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A Study of the Mechanism of Film Formation in the Spray-Coating of  
Paper with Nitrocellulose Lacquers

by Philip E. Shick

May, 1943

**A STUDY OF THE MECHANISM OF FILM FORMATION IN THE  
SPRAY-COATING OF PAPER WITH NITROCELLULOSE LACQUERS**

**A thesis submitted by**

**Philip E. Shick**

**B.S. 1939, Harvard University**

**M.S. 1941, Lawrence College**

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## INTRODUCTION

At the present time, the use of paper products in packaging is increasing rapidly, not only as a substitute for metal or glass but also in new fields. Although this increase has been brought about, in part, by pressure resulting from the shortage of more critical materials, it is indicative of an awareness of the innate advantages of paper, such as cheapness, low weight, convenience, and ease of disposal—a trend already evident before the war in the substitution of paper for glass in the milk industry.

For many packaging uses where liquids are to be retained, gain or loss of moisture reduced, or access of air prevented, the inherently porous and permeable nature of paper is a disadvantage which must be offset by some method of proofing—i.e., the paper must be rendered more resistant to penetration by liquids or vapors.

There are four approaches in the proofing of paper. The first comprises the treatment of the pulp before the sheet is formed. Addition of resin emulsions and prolonged beating are examples. The second involves the treatment of the paper or finished product; an example is the production of parchment paper by an acid treatment. A third method is that of impregnation of the sheet with materials which will impart the desired properties; fully waxed paper is an example of such a product. The fourth method consists in coating the sheet to produce a surface film having the desired characteristics; surface-waxed or resin-coated papers fall into this class.

Of the four procedures, coating offers advantages in economy of material and assurance of imperviousness. The continuous application of coating materials to paper in sheet form, as by roll coating, is an accomplished fact in the industry. However, the problem of coating finished containers has not been satisfactorily solved. For example, dipping or immersion techniques lead to thick films in the case of viscous materials; on the other hand, thin coating materials soak into the paper.

The object of the present work has been the study of the mechanism of thin film formation on paper, using a method of application suitable for the coating of finished containers. Spraying was chosen as such a method. Although the work was carried out on flat paper samples, it is felt that, by the use of extension nozzles and other equipment already in existence, a similar technique might be developed for finished paper containers and that the same variables and mechanism will prevail.

The field was further narrowed by the choice of nitrocellulose lacquers as the coating material. Such lacquers are typical of non-aqueous coatings and have been widely used. By suitable changes in their formulations—e.g., the addition of waxes or resins and change of plasticizer—the final film properties may be varied to suit many requirements.

# HISTORICAL SURVEY

References to literature on the production and properties of resistant or impervious papers have been compiled in an annotated bibliography by West (1). A general discussion of the field is given by Bauer (2). Most of the literature on the proofing of paper deals with the materials used, methods of application, testing, and properties of the final product. No comprehensive study of the variables and mechanism of coating is known. However, various phases of the problem have been investigated, although not always with the coating of paper in mind.

The porous structure of paper and its penetration by liquids have been described. The most illustrative description, "The pores in the sheet through which liquids move are, in general, not even approximately tubular in nature but are more of the nature of the interstices of a compressed brush heap," appears in an article by The Institute of Paper Chemistry (3).

Theoretical considerations of the flow of fluids in capillaries and adaptations of such equations to penetration and porosity studies of paper are treated in the same article. Perhaps the most useful expression in predicting the effects of various variables on penetration resulting from capillary action is Equation (1):

$$L^n = (T \cos \theta R t) / (2 \gamma), \quad (1)$$

in which  $L$  is the depth of penetration,  $n$  is approximately equal to 2,  $T$  is the surface tension of the fluid,  $\theta$  is its contact angle on the



fibers of the sheet,  $R$  (the effective capillary radius) is a measure of the porosity of the sheet,  $t$  is the time of penetration, and  $\eta$  is the viscosity of the fluid.

The importance of high lacquer viscosities in coating porous papers is stressed by Hollabaugh (4). He found a straight line relationship between a porosity factor (porosity x thickness in inches x 1000) and the minimum viscosity of the lacquer phase required for negligible penetration of the porous surface in coating with emulsified lacquers.

Bowlby (5) mentioned the better performance with high viscosities in roll coating.

Doolittle (6), in discussing coating with vinylite and a flash baking technique, pointed out the advantage of a short drying time in preventing penetration. However, he attributed the greatest cause of failure of thin films to the wicking action of wild fibers.

Stewart and Hook (7) concluded that high surface tension is responsible for the thinning out or drawing away of lacquer films at sharp edges. Although their observations were made on metal plates and wooden blocks, the same effect may be expected for wild or projecting fibers.

A general treatment of lacquers, their formulation, properties, and vagaries have been discussed in a number of publications. One which has been most helpful is the first volume of the treatise edited by Mattiello (8), particularly the chapter by Bogin on lacquer solvents.

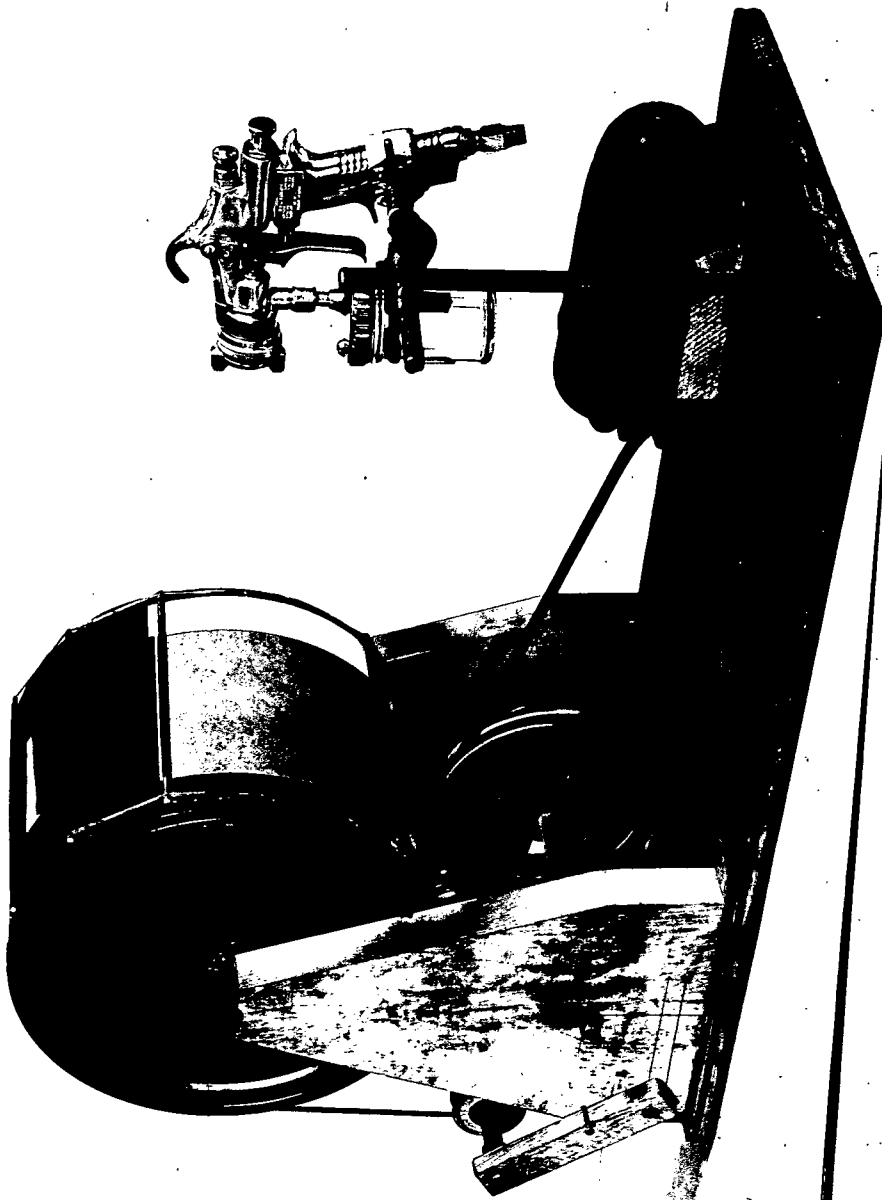
## APPROACH, APPARATUS, AND METHODS

With the objective of gaining greater insight into the mechanism of film formation in the protective coating of paper and paper-board, the following approach was used: Spraying was adopted as the coating technique because this process is suitable for the coating of formed containers. The field of investigation was restricted further by the selection of nitrocellulose as the film-forming constituent of the spraying lacquers. The study was then resolved into the following divisions: first, the standardization, in so far as possible, of the conditions of spraying; second, the variation of the properties of the nitrocellulose lacquers associated with changes in formulation; third, both absolute and relative measurement of these properties for comparison during the formation and drying of the films; fourth, the study of the spray coating of cellophane, a greaseproof paper, and three paper-boards of different porosities; and fifth, the measurement of the continuity of the dry films of various weights formed from each lacquer.

### THE SPRAYING TECHNIQUE

The paper and board samples were mounted on a revolving drum and sprayed with a commercial spray gun mounted in a fixed position. The apparatus in its final form is shown in Figure 1.

A DeVilbiss type MBC spray gun, supplied with cap 30 and nozzle E, was used. The gun was mounted at a distance of 10 inches from the periphery of the drum with the spray fan in a plane with the drum axis. The gun was adjusted for a fan width of 10 and the fluid control



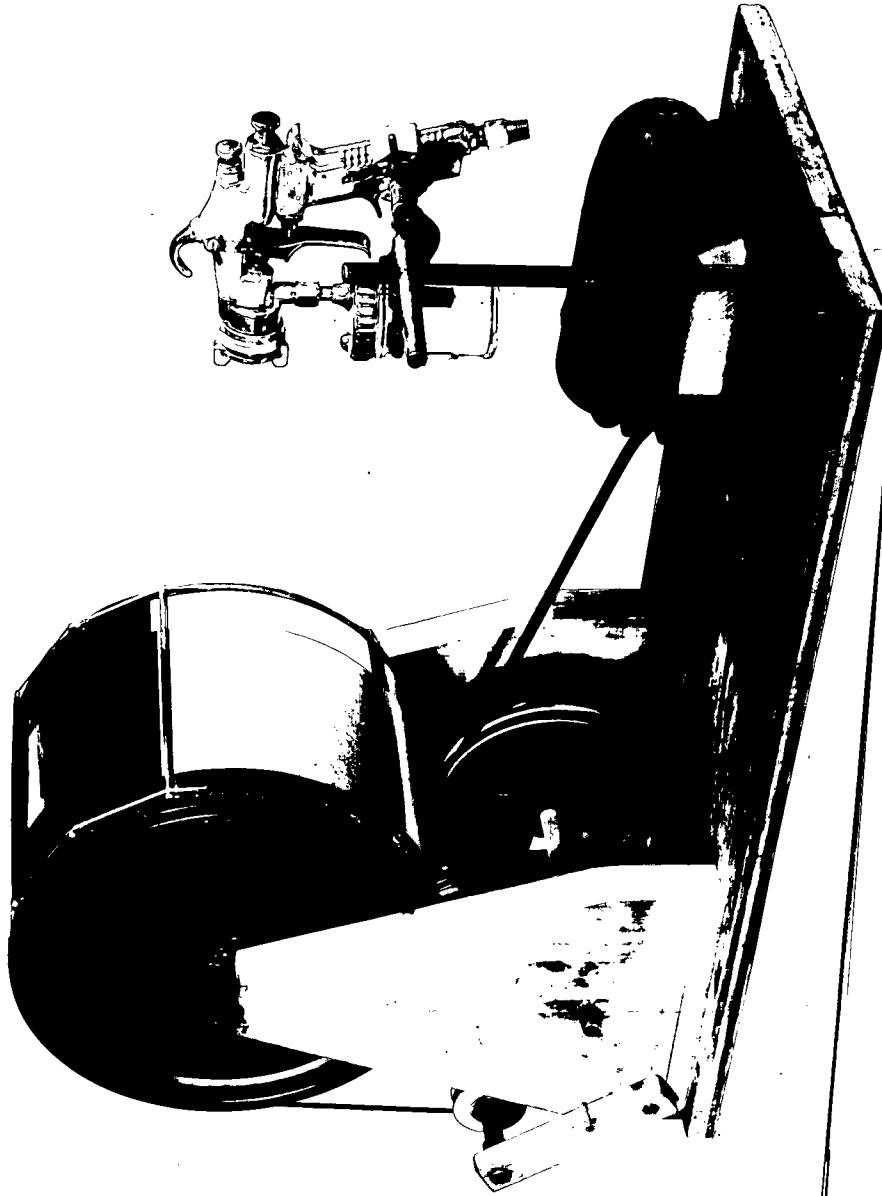
Diameter of drum: 11.5 inches

FIGURE 1 Distance from spray gun to drum: 10 inches

SPRAYING APPARATUS

1000

100  
100  
100



Diameter of drum: 11.5 inches

FIGURE 1 Distance from spray gun to drum: 10 inches

SPRAYING APPARATUS

valve opened 4 revolutions (completely open). The fluid cup was filled before each spraying.

