
20	0	25	0	13	0	20	0	25	0
30	0	30	0	25	0	33	0	35	0.2
50	1.0	60	1.5	40	0.5	55	1.6	57	1.7
67	1.9	75	2.6	65	2.1	85	3.2	92	3.6
80	3.0	95	3.3	90	3.5	120	4.6	119	4.5
100	3.8	120	4.4	130	4.9	160	5.8	165	5.4
125	4.8	155	5.4	170	5.8	220	7.3	235	6.5
160	5.7	180	5.9	230	6.8	255	7.0	260	6.8
185	6.1	250	7.0	325	7.6	310	7.5	325	7.3
260	7.1	295	7.4	375	8.1	400	8.4	390	7.7
300	7.6	380	8.2					465	7.8
365	8.1	445	8.9	T - - Time in Minutes					
390	8.5			G - - Rer Cent Gain in Weight					
450	8.9								

A - #00 Varnish Containing 0.2069 % Cobalt
B - #00 Varnish Containing 0.2069 % Cobalt and 5.0 % Toluidine Red Pigment
C - #00 Varnish Containing 0.2069 % Cobalt and 20.0 % Toluidine Red Pigment

TABLE 5

EFFECT OF PIGMENTATION WITH 5.0 PER CENT CARBON BLACK PIGMENT ON GAIN IN WEIGHT OF #00 VARNISH CONTAINING 0.2069 PER CENT COBALT AS COBALT NAPHTHENATE

A #00 Varnish Containing 0.2069 Per Cent Cobalt				B #00 Varnish Containing 0.2069 Per Cent Cobalt and 5.0 Per Cent Carbon Black			
Film Thickness				Film Thickness			
22.9 Microns		24.0 Microns		O 23.8 Microns		□ 24.0 Microns	
Time (min.)	% Gain in Weight	Time (min.)	% Gain in Weight	Time (min.)	% Gain in Weight	Time (min.)	% Gain in Weight
20	0	25	0	25	0	40	0
30	0	30	0	50	0.3	55	0.3
50	1.0	60	1.5	75	1.4	80	1.8
67	1.9	75	2.6	105	3.7	100	3.6
80	3.0	95	3.3	133	5.0	130	4.9
100	3.8	120	4.4	155	5.6	152	5.7
125	4.8	155	5.4	180	5.9	182	6.1
160	5.7	180	5.9	200	6.5	205	6.6
185	6.1	250	7.0	230	6.9	320	7.9
260	7.1	295	7.4	325	7.8	375	8.3
300	7.6	380	8.2	385	8.5	430	8.8
365	8.1	445	8.9	440	8.9		
390	8.5						
450	8.9						

TABLE 6

EFFECT OF DRIER CONCENTRATION ON GAIN IN WEIGHT OF #00 VARNISH CONTAINING COBALT NAPHTHENATE DRIER DURING 15 MINUTE INTERVALS

Time (min.)	Gain in Weight (Grams Gain for 100 Grams #00 Varnish during 15 Minute Intervals)				
	A 0.2069 % Cobalt ●	B 0.0770 % Cobalt O	C 0.0259 % Cobalt Δ	D 0.0077 % Cobalt □	E 0.0026 % Cobalt ◇
0	0	0	0	0	0
15	0	0	0	0	0
30	0.42	0.15	0	0	0
45	0.91	0.58	0.53	0.22	0
60	0.91	0.62	0.52	0.27	0.06
75	0.93	0.68	0.44	0.28	0.08
90	0.97	0.69	0.39	-	0.09
105	0.77	0.69	0.39	-	0.15
120	0.57	0.66	0.32	-	0.19
135	0.44	0.60	0.34	-	0.19
150	0.32	0.46	0.34	0.28	0.19
165	0.29	0.43	-	-	-
180	0.19	-	-	-	-
200	-	0.32	0.25	0.27	-
240	0.14	-	-	-	-
250	-	0.12	0.18	-	0.18
275	0.09	-	-	0.19	-
350	0.09	0.12	0.18	0.17	0.15