Compressed nitrogen was used in spraying to eliminate the possibility of water droplets in the spraying air, as might be the case were a compressor employed. The nitrogen tank was connected through a reduction valve and 20 feet of tubing to the gun. Before each spraying, the reduction valve gage was adjusted to read 30 pounds per square inch when the trigger of the gun was depressed. All sprayings except one were made in a spray-hood with the exhaust fan in operation.

The drum was made by cutting down a 5-gallon can and soldering the lid in the open end. It was driven through a pair of steel pulleys by a Precision Scientific Company variable-speed motor of the Kilmaster type. The maximum time of rotation was 41, and the minimum was 2.3 seconds per revolution, corresponding to peripheral speeds of 0.072 and 1.28 feet per second (2.95 feet per revolution). The speed was determined by measuring the time for one or more revolutions with a stop watch. A special fitting was made to replace the usual chuck supplied with the motor, to adapt it for belt drive.

The specimens were mounted on the drum by means of rubber bands and wooden crosspieces, as indicated on the lower portion of the drum in Figure 1. In some sprayings, a strip of paper covered one side of the specimens so that a portion was not coated.

After spraying, the drum was allowed to rotate until the films were dry to the touch. The specimens were then removed and hung in another room for at least 2 days before testing.

Tin plates, used for film-weight determinations, were fastened on the drum under a mask. It had an opening 5 cm. wide and 10 cm. long. A film-weight plate appears at the top of the drum in Figure 1. The plates were dried at 50° C. to constant weight to give an average dry weight for each spraying.

Different film weights were obtained by using different drum speeds. Only one coat was applied in the regular sprayings to obviate the further variables introduced by applying multiple coats.

Some variables of spraying were not completely controlled, such as those arising from the lacquers themselves. The relatively small differences resulting from longer spraying time and slower rotation of the drum in producing heavy coats, as compared with the shorter time and more rapid rotation for lighter films, could not be avoided. The humidity and, to a certain extent, the temperature of the air in the spray booth were some of the other variables.

#### LACQUERS

In preliminary experiments, a commercial lacquer--Roger's brushing lacquer for linoleum--was diluted to spraying viscosity with a 50:50 mixture of toluene and ethyl acetate and colored with Victoria green. It is designated as Lacquer R. Six other lacquers were prepared, the first of which was still preliminary in nature. The formulations are given in Tables I, II, and III.

TABLE I

FORMULA FOR LACQUER R

Roger's lacquer	200 ml.
Ethyl acetate	24.5 ml.
Toluene	24.5 ml.
Victoria green	0.04 g.

TABLE II

FORMULA FOR LACQUER 1

Nitrocellulose (16 sec.)	28 g.
Alcohol in nitrocellulose	13.5 g.
Dibutyl phthalate	12 g.
Sudan III	0.08 g.
Toluene	450 ml.
Butyl acetate	225 ml.
Ethyl acetate	225 ml.

TABLE III

FORMULAS FOR LACQUERS 2 TO 6

Lacquer 2

Nitrocellulose	28 g.
Type	162 sec.
Dibutyl phthalate	12 g.
Sudan III	0.08 g.
Solvent	1490 ml.

Lacquer 3

Nitrocellulose	35 g.
Type	16 sec.
Dibutyl phthalate	15 g.
Sudan III	0.10 g.
Solvent	1128 ml.

Lacquer 4

Nitrocellulose	49 g.
Type	5-6 sec.
Dibutyl phthalate	21 g.
Sudan III	0.14 g.
Solvent	1250 ml.

TABLE III (Continued)

FORMULAS FOR LACQUERS 2 TO 6

Lacquer 5

Nitrocellulose	77 g.
Type	0.5 sec.
Dibutyl phthalate	33 g.
Sudan III	0.22 g.
Solvent	877 ml.

Lacquer 6

Nitrocellulose	84 g.
Type	0.25 sec.
Dibutyl phthalate	36 g.
Sudan III	0.24 g.
Solvent	701 ml.

The solvent mixture used for Lacquers 2 to 6 was the same.

Its composition is given in Table IV.

TABLE IV

SOLVENT COMPOSITION FOR LACQUERS 2 TO 6

Solvent or Diluent	Percentage by Volume
Toluene	50
Butyl acetate	20
Ethyl acetate	10
Butyl alcohol	10
Ethyl alcohol	10

Dyes were added to make the thin sprayed films visible.

Victoria green had a higher tinctorial strength than Sudan III, but was not soluble in the vehicle used for Lacquer 1. The choice of dye was made from observations of the solubility in benzene, alcohol, and acetone and of the relative tinctorial strength in solution and on paper of the following dyes: DuPont Nigrosine SSB powder, DuPont Oil black BG, DuPont Victoria green, DuPont Methylene blue, DuPont Oil brown H, DuPont Safranin T extra, and Sudan III.



In an effort to utilize the high tinctorial strength of the basic dyes, attempts were made to prepare the oil-soluble bases of Victoria green, Methylene blue, and Safranine. Water solutions were treated with ammonium or sodium hydroxide, and extracted with ether or benzene. The bases--yellow, purple, and red, respectively--were of low tinctorial strength and, except for Victoria green, were difficult to prepare. Solutions of the bases poured onto paper returned to the color of the salt upon drying and exposure to the air.

Formation of lakes of the three basic dyes with Pontacyl Fast red AS gave acetone-soluble, water- and oil-insoluble dyestuffs of medium tinctorial strength.

The nitrocellulose samples used in preparing Lacquers 1 to 6 were furnished by the Hercules Powder Company. The percentages of alcohol with which the samples were shipped were approximately determined by drying a portion of each in a weighing bottle at 50° C. Such a value was used for calculation of the weights of nitrocellulose and alcohol employed in formulating Lacquer 1. However, because of possible non-uniformity in the samples and evaporation losses during weighing, this method of formulation was not considered to be sufficiently accurate. The nitrocelluloses for Lacquers 2 to 6 were dried at 50° C. until there was no odor of alcohol. They were then weighed for the lacquer formulation.

In preparing the lacquers, the nitrocellulose, dibutyl phthalate, and Sudan III were weighed out and placed in 2-quart Mason jars. A portion of the vehicle was added, and the jars were sealed and then

shaken. In a like manner, more solvent was added until the solutions approached the spraying viscosity of 40 centipoises, which was chosen for all the lacquers. This value is in the range of viscosity usually employed for spraying. The final viscosity was approached by successive smaller additions of solvent, and was not reached until the lacquers had been allowed to stand overnight to effect good dispersion. Proper dilution to the required viscosity was simplified by reference to a plot of logarithm of viscosity versus concentration. At low viscosities, the curves were found to be nearly straight lines and to approach a common origin at zero concentration.

The lacquers were stored in the jars. No appreciable changes were observed during the storage time.

#### MEASUREMENT OF LACQUER PROPERTIES

Unless otherwise noted, all the measurements of the physical properties of the lacquers were made at 25° C. A large battery jar, filled with water and equipped with a motor-driven stirrer and bayonet immersion heater, was used as a constant temperature bath for the measurement of viscosity, specific gravity, and interfacial tension. The temperature was held within  $\pm 0.1^\circ$  C. and was checked before and during the course of each measurement.

The concentration (percentage of nonvolatile material) of the lacquers was determined by pipetting samples into weighing bottles and drying at 50° C. to constant weight. The nonvolatile portion is considered to be the nitrocellulose, the dibutyl phthalate, the small

amount of dyestuff, and the tenaciously held solvent (and resins in the case of the commercial lacquer).

Specific gravities were determined by the use of a 10-ml. pycnometer bottle calibrated with boiled distilled water. They are referred to water at 25° C. and are uncorrected for differential air buoyancy.

Viscosities were determined in a simple eccentric falling ball viscosimeter of the Hoeppler type (9), illustrated on the right in Figure 2. It consists of Pyrex tubing, approximately 6 ml. in bore, drawn out at the lower end. The outside of the tube bears etched marks at intervals of 2, 1, 3, 5, 5, and 5 cm., starting at a point 5 cm. from the top. A rubber policeman closes the lower end and a glass plug closes the top, thus reducing evaporation losses. A stand and special clamp held the tube at a constant angle of about 10 degrees from the vertical. Nine steel bearing balls, of 7/32-, 6/32-, and 5/32-inch nominal diameters, were used.

The operation of the viscosimeter is based on the empirical principle that, in the region of viscous flow, the rate of fall for any given ball and tube diameter is proportional to the difference in density between the ball and the fluid and inversely proportional to the viscosity of the fluid. For a uniform tube, after reaching an equilibrium rate, the time of fall over a given distance is then proportional to the quotient of the viscosity and the density difference. This is expressed in Equation (2).