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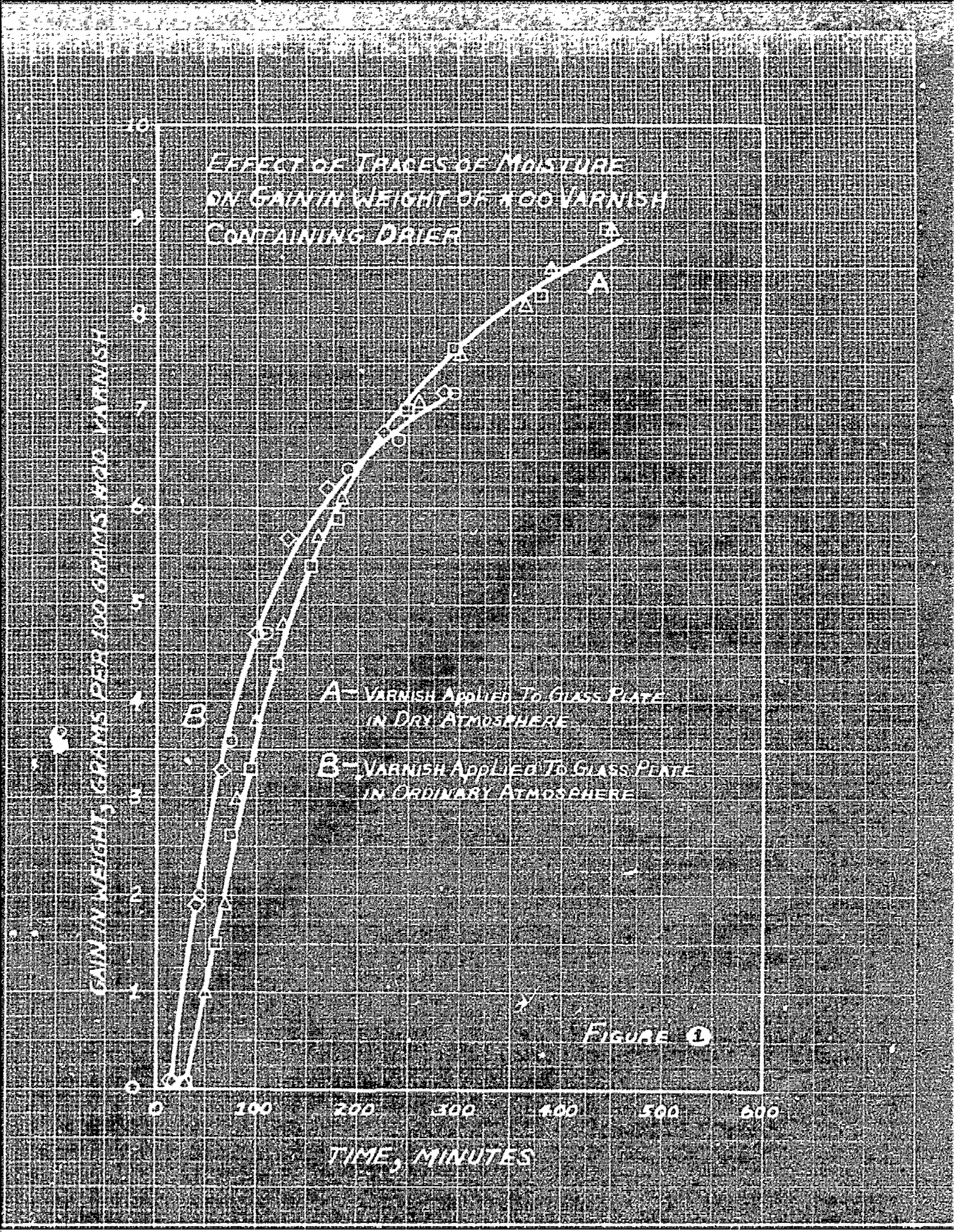