$$t = k\eta/(\rho_b - \rho_l). \quad (2)$$

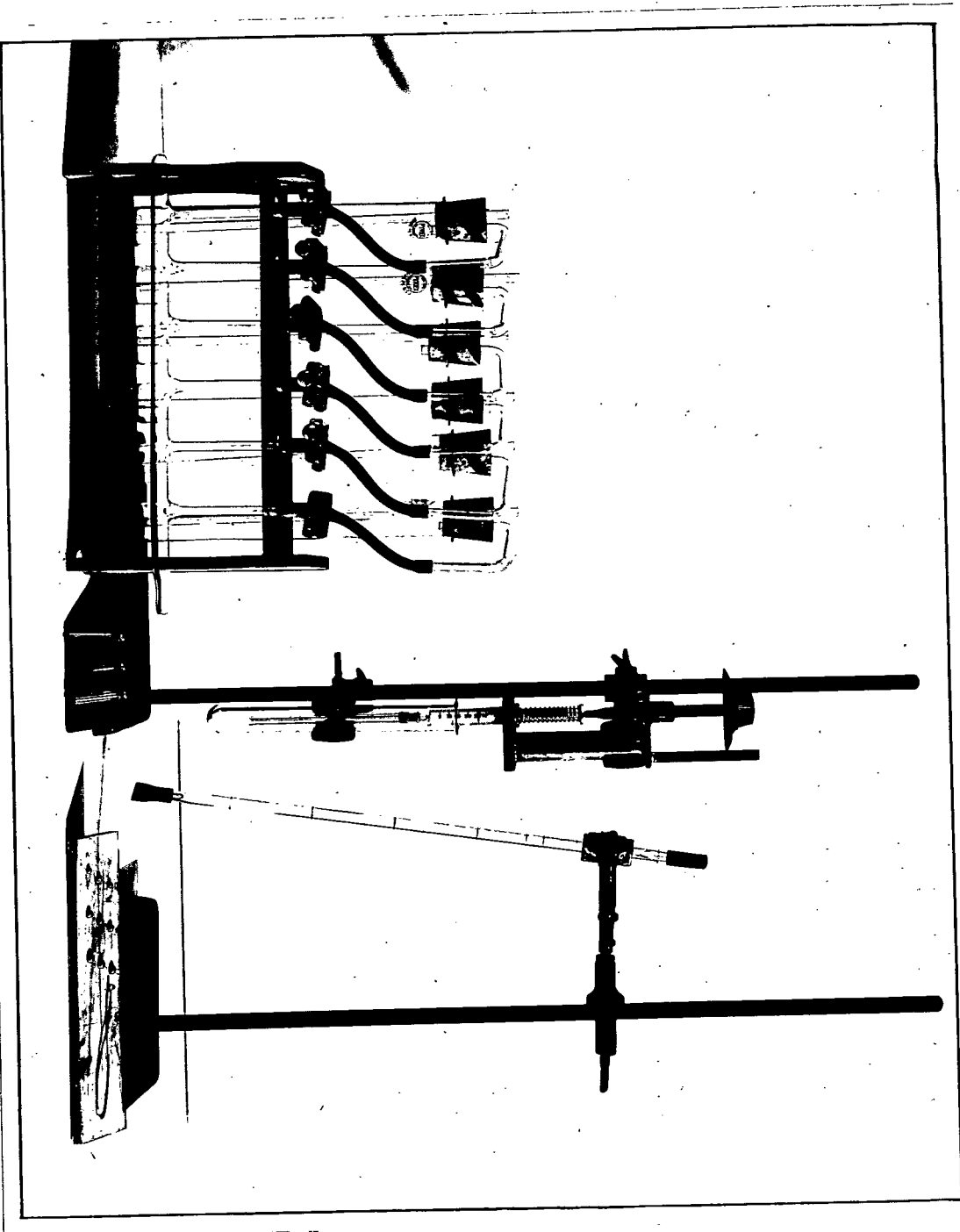


FIGURE 2

EVAPORATION, INTERFACIAL SURFACE TENSION, AND VISCOSITY APPARATUS

14-5

100  
100  
100

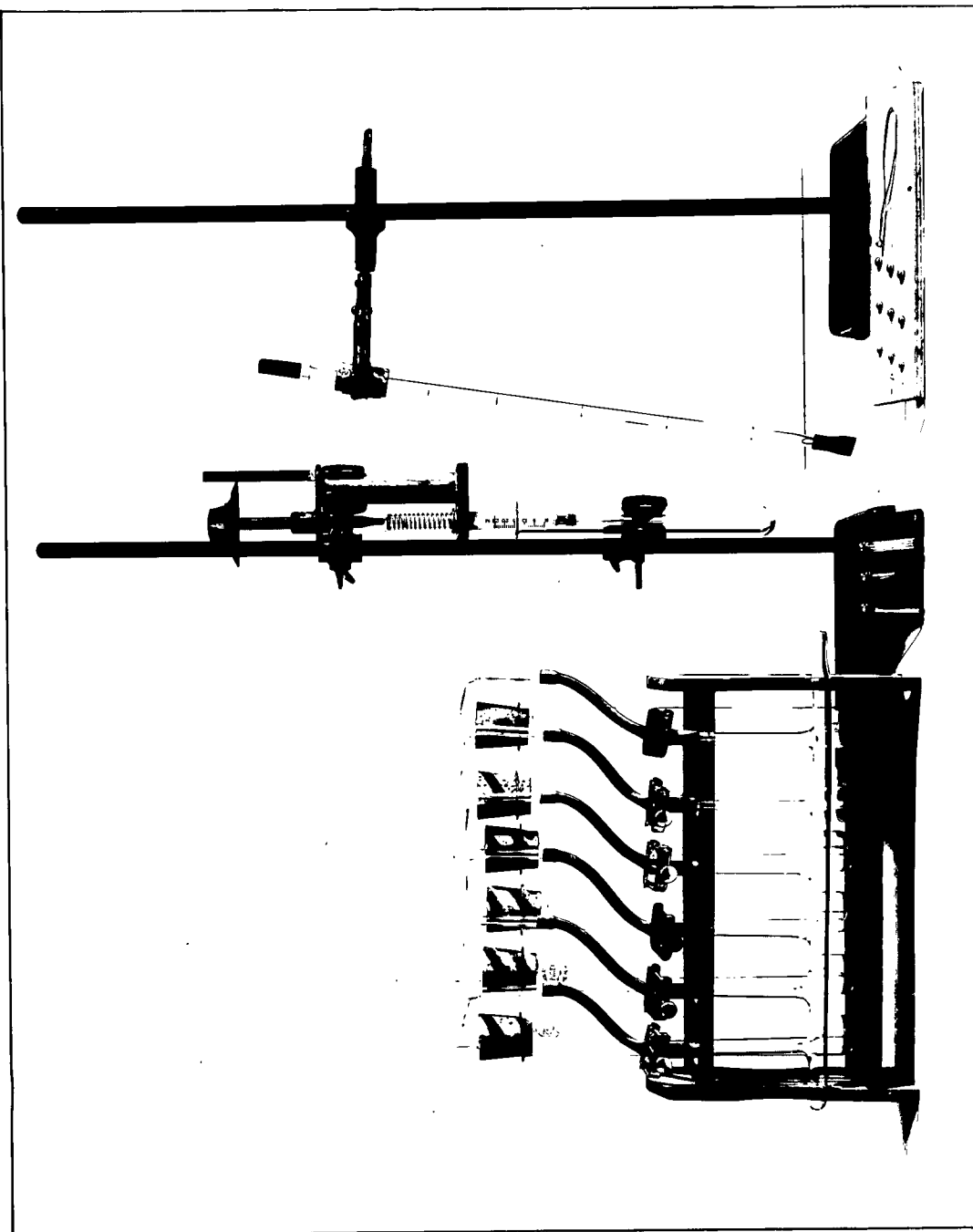


FIGURE 2  
EVAPORATION, INTERFACIAL SURFACE TENSION, AND VISCOSITY APPARATUS

where  $t$  is the time of fall,  $k$  is a constant,  $\eta$  is the viscosity of the fluid,  $\rho_b$  is the density of the ball, and  $\rho_l$  is the density of the liquid.

Equation (2) may be rewritten to express the viscosity as a function of the density difference and the time of fall:

$$\eta = k_b (\rho_b - \rho_l) t, \quad (3)$$

where  $k_b$ , the ball constant, is  $1/k$ .

Equation (3) will still hold for a round tube which is not absolutely uniform in bore provided the change in rate of fall caused by change in tube diameter is small enough so that acceleration effects are negligible, because the simple theory will still hold for any differential length. At small rates of fall, changes in rate must be correspondingly small. If the time of fall over every differential length remains proportional to viscosity and inversely proportional to the density difference (each of which is constant), the total time over the total distance must also be proportional to their quotient;  $k_b$  then becomes an average value.

Much the same reasoning may be used for a tube which is not round; in any event, for small deviations the effect should be of the second order.

Because the tube employed was not uniform, different constants were determined for the different distances. The shorter intervals at the top were intended for use with very viscous lacquers. Actually, most of the measurements were made over the first 5-cm. interval.

The ball constants were determined by standardization with U.S.P. glycerin using the viscosity data of Sheely (10), and by comparison of one ball against another in castor oil and sucrose solution.

The density of the balls was calculated from their weights and the volumes computed from their nominal sizes. The use of specific gravity instead of density of the lacquers in the calculation of the density difference does not introduce an appreciable error.

In use, the viscometer was filled to the top mark in the same manner as a pipet, the ends were closed with the rubber policeman and plug, and the tube was fastened in the holder. The stand was placed in a fixed position beside the constant temperature bath, with the tube immersed to the clamp. After at least 15 minutes, the plug was removed, a ball was dropped in the top of the tube, and the time of fall between two marks was measured with a stop watch. The time of fall of two or more balls was determined. Check values rarely deviated from each other by more than 1 per cent.

The viscosity apparatus has the following advantages: It is easy to fill and clean, and requires only a small amount of fluid. It is simple to use, and checks may be run quickly. By employing balls of different sizes, one piece of apparatus suffices for a wide range of viscosity. The uncertainty in centering which would arise for a coaxial falling ball viscometer of similar fluid capacity is absent.

A Cenco-du Noy interfacial tensiometer was used in surface tension determinations. The instrument was adjusted for direct reading

in dynes per cm., following the standard procedure using a small weight (11). The corrections of Harkins and Jordan (12) were applied. The measurements are considered to be accurate to within 0.1 dyne per cm. The lacquer samples were protected somewhat from evaporation by covering the dish containing them with a metal plate having a small strip cut out to accommodate the ring suspension. No special precautions with respect to temperature were taken other than maintenance of the room within reasonable limits. A variation of several degrees was possible and represents the greatest source of error.

Interfacial tension against water has been suggested and applied by Gardner (13) in the differentiation of oils for varnishes. It was thought that such a measurement might be applied to lacquers and possibly would be indicative of their wetting characteristics on paper. Furthermore, to reduce the possibility of gelling at the interface, which might occur with water, and in the hope of finding a different behavior which would be more like that of cellulose, measurements of interfacial tension of lacquer against 95 per cent glycerin were also made. For purposes of comparison and better interpretation of results, a number of interfacial tension determinations were likewise carried out with organic liquids against glycerin.

One of the most satisfactory methods of measuring interfacial tensions is the drop-weight determination. A description of surface tension methods is found in Adam (14). The ring and capillary methods both require a knowledge of contact angles at the junction of the interface and ring or capillary wall, whereas the drop-weight method requires



only a knowledge of the densities of the two liquids in addition to the constants of the apparatus.

Unlike the ring and drop-weight methods, the capillary method does not require corrections other than for contact angle; however, it does suffer the disadvantage that it cannot be used for viscous materials.

There are two types of drop-weight apparatus. In one, perhaps the more common, the number of drops formed from a certain volume or weight of liquid is determined. In the other, the weight or volume of individual drops is determined. Considering the time required for the careful formation of the drops (1 to 10 minutes, depending upon how they are formed) and that necessary for the interface to approach equilibrium, the latter method is certainly the more convenient.

The theory and use of the drop-weight determination of surface tension have been extensively studied. In the simple theory, the weight of the drop at the time of fall is equal to the product of the surface tension of the liquid and the circumference of the tube. This is expressed in Equation (4):

$$\underline{mg} = 2\pi \underline{r}\gamma, \quad (4)$$

where  $\underline{m}$  is the mass of the drop,  $\underline{g}$  is the acceleration due to gravity,  $\underline{r}$  is the radius of the tip, and  $\gamma$  is the surface tension of the liquid.

Since the drop hangs from the boundary of the wall of the tube and the bottom (i.e., a sharp edge), contact angle is of no importance. However, the surface is not necessarily vertical at the line of contact

with the tube, and a deviation from the simple theory may be introduced. In addition, a portion of the drop remains on the end of the tube after the main body has fallen. The simple theory, expressed in Equation (4), is approached in practice for the case of a large drop and small tip.

From dimensional analysis and experimental study, Harkins and Brown (15) have shown that the shape of drops at the moment of separation is a function only of the diameter of the tip and the volume of the drops. Adam (16) points out that this reasoning is valid whether the drops are formed in air or in another liquid.

The drops free themselves from the tip by constricting in the upper portion. As they fall, the constricted portion strings out and breaks, forming one or more small drops. Often three are formed, the center one being somewhat larger than the other two, and all being quite small in comparison with the main body which has pulled away. The mechanism of breaking away has been studied by means of high speed photography. The most recent work is that of Hauser, et.al. (17).

In the measurements on lacquers, the same phenomena could be seen in slow motion. In some cases the connecting portion broke into numerous very small droplets. It is believed that differences in the stringing out which may result from viscosity differences do not introduce a large error; however, in the absence of proof it is perhaps best to consider the data, particularly with regard to the lacquers, as relative and of the right order rather than as absolute.

Harkins and Brown (15) have determined the corrections for use in drop-weight measurements, using capillary tubes with flat ends. They point out that Rayleigh (18) obtained essentially the same results using knife-edge tubes, but with somewhat larger experimental error. Hence, it was felt that their corrections could be applied in these measurements, whether the drop hangs from the inside edge (equivalent to a knife edge), or the outside edge of the tips (equivalent to a flat-ended tip).

The apparatus used for the drop-weight determination of interfacial tension appears in the center of Figure 2. The essential parts are the microburet and glass tips. The use of a hypodermic syringe and micrometer screw as a microburet and for drop-weight (volume) determination is not new (19, 20).

The buret was calibrated by weighing distilled water discharged as the micrometer screw was turned down. Over-all linearity was tested by making several determinations along the scale, and the linearity of the dial was checked by comparing the volumes of small drops of water, using a cut-off hypodermic needle as a tip. A value of  $2.830 \times 10^{-4}$  ml. per division of the dial was adopted and is considered accurate to within 0.1 per cent over the first three quarters of the range, and within 0.5 per cent for the last quarter. This accuracy is better than the reproducibility of drop volume in actual measurements.

The tips were made from Pyrex tubing by grinding one end flat on a glass plate using fine carborundum, and cementing the other end with De Khotinsky cement to joints cut from hypodermic needles. During

the grinding, the tubes were inserted in holes in a wooden block to maintain them in a vertical position and to reduce chipping. After grinding, the sizes were determined across four diameters with a measuring microscope, and the averages taken. The dimensions are given in Table V.

TABLE V  
SIZE OF TIPS USED IN DROP-WEIGHT DETERMINATION  
OF INTERFACIAL TENSIONS

Tip	Outside Radius cm.	Inside Radius cm.
1	0.3188	-
2	0.3030	0.2009
3	0.2144	0.1146
4	0.1860	-

In the determination of the interfacial tension of organic liquids against glycerin, equal volumes of the liquid and 95 per cent glycerin were placed in a test tube held in a rack in the constant temperature bath. The test tube was shaken at intervals. After allowing the layers to separate, the microburet was filled from the lower layer. A few drops were run out rather rapidly from the tip into the upper layer to "get the range," and then the time for the final period of formation for the drop was increased. The final volume was reached by turning the dial one division at a time. When further increase in time of formation no longer decreased the size of the drops, an average of the constant values was taken.

u  
A

The densities of the mutually saturated glycerin and organic liquids were determined by the pycnometer method mentioned above, and the difference calculated.

A knowledge of the density difference, the drop volume, and the radius of the tube permitted calculation of the interfacial tension by the equation,

$$\gamma_{lg} = (\underline{v}(\rho_g - \rho_l) g \underline{F})/\underline{r} \quad (5)$$

where  $\gamma_{lg}$  is the interfacial tension,  $\underline{v}$  is the drop volume,  $\rho_g$  and  $\rho_l$  are the densities of the glycerin and liquid, respectively,  $g$  is the acceleration due to gravity (980.5),  $\underline{r}$  is the radius of the tube, and  $\underline{F}$  is the correction factor (a function of the dimensionless quantity,  $\underline{v}/\underline{r}^3$ ) and includes the  $2\pi$  found in Equation (4).

The same procedure was followed in the measurement of the interfacial tension of the lacquers against glycerin and water, except that the two phases were not shaken together, since rather stable emulsions would result and contact with a large volume of water or glycerin would greatly change the solvent formulation of the lacquers. In calculation, the densities of water, the glycerin, and the lacquers were used as measured separately. Changes in the volume and density of the drop as well as of the surrounding lacquer, caused by diffusion, were sources of error. Furthermore, the drops were not as stable as would be the case if the liquids had been allowed to come to equilibrium before the measurements. It was observed that, the higher the viscosity of the lacquer, the greater was the stability. Because the forces at the interface decreased with time as a result of diffusion and the density and volume also changed, a compromise was adopted in forming the drops over a constant period of 5 minutes, rather than attempting to wait for equilibrium. In the case of the more viscous (evaporated) lacquers, a longer time was allowed so that a drop could assume its normal shape and fall, but diffusion effects were also reduced.