Figure 1

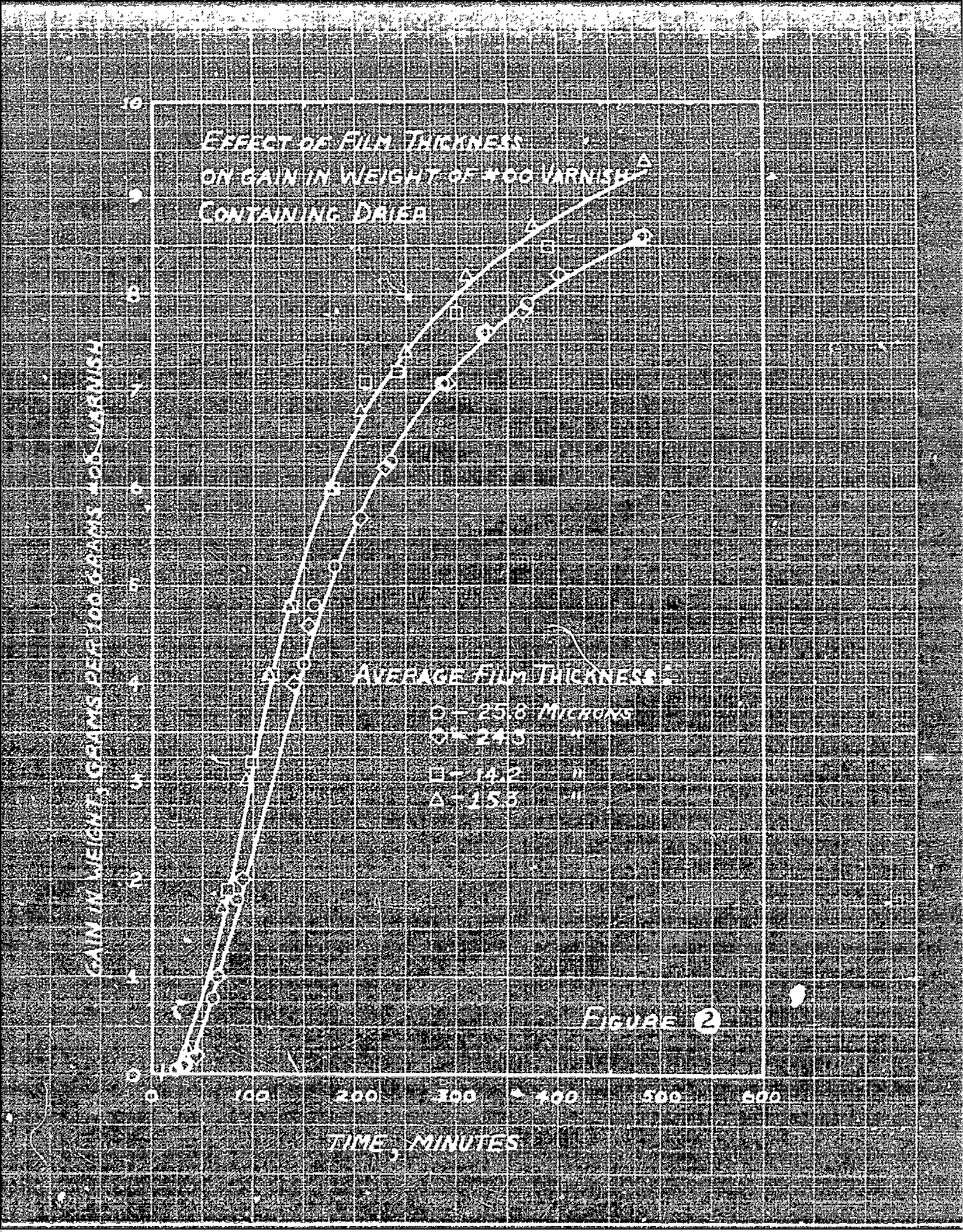
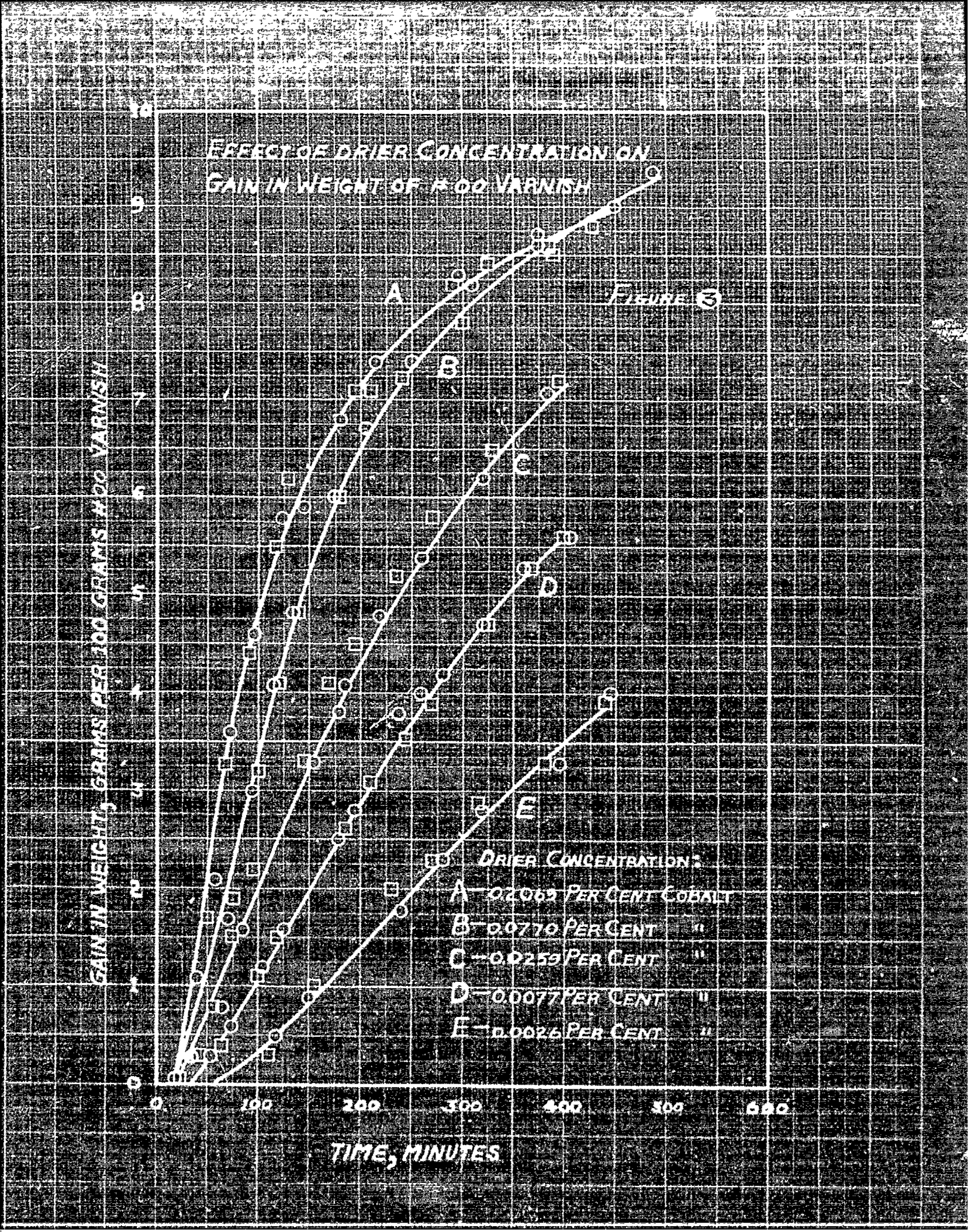