Advancing contact angles were determined by a drop-projection method similar to the suggested TAPPI procedure (21). A microscope equipped with a mechanical stage was tilted so that the tube was in a horizontal position. The eyepiece, mirror, and back lens of the Abbe' condenser were removed. A research microscope illuminator was directed on the condenser, and the field projected on a screen. For best results, it was found desirable to close the iris of the condenser until it began to limit the field. A strip of one of the paper or board samples was placed in a horizontal position on the crossarm of the mechanical stage, and a drop of lacquer applied with an eyedropper, the tip of which had been drawn out. A drop 2 to 3 mm. in diameter was used. The position of the sample and the drop was adjusted by means of the mechanical stage, and the image was focused on the screen using the 32-mm. objective. The angle between the projected image of the board surface and the side of the drop was measured directly with a protractor, one measurement being made on each side. A horizontal line was not used as a reference since some of the samples—e.g., the callophane—were often puckered or curved. At least four values were determined and averages taken.

Possibly the greatest source of error in the measurement of contact angles, particularly for lacquers of low viscosity, was the roughness and absorbency of some of the samples. As in the surface tension measurements, the temperature was not completely controlled. Variations in drop size and unavoidable differences in the technique of application were also sources of error. Measurements were made sufficiently quickly so that it is believed evaporation losses were not significant. Because the drops had ceased to advance when the measure-

ments were made, it may be said, with the possible exception of the most viscous lacquers, that the probable effect of errors was to give low values.

Evaporation of samples of the lacquers for the determination of the changes in their properties during drying was accomplished in the apparatus shown at the left in Figure 2. The test tubes were filled two-thirds full and air was bubbled through the lacquer to effect the desired reduction of solvent, estimated by the change in volume. A different sample of each lacquer was used for each interval. In the early, less viscous stages, efficient stirring was supplied by the current of air. The more viscous samples were stirred at intervals and allowed to approach uniformity before testing.

The rate of evaporation of the lacquers is of importance not only from the standpoint of the time of drying, but also as it affects the rate of change of the physical properties with increasing concentration. A combination of drying rate studies and the physical measurements on the evaporated lacquers permits an estimation of the changes and relative rate of change taking place in a sprayed film.

Rieger and Grove (22) discussed the various methods which have been used in evaporation rate studies. A method similar to the one developed by Rieger and Grove was employed in this work. Where they used a deflection balance, a Chainomatic analytical balance was employed. Instead of cast films on glass slides, the samples were allowed to spread over the bottom of tin lids, a heavier film being required to compensate for the reduced accuracy in weighing. Approximately 0.75 ml. of lacquer

from an eyedropper was allowed to cover the central portion (4.5 cm. in diameter, 16 sq. cm. in area) and was retained by a circular ridge in the lid. The advantage of this procedure was that a thick region resulting from surface effects was not present, as would be the case were the lid filled to the edge. A stop watch was started immediately after the film was formed. The lid was leveled on the balance pan. The door of the balance was closed to a stop  $3/8$  inch from the bottom to reduce the effect of stray air currents, and weighings were made at intervals. The temperatures in the balance case and of the room were observed throughout the determination. The films were finally dried at  $50^{\circ}$  C. to constant weight. A knowledge of the weight of the lid then permitted the calculation of film weights and concentration.

Two determinations of film weight versus time and calculated values of concentration versus time for Lacquer 2 are shown in Figure 3. Check values of the time for equivalent concentration change, corrected for difference in film weight, agreed within 2-4 per cent.

The experimental agreement with the assumption that drying time (i.e., time for the same change in concentration) is proportional to the original film weight (23) is considered good enough to justify correction of evaporation data for differences in initial film weight. Results on the evaporation of Lacquer R on lids are given in Table VI. It should be noted that the ratios given in the last column of the table are independent of film weight.

Preliminary experiments in which the film-weight plates were removed from the drum immediately after spraying and weighed at intervals



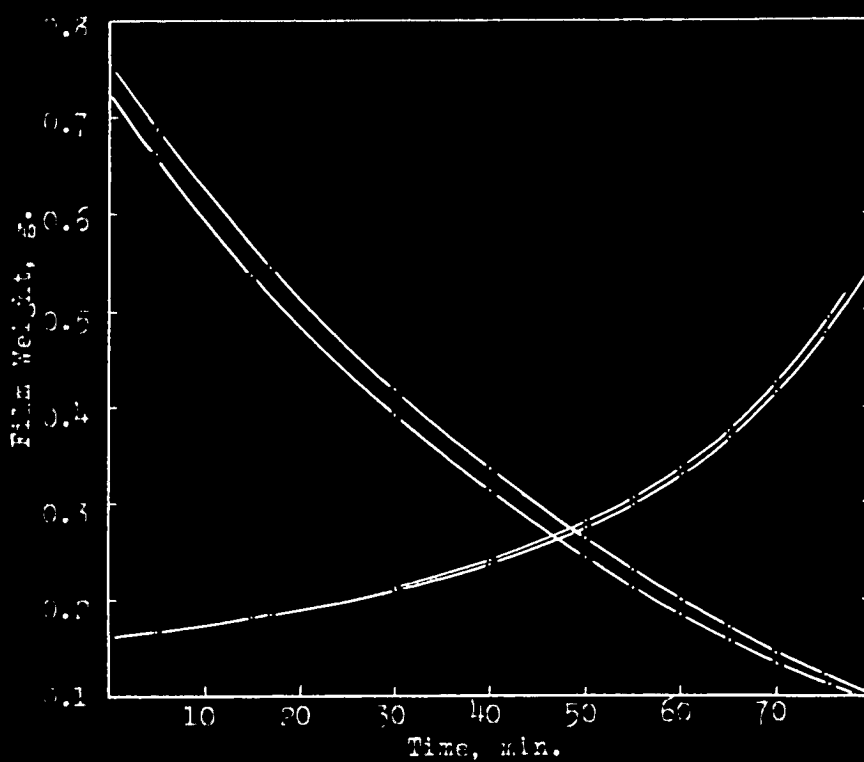


FIGURE 3

#### EVAPORATION OF LACQUER 2

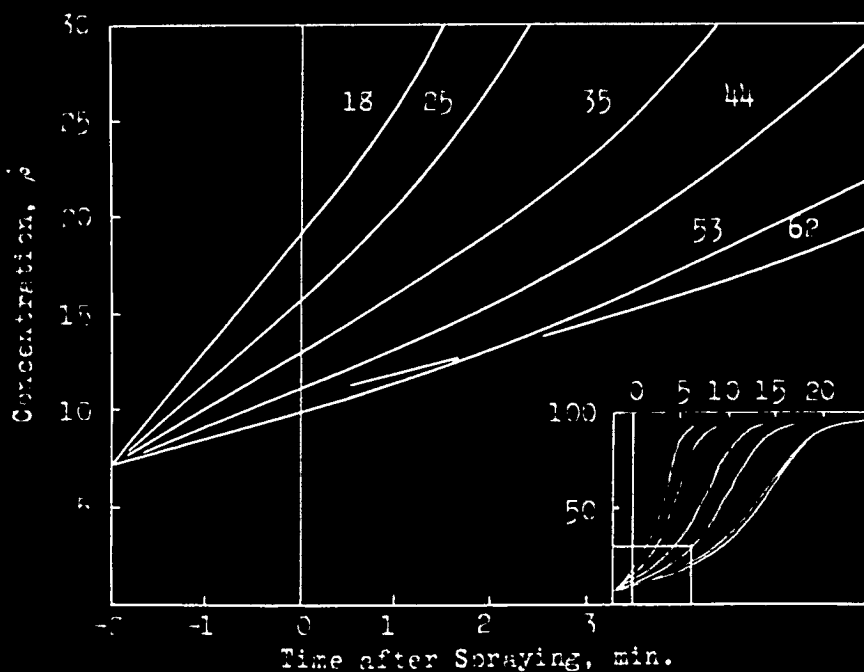


FIGURE 4

EXTRAPOLATION FOR EVAPORATION ON FILM-WEIGHT PLATE

TABLE VI

DRYING TIME AS A FUNCTION OF FILM WEIGHT

Dry Film Weight g.	Change in Concentration %	Time for Change in Concentration min.	Time for Change Dry Film Weight
0.1000	17.6 to 20	9.5	95
0.1016	17.6 20	8.0	79
0.2089	17.6 20	17.0	81
0.1000	17.6 30	61	610
0.1016	17.6 30	63	620
0.2089	17.6 30	124	590
0.1000	20 30	50.5	505
0.1016	20 30	55	540
0.2089	20 30	107	510

were not nearly as satisfactory nor as reproducible as the method finally adopted.

For a comparative study of the lacquers, it was considered desirable to represent their properties as a function of time after spraying for ideal films of unit initial weight (1 mg./sq. cm.). The results would be expected to represent qualitatively the actual changes with time in the sprayed films, and to permit estimation of relative rates. Such a procedure requires a knowledge of the lacquer concentration immediately after spraying.

Two previous studies of volatiles lost in the spraying operation have been made by Bogin. In one case, a solvent mixture was sprayed on a metal shield, which drained into a funnel to collect the unevaporated portion (24); in another, a lacquer spray was directed through a glass tube into a receiver (25). Both methods were unsatis-

factory for this work, because they did not reproduce actual spraying conditions and had the further disadvantage that relatively large quantities of lacquer would be required.

It was first hoped to determine the concentration after spraying from evaporation rate measurements on the film-weight plates. By extrapolation of the curves of concentration versus time to zero (i.e., to the time of spraying), the initial wet film concentration would be given. However, in practice the extrapolated values for sprayings of different weights did not agree, the heavier sprayings giving effectively a lower concentration—that is, a lower spraying loss. It is inconceivable that the actual percentage loss during spraying should depend upon the weight of the sprayings or, if it did, that the heavier sprayings should suffer the least loss, since they require a longer time.

Two explanations come to mind, and both may play a part. The initial evaporation rates may be greater than that measured on the balance, because the plates, originally at room temperature, are cooled by the sensible heat capacity of the cold sprayed droplets and possibly by the initial evaporation from the film. The second explanation is that a fairly constant loss in weight, above the rate measured, takes place immediately after spraying as a result of the air currents of the hood and during the transfer to the balance. Extrapolation of the curves beyond the spraying time to a point of intersection would compensate for such a constant loss, whether it be from cooling the plate or the result of air currents. By such treatment, curves for different weight films may be extrapolated to the same initial concentration.

The extrapolated portion is shown in detail for a series of sprayings with Lacquer 1 in Figure 4. The box in the lower right-hand corner shows the shape of the complete curves and is included because evaporation was allowed to proceed further than in the final method using tin lids. The numbers on the curves in Figure 4 represent the dry film weights, which are proportional to initial film weights. It may be seen that the curves for all sprayings except one can be extrapolated to the same point. The poor behavior of the heaviest spraying, not only on extrapolation but also in general relation to the other curves, must be the result of an error in dry film-weight determination, recording of time, or difference in temperature. Temperature was not checked as consistently during these measurements as it was in the final method.

Whereas the value for initial concentration obtained by extrapolation of the evaporation curves depends on the judgment used in extrapolation, and because it was found that better evaporation data could be secured with less effort in a measurement separate from the spraying operation, the study of evaporation rate on film-weight plates was abandoned. A new and simpler procedure for the determination of spraying loss also was adopted. A piece of greaseproof paper was attached in the position of the samples on the stationary drum. A fairly heavy spraying was made so that the lacquer began to sag or run; a portion of this sprayed film was immediately scraped into a puddle with a spatula and transferred to a weighing bottle, in which it was dried to constant weight. The wet weight, dry weight, and tare permitted calculation of the concentration. The result obtained for Lacquer 1 was used in the extrapolations in Figure 4.

The temperature drop during spraying was not evaluated, although changes of 14 and 16° C. are reported by Bogin (25). A knowledge of the temperature drop alone without a study of the temperature coefficients of evaporation rate, viscosity, and other variables of the lacquers could not be interpreted. The thermal interaction between the lacquer and paper samples would further complicate such a study. Instead, it is assumed that, for any particular sample, the temperature changes and the effects of the changes on the lacquers are roughly equivalent. For lacquers of similar formulation, the more volatile the solvent mixture and the greater the latent heat of vaporization, the greater the temperature drop to be expected.

#### PAPER AND BOARD SAMPLES

The samples used and their physical properties are listed in Table VII. Sample 1 was No. 300 Plain Transparent Cellulose Paper, referred to as cellophane in this report. Sample 2 was 40-pound bleached, uncalendered, uncoated greaseproof paper. Sample 7, a sulfite waxing stock, was used only in some preliminary tests, but not in the controlled sprayings. It is included because comparison makes possible a better understanding of the properties of the other boards.

The smoothness and porosity were determined on the Bekk smoothness tester (26, 27), by measuring the time in seconds required for a definite amount of air to leak between the sheet and a glass plate (for smoothness) or through the sheet (for porosity); the higher the Bekk value, the smoother or denser the sheet. Smoothness was determined by the standard procedure, in which the sample is backed with a rubber disk.

TABLE VII

## PROPERTIES OF PAPER AND BOARD SAMPLES

Sample	Material	Caliper in.	Apparent Density g./cm. <sup>3</sup>	Bekk Smoothness sec.	Bekk Porosity sec.	Porosity/Caliper	Contact Angle (Water) degrees
1	Cellophane	0.0008	1.4	∞	∞	-	very small
2	Greaseproof paper	0.0027	0.96	9.0	200,000	-	86
3	Groundwood board	0.036	0.47	1.0	1.8	0.05	104
4	Kraft lined board	0.018	0.77	23.2	11.9	0.64	80
6	Bleached sulfite lined board	0.023	0.70	13.9	7.0	0.30	98
7	Sulfite varying stock	0.018	0.81	15.4	3.0	0.17	-

In the measurement of porosity, the edges of the specimens were sealed to the glass plate with vaseline to prevent leakage. In both measurements, the time for the vacuum to drop from 380 to 360 mm. of mercury was recorded. This pressure increase corresponds to the passage of 10 ml. of air. The sheets are ranked in the same order by visual judgment as by the recorded values of smoothness and porosity. Bekk porosity divided by caliper is included in the table, as it gives a better idea of true porosity.

As would be expected, there is a correlation between apparent density and porosity. However, Sample 7 seems to be out of line. This is attributed to the fact that it is made of virgin fiber, not greatly hydrated, but calendered to give smoothness and density. In comparison with Samples 4 and 6, both of which contain hydrated or cut stock either in the liner or base. Sample 7 may be expected to have larger pores, although perhaps fewer of them, for the same density. In such a porosity measurement, pore diameter enters to the fourth power. This statement is made with the Poiseuille equation for flow in capillaries in mind (3).

The porosities of the boards do not give, in every case, a true picture of the porosities of the liners. Samples 3 and 7 were quite uniform. The liner of Sample 4 did not differ greatly from the base stock, whereas the liner of Sample 6 was certainly more porous and by visual estimation appeared to be comparable to Sample 7. The structure was so expanded in splitting the liner from the base stock that a separate measurement was considered impractical.

The contact angle of water against the samples was measured in the same manner as the contact angle of lacquer. It indicates the degree of sizing. As indicated in the section discussing the experimental data, the great differences observed for water (0 to  $104^{\circ}$ ) were not noted for lacquer.

Some nonuniformity of wetting for water was observed with a surface tester, which has been used at the Institute to predict behavior in air-knife coating, but the same effect was not found with organic liquids.

The values given in Table VII for the physical properties of the boards are typical values. During the course of the work, particularly in the testing of the dry films, a surprising amount of nonuniformity was observed. Fifty per cent variations in the porosity of any one board were found in some cases.

#### TESTING OF THE DRY FILMS

The final films were tested for continuity. A turpentine test applicable to boards was devised and, although it was later abandoned in favor of a porosity test, it deserves mention. By placing the coated side down and using a piece of tissue or thin bond paper as an indicator, the adverse effect of the thickness of the boards could be avoided and results comparable with the usual turpentine tests on coated paper obtained. A strip 1 inch wide was cut across the sprayed sample. It was placed on the indicator paper, which lay on a glass plate. Five short pieces of iron pipe, of an outside diameter of  $7/8$  inch, were



placed upright so as to cover the middle 5 inches of the sample strip. An excess of turpentine was dropped into the pipes with an eyedropper, and the time for the first spot to appear under each was observed from below. In 15-30 minutes the turpentine would work under the edges if it had not penetrated the film, and the test would have to be discontinued.

Most of the testing was carried out employing the Bekk smoothness tester. Samples 3/4-inch square were sealed, with the film side down, over the round hole (1 sq. cm. in area) in the glass plate with a little vaseline. The porosity attachment was used, and the time of fall from 500 to 480 mm. was measured or estimated from the distance fallen in 5 minutes in the case of a nearly continuous film. If no change could be detected in 5 minutes, the film was considered to be impervious. Three or four samples taken from the center of a strip across each board were tested.

The porosity test had several advantages over the turpentine test, in that less was left to the judgment of the operators, the same samples could be retested, and the time of testing was reduced.

In Figure 5, values observed with the turpentine test are plotted against those obtained with the Bekk porosity test for a number of sprayings. A correlation is evident. Corrected for blanks (values for uncoated samples), the curve would be nearer a straight line.

For the purposes of this work, zero air porosity as measured by the Bekk test defines a continuous film. In practice, the word

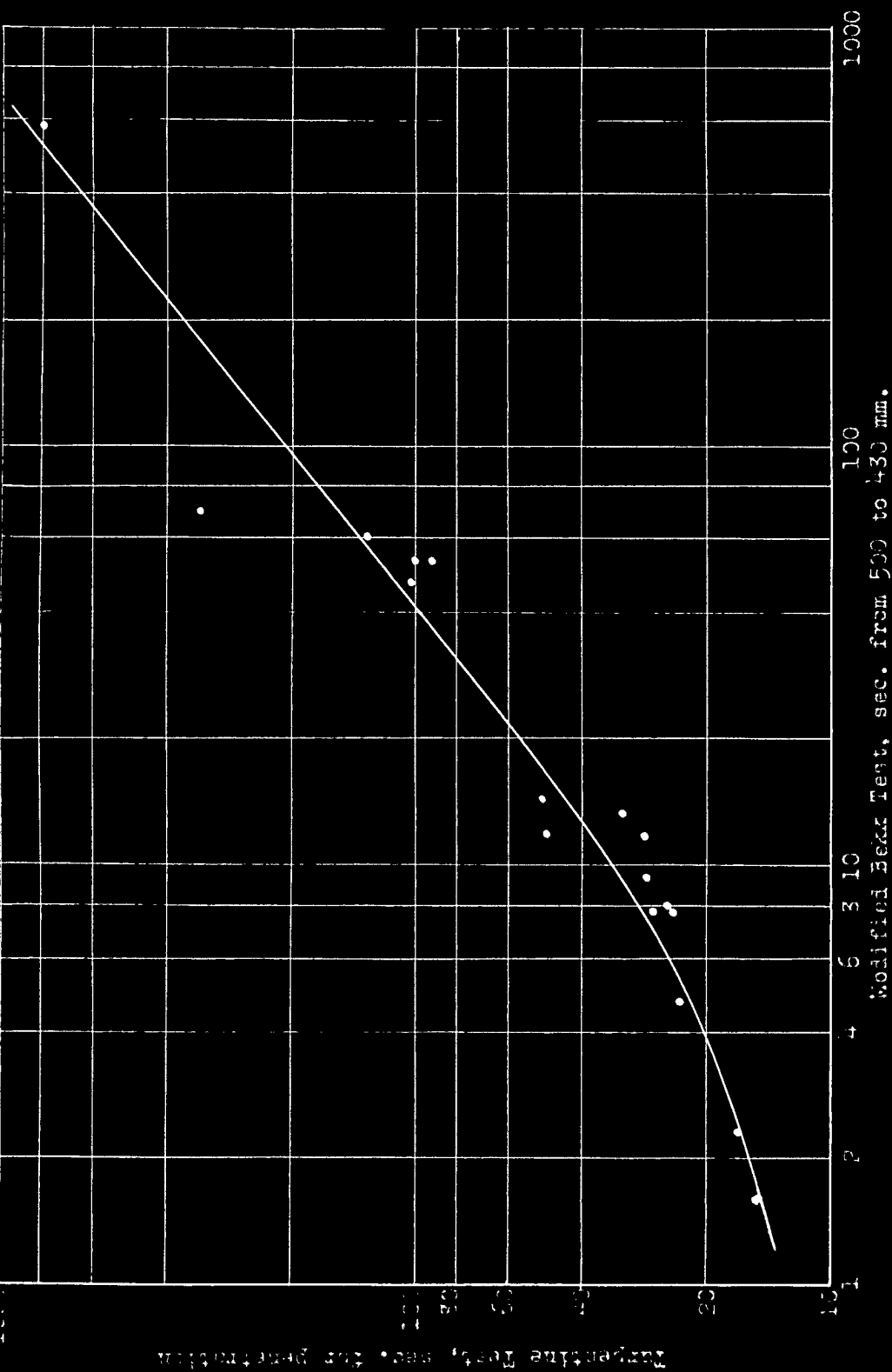


FIGURE 5  
COMPARISON OF TURPENTINE AND POROSITY TESTS

continuous is often used interchangeably with impervious. However, there is a distinction. A film which is not continuous certainly is not impervious. A film which is macroscopically continuous may be pervious to air, vapors, or liquids.

It seems justifiable to say that imperviousness for a macroscopically continuous film is a function of the film-forming material and its inherent submicroscopic structure. For instance, a cellophane sheet is found to be continuous by the Bekk test and is impervious to oil but it is slightly permeable to gases and very permeable to water vapor. A film of nitrocellulose has low permeability to gases, but is not especially good from the standpoint of water vapor. Wax films, in general, offer good resistance to water vapor but may be dissolved by oils.

In short, the first requirement of an impervious film is that it be continuous; the second requirement is that the material itself be resistant. The physical nature--i.e., density, absence or presence of cell structure, amorphous or crystalline nature, and solubility--as well as its chemical properties, determines the resistance of the film material.

The cellophane and greaseproof samples could be tested neither by a porosity nor by the turpentine test. Also, the film material was not sufficiently resistant to make water-vapor permeability of value as a test. Hence, the continuity of films on these materials was estimated by visual examination, using a microscope as well as a hand lens.

## EXPERIMENTAL DATA

The approach to the problem of studying the mechanism of film formation was divided into several sections, and it seems logical to discuss the results according to the divisions in which they fall.

The standardized conditions of spraying have been set forth in the preceding section, as well as the formulations of the lacquers and the physical properties of the samples sprayed. The techniques of measurement and the apparatus developed may also be considered a part of the thesis results and likewise have been discussed in the foregoing section, so that for the most part no further consideration need be given them.

For purposes of discussion, the balance of the experimental data will be presented under the following headings: physical properties of the lacquers, changes during the spraying operation, tests on dry films and, finally, other observations not directly related to film formation.

### PROPERTIES OF THE LACQUERS

The values obtained in the measurement of the physical properties of the original lacquers and evaporated samples are given in Table VIII. A knowledge of the specific gravity (0.855) of the solvent mixture and the formulations of Lacquers 2 to 6 permits a calculation of the concentrations of the original lacquers from the weights of the nonvolatile portion and the solvent. The calculated values were found to be in good agreement with those found in Table VIII, as determined by measurement. A comparison is made in Table IX.

TABLE VIII

PHYSICAL PROPERTIES OF THE LACQUERS AT VARIOUS CONCENTRATIONS DETERMINED ON  
ORIGINAL LACQUERS AND EVAPORATED SAMPLES

Lacquer	Concen- tration %	Specific Gravity	Viscosity cps.	Surface Tension, dynes/cm.	Interfacial Tensions, dynes/cm.		Contact Angles, degrees					
					Glycerin	Water	Paper or Board		Samples		Tin Plate	
							1	2	3	4	5	6
R	17.6	0.9194	40.5	25.5	1.9	4.2	21	21	8	20	18	—
	23.7	0.9434	280	25.7	3.3	5.7	32	33	29	36	34	—
	38.8	0.96	18,000	26.3	6.3	—	76	73	77	73	74	—
1	4.77	0.8889	40.1	25.4	2.6	3.6	20	25	10	25	20	21
	6.77	0.8946	181	25.8	3.1	4.9	37	35	30	42	35	—
	8.30	0.8992	454	26.1	3.4	5.1	45	44	42	46	45	—
	11.75	0.908	2,010	26.2	3.8	5.4	58	56	60	62	58	—
2	3.04	0.8658	40.2	25.5	1.6	2.2	25	25	—	28	24	—
	5.67	0.876	403	25.6	—	—	—	—	—	37	—	—
	7.96	0.884	1,660	25.8	—	—	—	—	—	59	—	—
	12.97	0.903	16,600	25.9	—	—	—	—	—	72	—	—
3	4.95	0.8726	40.3	25.6	1.4	2.0	25	25	—	28	25	—
	9.07	0.888	384	25.7	—	—	—	—	—	38	—	—
	13.80	0.906	2,240	25.9	—	—	—	—	—	58	—	—
	21.22	0.935	21,500	26.0	—	—	—	—	—	77	—	—
4	6.00	0.8770	39.7	25.7	1.4	1.9	30	28	—	28	26	29
	10.76	0.895	307	25.8	—	—	—	—	—	44	—	41
	16.18	0.916	1,820	25.9	—	—	—	—	—	57	—	55
	29.3	0.965	54,500	26.3	—	—	—	—	—	104	—	97
5	12.62	0.9018	39.8	25.9	1.1	2.2	25	24	—	28	21	26
	24.2	0.946	644	26.3	—	—	—	—	—	54	—	50
	33.2	0.980	4,290	26.7	—	—	—	—	—	69	—	64
	45.5	1.027	49,500	27.2	—	—	—	—	—	—	—	—
6	16.40	0.9167	39.6	26.1	1.0	1.8	26	24	—	27	21	—
	30.3	0.969	692	26.6	—	—	—	—	—	51	—	45
	40.9	1.009	6,050	26.9	—	—	—	—	—	76	—	72
	49.1	1.040	35,100	27.5	—	—	—	—	—	—	—	—

TABLE IX

COMPARISON OF MEASURED CONCENTRATIONS OF ORIGINAL LACQUERS  
AND VALUES CALCULATED FROM THEIR FORMULAS

Lacquer	Measured Concentration %	Calculated Concentration %
2	3.04	3.04
3	4.95	4.93
4	6.00	6.15
5	12.62	12.80
6	16.40	16.70

The small differences may be the result of inaccuracy in weighing the nitrocellulose or in measuring the solvent, since an ordinary platform balance and graduated cylinders were used, or they may be the result of incomplete removal of the alcohol in the nitro-cellulose samples.