FIGURE 2



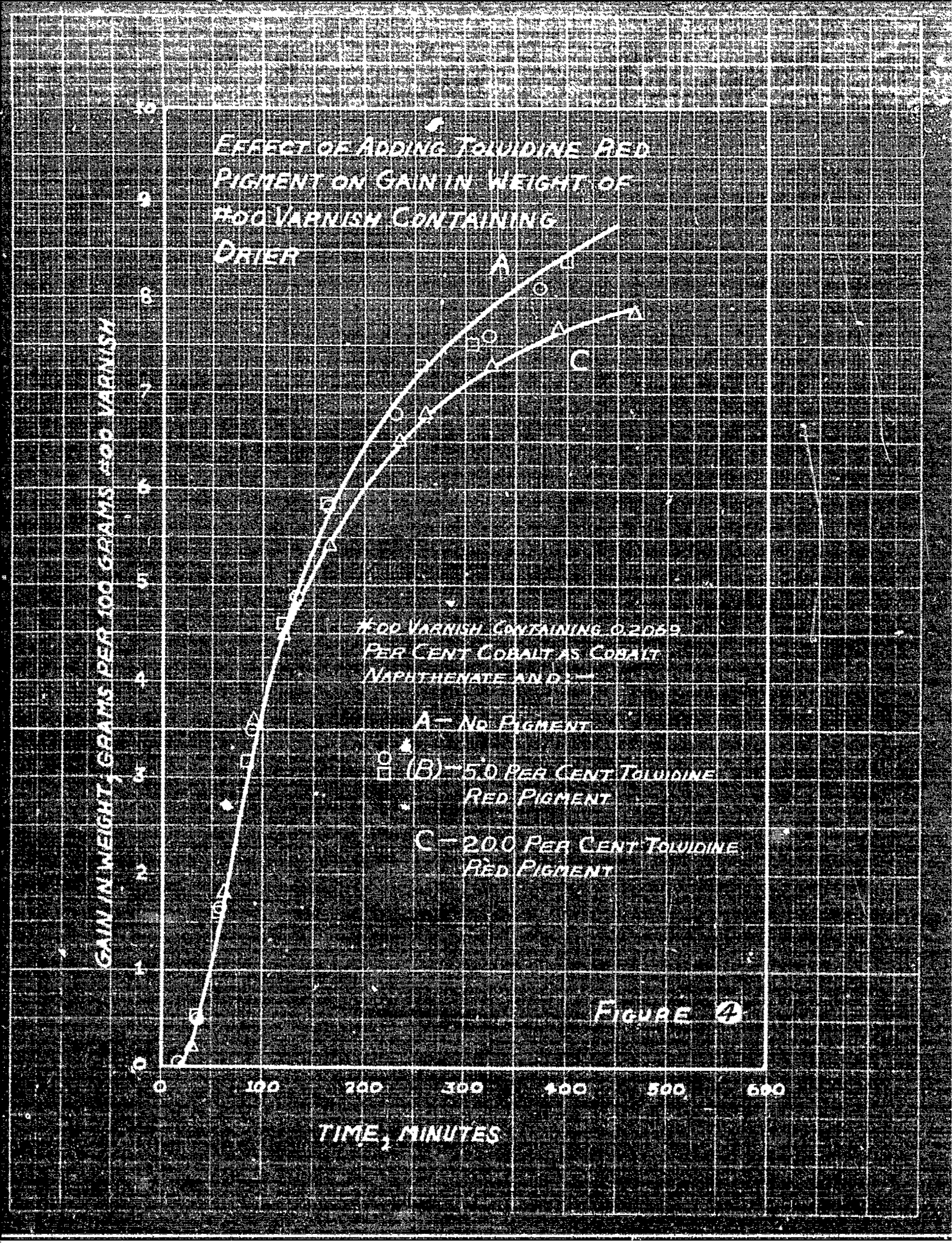