The specific gravities probably are not of great importance in film formation, even though they might be employed in correcting film weight to film volume or thickness; however, they do enter into surface tension, interfacial tension, and viscosity measurements.

In the measurements on the original and evaporated samples of Lacquer 1, specific gravity was found to be nearly a linear function of concentration; the values obtained for the original Lacquers 2 to 6 could be quite accurately expressed by the linear equation

$$\rho = 0.854 + 0.00380 \underline{C}, \quad (6)$$

where  $\rho$  is the specific gravity and  $\underline{C}$  is the concentration or percentage of nonvolatile material.

The values for specific gravities reported to four decimal places in Table VIII were measured. The other values were estimated by extrapolation for Lacquers R and 1, and from Equation (6) for Lacquers 2 to 6. Whereas no interfacial tension measurements were made on the evaporated samples of Lacquers 2 to 6, greater accuracy is not required—i.e., in the calculation of viscosities and surface tensions.

The viscosities of the original lacquers were essentially the same, with a total range from 39.6 to 40.5 centipoises.

The values of viscosity versus concentration have been plotted in Figure 6. Each curve bears the number of the corresponding lacquer. Those for Lacquers 1 to 6, in which the nonvolatile composition differs only in the nitrocellulose type (inherent viscosity), represent a definite family. Lacquers 1 and 3 had the same nonvolatile composition, but differed in solvent composition. The greater dilution required to reach spraying viscosity, as well as the more rapid increase of viscosity with concentration for Lacquer 1 as compared with Lacquer 3, may be attributed to the greater alcohol content of the latter, alcohol being effective in decreasing viscosity in the presence of both a true solvent and a diluent.

The more rapid increase in viscosity for Lacquer R and non-conformity with the family of curves for the other lacquers may be attributed to its resin content.

All the curves may be expected to rise more sharply at high concentrations if they are to give solid films, as they do. Such an

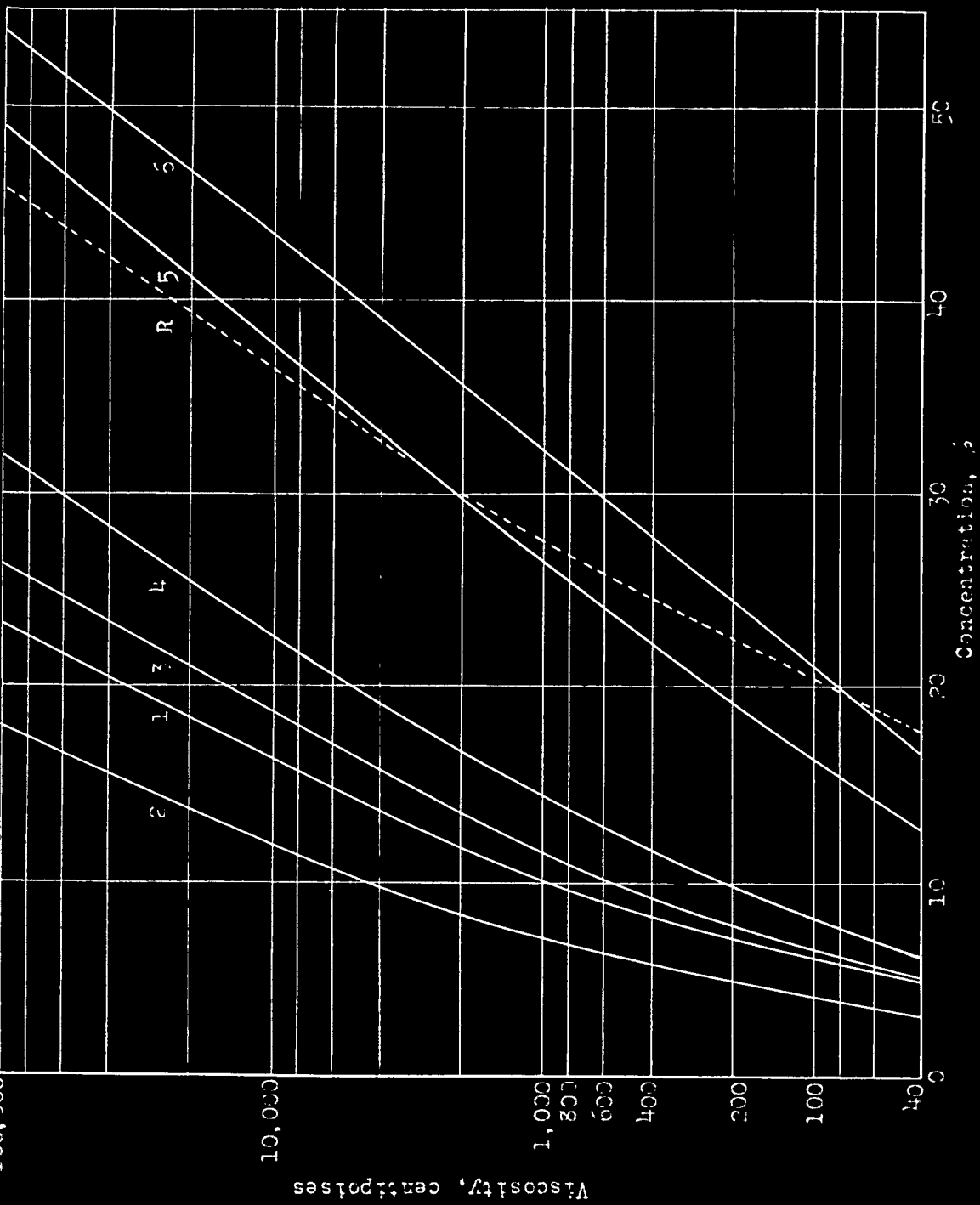


FIGURE 5

RELATIONSHIP BETWEEN VISCOSITY AND CONCENTRATION OF A SUBSTANCE



increase in slope appears for Lacquer 6, the most concentrated lacquer.

The surface tensions of the unevaporated lacquers ranged from 25.4 to 26.1 dynes per cm., and increased with increasing concentration. The highest value measured for the evaporated samples was 27.5 dynes per cm. for Lacquer 6. The lowest value, 25.5 dynes per cm., in the series of Lacquers 2 to 6 corresponded to that observed for the solvent mixture. Had petroleum thinners instead of toluene been used as diluents, lower surface tensions would have been expected in accordance with the findings of Stewart and Hook (7). The increase with evaporation probably is not the result of increasing nitrocellulose concentration, but of variation in the solvent composition. In evaporation, the more volatile components, as well as those of lower surface tension, are lost more rapidly. In the original lacquers (2 to 6), the quantity of dibutyl phthalate increases with increasing concentration. It may be considered as a part of the solvent in the liquid lacquers and has the relatively high surface tension of 32.4 dynes per cm.

Interfacial tensions of the lacquers against 95 per cent glycerin and water were not determined for all the evaporated samples. In the case of Lacquers R and 1, both interfacial tensions were found to increase with increasing concentration, the effect being more rapid for Lacquer R than for Lacquer 1. The increase for Lacquer 1 from 2.6 to 3.8 dynes per cm. against glycerin and from 3.6 to 5.4 dynes per cm. against water may be fictitious and may be caused by the effect of increasing lacquer viscosity on diffusion. Values obtained for the larger first drops, which were rapidly formed, were more uniform in the evaporation series and corresponded more nearly to the values observed for drops

formed slowly at high concentrations and viscosities. On the contrary, the initial drop size for Lacquer R increased with increasing concentration. The difference in behavior is attributed either to the loss of alcohol during evaporation or to the different nature of the non-volatile content (resins) of the latter.

Lacquer 1 was formulated with a minimum of alcohol, with the idea of obtaining a lacquer of high interfacial tension against glycerin and water. A value of about 8 dynes per cm. or more was expected for glycerin. The low value of approximately 3 dynes per cm. was a distinct surprise. Approximate interfacial tensions against glycerin of various combinations of the materials used in formulating the lacquer were roughly measured to determine the cause of the low value. The results are presented in Table X.

TABLE X  
APPROXIMATE INTERFACIAL TENSIONS AGAINST GLYCERIN

Materials	Interfacial Tension dynes/cm.
Butyl acetate	7
Butyl acetate Sudan III	7.5
Butyl acetate, 10 ml. Ethyl alcohol, 0.1 ml.	6
Butyl acetate, 5 ml. Ethyl acetate, 5 ml. Toluene, 10 ml. Ethyl alcohol, 0.3 ml.	9
Butyl acetate, 5 ml. Ethyl acetate, 5 ml. Toluene, 10 ml. Ethyl alcohol, 0.6 ml.	7.5
Butyl acetate Dry nitrocellulose	3
Butyl acetate More dry nitrocellulose	2.5
Butyl acetate Dry nitrocellulose Dibutyl phthalate	3

The conclusion is reached that the nitrocellulose itself is surface active; considering the colloidal nature of the solution and the polar as well as the hydroxylic nature of this material, the low value of the interfacial tension should have been no surprise at all.

In the measurement of interfacial tension of the original lacquers (2 to 6), the drops were quite unstable. The low values, 1 to 1.5 dynes per cm. against glycerin and 2 dynes per cm. against water, may be attributed to the alcohol content of the solvent. Values of approximately 3 dynes per cm. against glycerin and 1.5 to 4 dynes per cm. against water were obtained for the solvent mixture. In the series of unevaporated lacquers, the value against water remains about the same, whereas that against glycerin decreases with increasing concentration in accordance with the surface activity already observed for the nitrocellulose.

No evidence of gelling of the lacquers at the drop interface was found; however, upon standing, the attenuated lacquer films between the drops which had settled to the bottom of the test tubes had a blushed or milky appearance when water was used.

In the evaporation series for Lacquers R and L, both interfacial tension and advancing contact angle increased with increasing concentration. It is reasonable to expect a correlation between these two measures of surface properties; upon cursory inspection, the results for the two lacquers might be taken as proof of a relationship. However, a plot of contact angle versus viscosity (the solid points, Figure 7) for all the lacquers on board Sample 4 suggests that advancing contact angle, as measured, is a function of viscosity and, consequently,

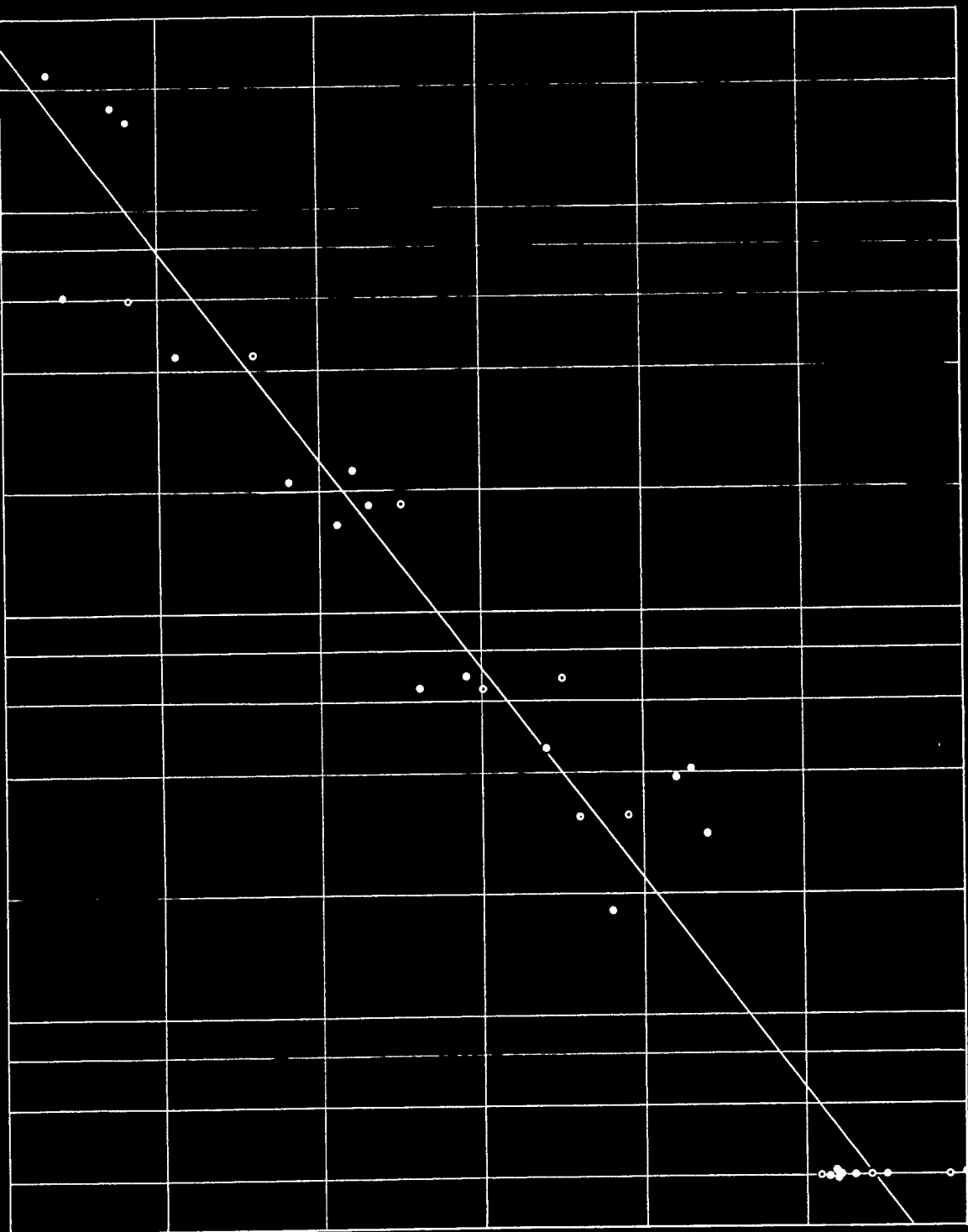


Figure 1: Scatter plot showing a negative linear correlation between two variables.