FIGURE 4

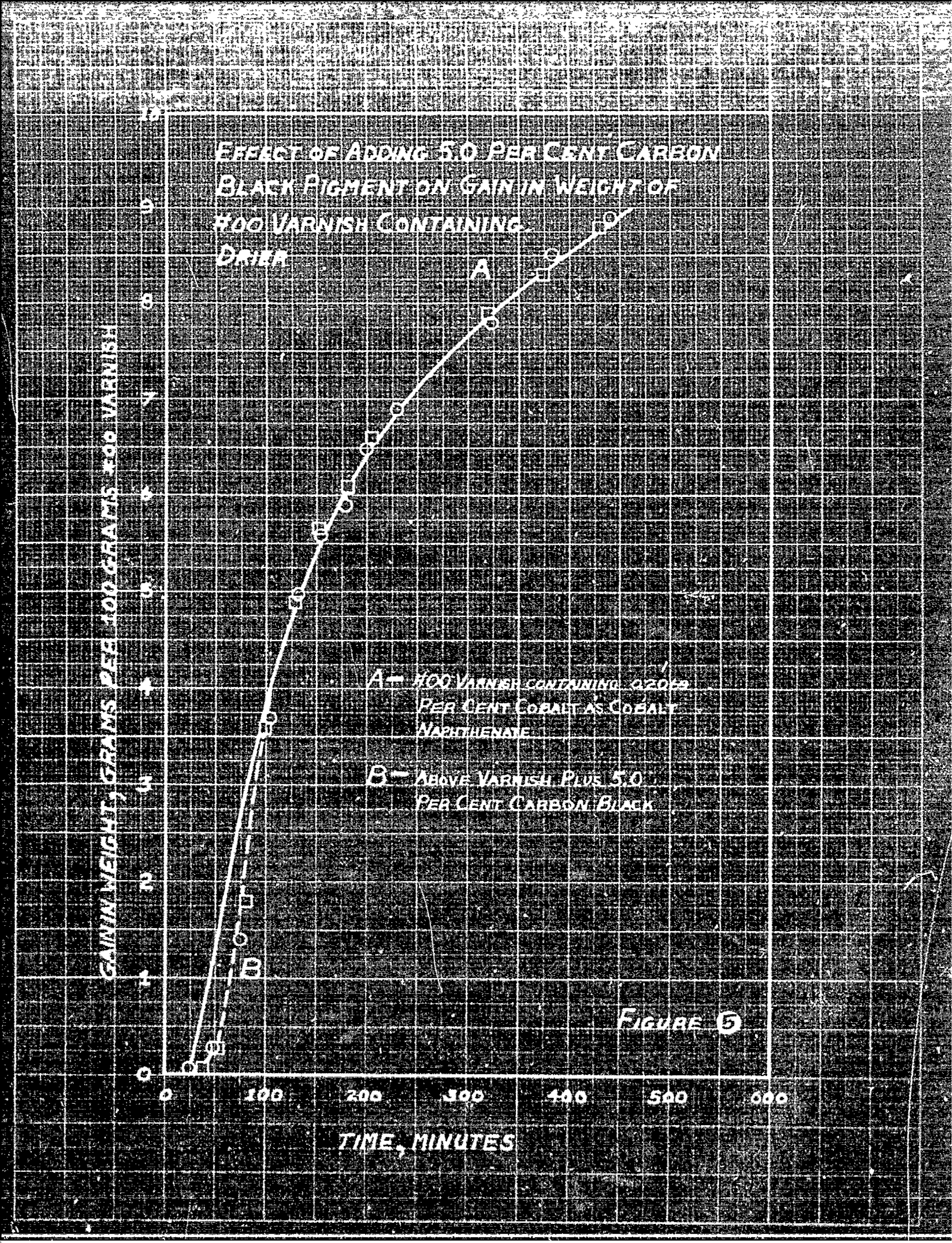


FIGURE 5

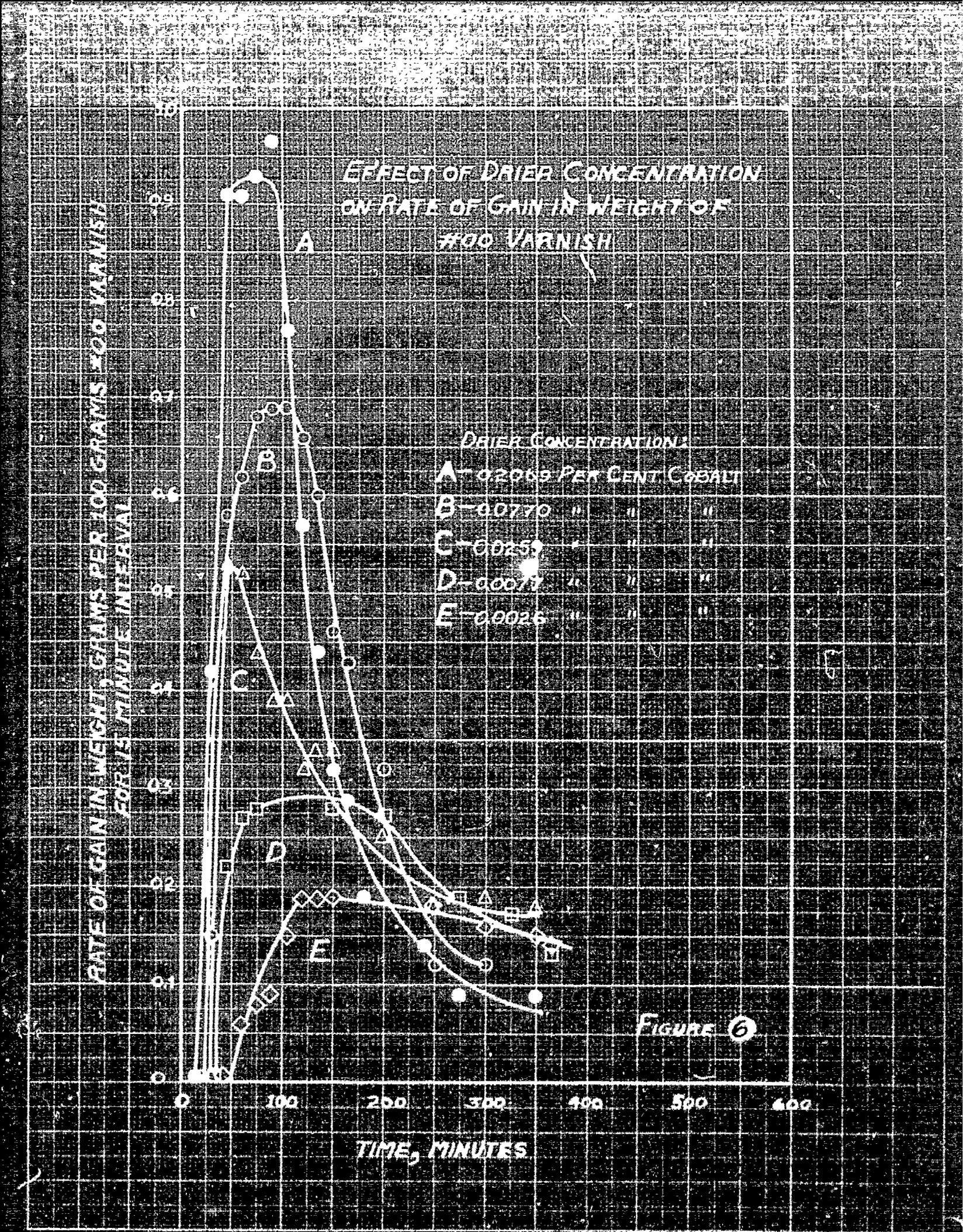


FIGURE 6