comparisons may be made only at the same viscosities. In general, the points for individual lacquers do not lie on straight lines or even smooth curves, so that the scattering of the points from a single line probably represents experimental error. However, the three points for Lacquer R do lie very close to a straight line, and only three points for all the other lacquers lie below that line. Since Lacquer R has a higher interfacial tension than the other lacquers, the opposite conclusion would be reached—namely, that advancing contact angle on paper decreases with increasing interfacial tension against glycerin or water. With so little evidence, it is better to draw no conclusion at all.

The surface tensions, discussed above, are nearly the same at any viscosity for all the lacquers, and in the range studied do not increase markedly with evaporation. Therefore, it seems justifiable to disregard them in the discussion of contact angle.

Although the paper and board samples showed considerable differences in the contact angles of water, this was not true in the case of the lacquers (see Tables VII and VIII). The results on the various paper or board samples for the evaporation series of Lacquers R and 1 and the initial Lacquers 2 to 6 may be considered the same within the range of experimental error. The low values against board Sample 3 at low lacquer viscosities were caused by the rapid penetration of the lacquers into the sample and cannot be considered as a true measure of contact angle.

Some doubt might exist as to whether the true contact angle has been measured even for the dense and smooth samples. Foote (28)

found that the contact angles of alcohol, benzene, and formamide against sized or unsized papermaking fibers were zero. The contact angles against cellophane of the solvent mixtures used in the formulation of the lacquers were too small to be measured by the drop method used; yet, the lacquers gave measurable angles.

Contact angle along a linear edge is usually expressed from energy considerations or by resolution of forces in the equation derived by Young (29).

$$\sigma_s - \sigma_{sl} = \sigma_l \cos \theta, \quad (7)$$

in which  $\sigma_s$  is the free surface energy (surface tension) of the solid,  $\sigma_{sl}$  is the free surface energy of the interface,  $\sigma_l$  is the free surface energy of the liquid, and  $\theta$  is the contact angle.

In changing from measurements on a solvent to those on a lacquer,  $\sigma_s$  and  $\sigma_l$  are essentially unaffected. Therefore, according to Equation (7), if  $\theta$  is to increase,  $\sigma_{sl}$  must also increase. However, because of the natural tendency of any system to seek the lowest energy levels, components which lower surface energy are more effective than those which raise it; thus, a large increase is not to be expected. In fact, if it is postulated that there is a similarity between a paper surface and glycerin, a decrease in  $\sigma_{sl}$  might be expected in analogy with the data of Table X.

It is probable either that true equilibrium is not reached, or that variables exist which are not taken into account by Equation (7). It is true that this equation holds strictly only for a linear interface but the same reasoning is valid for the more complicated case

of a drop. The apparent relationship of contact angle and viscosity already mentioned (Figure 7) may provide some explanation; however, simple viscosity should make no difference if a reasonable time is allowed. If the lacquers had shown evidence of a plastic nature, a definite correlation of yield value and contact angle could be expected.

For the cases in which advancing and receding contact angles differ, an empirical theory involving a friction force along the surface has been developed by Adam and Jessop (30). There is every evidence that the receding contact angle for the lacquers is zero. An attempt to find a simple relationship between viscosity and a friction force, using the data obtained on the lacquers, was unsuccessful.

A phase change in which a portion of the solvent would be absorbed from the lacquer by the paper, leaving a plastic or very viscous film at the interface cannot be used to explain the existence of a contact angle. Contact angle measurements of Lacquers 1, 4, 5, and 6 against tin plate gave values essentially the same as, though perhaps slightly lower than, those found for paper. The small circles in Figure 7 represent the values for the films on tin plate.

Whether the results of contact angle measurements represent true equilibrium values or not, they may be expected to indicate the actual behavior of the lacquer in the coating operation. Perhaps this is of greater importance.

In considering a mechanism for film formation, and particularly film breakdown, such factors as the weight of film, viscosity, surface

tension, and elapsing time are of interest. There may be a wide variation in concentration for lacquers of similar physical properties. Furthermore, there may be a great difference in drying time. Hence, it is more logical to express the properties of the lacquers in the drying film as a function of time elapsed after spraying rather than as a function of concentration. They are then on a common basis.

Determination of the relative rates of drying permits a comparative expression of physical properties with time as the independent variable.

In a preliminary study of the evaporation method on tin lids, the evaporation rates of butyl acetate, toluene, and butyl alcohol were determined for comparison with reported rates. It is customary to express evaporation rates on the basis of technical butyl acetate as a standard, to which is assigned a value of 100. Thus, a material which loses weight twice as readily, or which evaporates in half the time, will have a relative rate of 200. Relative rates for toluene and butyl alcohol obtained by evaporation in tin lids are compared with those reported by Bogin (31) in Table XI.

Corrections for temperature were made possible by the assumption that the rates of evaporation are proportional to the vapor pressures of the liquids. The change in vapor pressures with change in temperature was calculated from the heats of vaporization listed by Bogin (31) and the thermodynamic equation,

$$\log P_1/P_2 = \frac{H_v(T_1 - T_2)}{2.3 R(T_1 \cdot T_2)}, \quad (8)$$



in which  $P_1$  and  $P_2$  are the vapor pressures at temperatures  $T_1$  and  $T_2$ .  $T_1$  and  $T_2$  are absolute temperatures,  $H_v$  is the molal latent heat of vaporization, and  $R$  is the gas constant.

It may be seen from the data of Table XI that the relative rates at 23° C. for the method used are in fair agreement with those reported. A better agreement is obtained if the values are corrected to 30° C.

TABLE XI  
COMPARISON OF EVAPORATION RATE MEASUREMENTS ON SOLVENTS

Solvent	Measured Rate mg./min.	Rate at 23° C. mg./min.	Relative Rates		
			Measured 23° C.	30° C.	Reported 30° C.
Butyl acetate	0.228 (23° C.)	0.228	100	100	100
Toluene	0.530 (24° C.)	0.504	221	214	195
Butyl alcohol	0.086 (23° C.)	0.086	38	41	45

The results of the evaporation studies for lacquers on the film-weight plates are summarized in Table XII, and those on tin lids in Table XIII. Because the rate of change of concentration is of more interest for the lacquers, concentration as a function of time is reported instead of evaporation rate.

TABLE XII

TIME FOR EVAPORATION ON FILM-WEIGHT PLATES

Spraying	Time from Spraying min.	Net Weight g.	Concn. %	Spraying	Time from Spraying min.	Net Weight g.	Concn. %
R-2	2	0.418	29.9	1-9	1.5	0.5	
	4	0.383	32.6		2.5	0.457	13.7
	7	0.338	37.0		3.5	0.414	15.1
	10	0.300	41.7		5	0.357	17.5
	19	0.212	59.0		6	0.322	19.4
	27	0.166	75.3		15.5	0.091	69
	33	0.149	83.9		25.5	0.065	90
	37	0.143	87.5		∞	0.0425	
	∞	0.1250					
R-3	1.75	0.600	27.9	1-10	2.5	0.370	13.9
	6	0.515	32.5		3.5	0.328	16.2
	9	0.462	36.2		5.5	0.257	21
	13	0.410	40.8		7.5	0.202	26
	24	0.290	57.7		11	0.129	41
	∞	0.1674			15	0.079	67
					23.5	0.056	95
1-1	1.5	0.10	20		∞	0.053	
	2.5	0.079	25.8				
	4	0.050	40.8	1-11	3	0.243	18
	7	0.025	81.6		4.5	0.192	23
	10	0.021	97		5.5	0.164	27
	12	0.021	97		7	0.128	34
	∞	0.0204			11.5	0.060	73
					17.5	0.047	94
1-2	1.5	0.0825	21.1		∞	0.044	
	2.5	0.0545	31.9				
	4	0.0325	53.5	1-12	2	0.184	19
	6	0.0205	85		3.5	0.138	25
	∞	0.0174			5.5	0.103	35
					7.5	0.063	56
1-3	2.5	0.0146	89		10	0.044	80
	4	0.0137	95		∞	0.035	
	5	0.0136	95.5				
	∞	0.0130		1-13	2	0.094	27
					4	0.053	47
1-4	2	0.018	66		6.5	0.030	83
	5	0.0121	98		9	0.027	93
	∞	0.0118			∞	0.025	
				1-14	1.5	0.061	30
					2.5	0.042	43
					3.5	0.030	60
					4.5	0.023	78
					∞	0.018	

TABLE XIII

TIME FOR EVAPORATION ON TIN LIDS

Lacquer R  
Temperature 23° C.

<u>Dry Weight 0.1000 g.</u>		<u>Dry Weight 0.1016 g.</u>		<u>Dry Weight 0.2089 g.</u>	
Time min.	Concn. %	Time min.	Concn. %	Time min.	Concn. %
1.5	17.99	2	18.34	5	18.55
2	18.11	5	19.13	15	19.7
4	18.60	10	20.5	30	21.3
6	19.12	25	23.4	45	22.7
10	20.1	41	26.1	60	24.1
15	21.1	55	28.7	75	25.4
26	23.1	70	31.6	90	26.8
35	25.0			105	28.1
45	26.7			120	29.6
60	29.8				
75	33.2				

Lacquer 1

<u>Temperature 23° C.</u> <u>Dry Weight 0.0385 g.</u>		<u>Temperature 23° C.</u> <u>Dry Weight 0.0396 g.</u>		<u>Temperature 24.5° C.</u> <u>Dry Weight 0.0405 g.</u>	
Time min.	Concn. %	Time min.	Concn. %	Time min.	Concn. %
5	5.63	5	5.54	5	5.55
20	7.39	15	6.66	10	6.05
35	9.80	30	8.5	15	6.62
50	13.5	45	11.1	30	8.57
65	18.9	60	14.9	45	12.05
80	27.9	75	20.8	60	17.2
95	43	90	31.2	75	25.3
110	67	105	49	90	39.7
125	90	120	73	105	63
				120	86

TABLE XIII (Continued)

TIME FOR EVAPORATION ON TIN LIDS

<u>Lacquer 2</u>			<u>Lacquer 3</u>		
Temperature 25° C.			Temperature 25° C.		
Dry Weight 0.0220 g.			Dry Weight 0.0230 g.		
Time min.	Concn. %	Time min.	Concn. %	Time min.	Concn. %
5	3.33	5	3.34	5	5.43
15	4.09	17	4.22	15	6.58
30	5.63	30	5.49	30	8.83
40	7.05	40	6.85	40	10.86
50	9.02	50	8.72	50	13.65
55	10.3	55	9.96	55	15.45
60	11.9	60	11.5	60	17.4
65	13.8	65	13.4	65	20.3
70	16.3	70	15.8	70	23.5
75.5	19.6	75	18.8	75	27.3
		80	22.5	80	32.3
				85	38.0

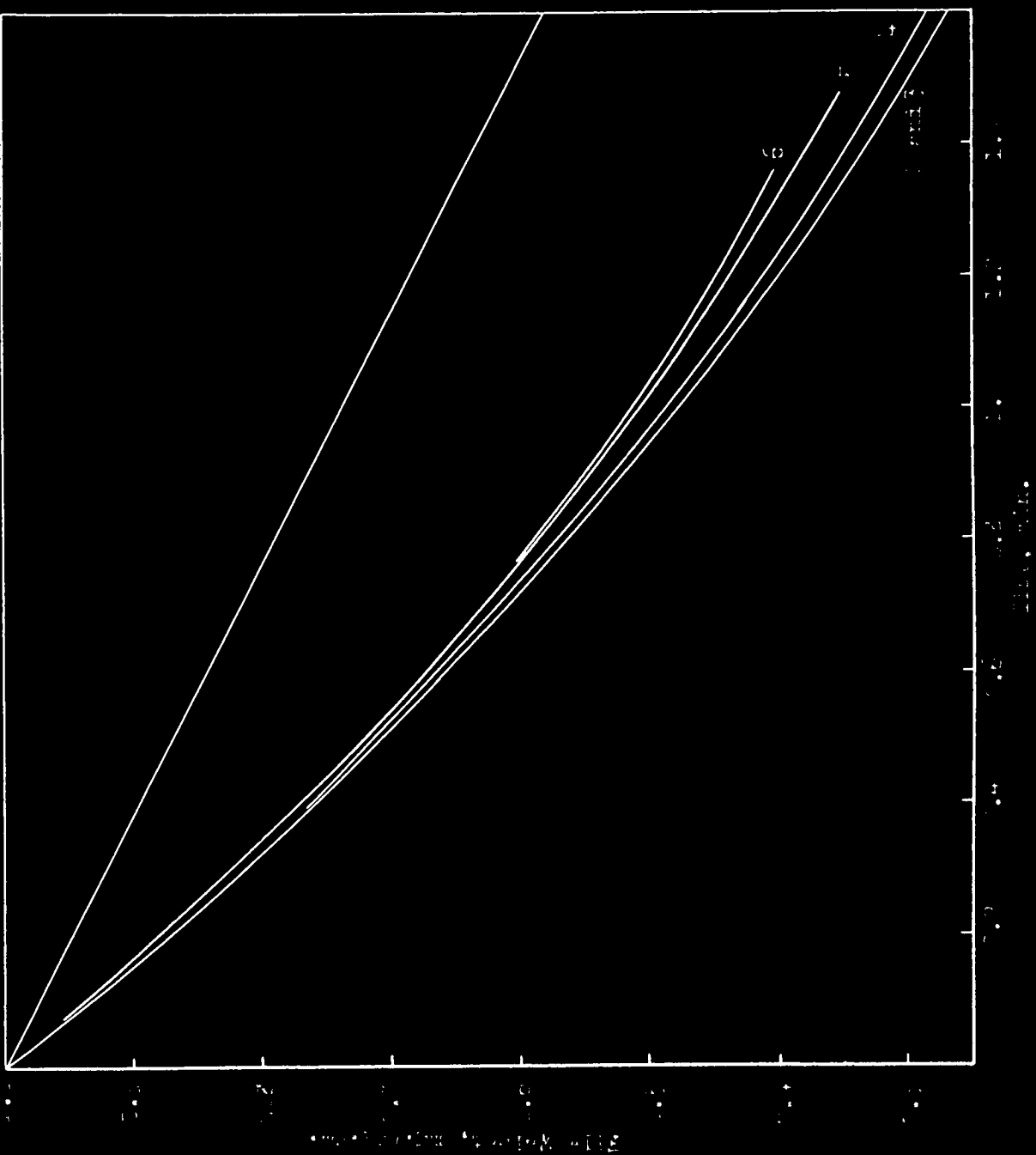
  

<u>Lacquer 4</u>			<u>Lacquer 5</u>			<u>Lacquer 6</u>		
Temperature 25° C.			Temperature 25° C.			Temperature 25° C.		
Dry Weight 0.0495 g.			Dry Weight 0.1045 g.			Dry Weight 0.1327 g.		
Time min.	Concn. %	Time min.	Concn. %	Time min.	Concn. %	Time min.	Concn. %	Time min.
5	6.80	5	14.03	5	18.20	5	18.20	
10	7.47	10	15.32	15	21.75	15	21.75	
20	9.00	20	18.25	30	28.35	30	28.35	
30	10.88	30	21.7	40	33.8	40	33.8	
40	13.2	50	31.1	50	40.6	50	40.6	
50	16.4	55	34.3	55	44.5	55	44.5	
55	18.3	60	37.8	60	48.8	60	48.8	
60	20.7	65	41.8	65	53.4	65	53.4	
65	23.5	70	46.1	70	58.3	70	58.3	
70	26.8	75	50.8	75	63.0	75	63.0	
75	30.7	80	55.9	80	67.7	80	67.7	
80	35.4	85	60.8	85	72.1	85	72.1	
85	40.7	90	66.0	90	76.3	90	76.3	
90	46.9							

A comparison of the ratio of time for equivalent change in concentration to dry film weight for the films of different weights of the same lacquer on the plates for the sprayings of Lacquers R-2 and R-3, 1-1 and 1-2, and 1-9 to 1-14, and the lids for Lacquer R leads to the conclusion that for the same lacquer, within the experimental error and in the range studied, the ratio is not changed by a change in film thickness. The results of the measurements with Lacquer R on lids are compared in Table VI. If time from spraying is used in calculating the ratio for the film-weight plate studies, each value must be increased by about 2 minutes, corresponding to the extrapolation discussed in the previous section and illustrated in Figure 4.

The changes of weight with time calculated for films of unit initial weight after spraying of Lacquers 2 to 6 are represented by the curves in Figure 8. Each curve bears the corresponding lacquer number. Lacquers 2 and 3 gave essentially the same results. If the values were corrected to film volume instead of film weight by division by the density, even less spread would be apparent. Evaporation studies of Lacquer R were made at 23° instead of 25° C. and have not been plotted. The film weight for Lacquer 1 decreases somewhat more slowly at first than that for the series 2 to 6 as a result of greater initial loss in spraying; however, in the later stages it would lie just below the values for Lacquers 2 and 3.

The straight line in the figure represents the weight of an equivalent film of butyl acetate also evaporating at 25° C., and is included for purposes of comparison. The negative slopes of the curves



at any point represent the instantaneous rates of evaporation in milligrams per minute per square centimeter.

The calculated values for time are of the same order as those observed for the actual sprayed films.

The rate of evaporation, in the early stages at least, would seem to be dependent on the solvent composition and its volatility, and not on the nonvolatile content. As the concentrations of the initial lacquers increase in passing from 2 to 6, the proportion of solvent decreases, so that the relative change of solvent composition during evaporation in films of the same original weight is greater for the more concentrated lacquers.

With the exception of concentration, viscosity, and contact angle, the lacquer properties are not only essentially equivalent, but remain relatively constant. As has been pointed out earlier, contact angle seems to be a function of viscosity. Therefore, of the physical measurements, only the variation of viscosity has been compared with time after spraying as the variable. The results are presented in Figure 5. The numbers on the curves correspond to the lacquers, 3 and 4 being essentially the same. The dotted curve for Lacquer 1 represents values calculated from evaporation rate measurements at about 23° C.; compared with the solid line for 25° C., this curve shows the effect of temperature on evaporation rate and viscosity change.

From the time of spraying to the time the viscosities reach 1000 centipoises, Lacquers 2 to 5 are approximately the same. Above 1000 centipoises, the divergence is greater; however, it may be expected

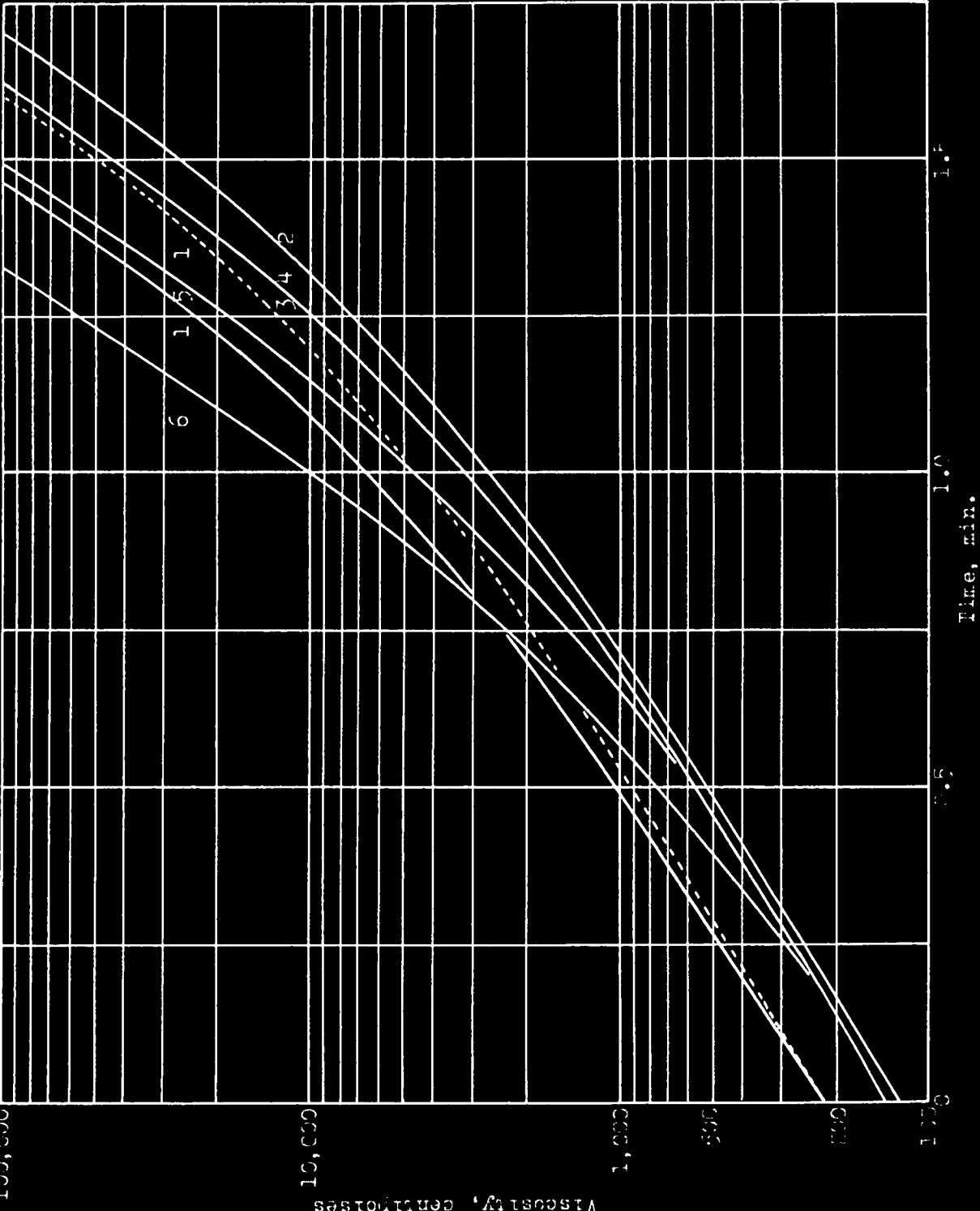


FIGURE 9

CHANGE IN VISCOSITY AS A FUNCTION OF TIME AFTER SHEARING



to have less effect upon penetration because, for flow changes taking place in the film and during penetration, the product of time and the reciprocal of viscosity should be the determining factor (see Equation (1)).

The viscosity of Lacquer 6 increases more rapidly with time, whereas Lacquer 1 shows a higher viscosity in the initial stages. It is interesting to note that Lacquer 3, of approximately the same concentration and with the same nonvolatile content as Lacquer 1, gives a parallel curve displaced on the time axis.

#### SPRAYING OPERATION

The loss of volatiles in spraying determines the concentration and viscosity of a lacquer during the formation of the film. The results of measurements on the spraying losses are given in Table XIV.

The high loss for Lacquer 1 corresponds to greater solvent volatility, but the change for Lacquer 4 seems too high and is probably in error. However, in view of the importance of temperature, the results may be considered satisfactory.

The occurrence of dry spray, very viscous droplets, or droplets covered by a skin of viscous lacquer, which do not flow out and coalesce on the sprayed surface, need not present a problem. No trouble was experienced in these sprayings. In general, by proper control of solvent volatility, with or without the addition of retardants (high boiling solvents), the evaporation loss during spraying may be controlled and made to fit such conditions as distance of the gun from the work, fan width, and temperature of spraying.

TABLE XIV

CHANGES TAKING PLACE IN LACQUERS DURING SPRAYING

Lacquer	<u>Concentration, %</u>		<u>Volatiles Lost, %</u>		Viscosity after Spraying cp. at 25° C.
	<u>Before</u>	<u>After</u>	<u>Based on Total Lacquer</u>	<u>Based on Total Volatiles</u>	
R	17.6	23.5	25.0	30.4	270
1	4.77	7.14	33.1	34.8	220
2	3.04	4.27	28.8	29.7	125
3	4.95	7.07	30.0	31.6	140
4	6.00	8.85	32.2	34.3	148
5	12.62	17.1	26.1	29.9	122
6	16.40	22.2	26.1	31.2	130

The other pertinent data on the sprayings are given in Table XV. The lacquer number and a number for the spraying identify each. The room temperature, time of rotation of the drum, dry film weight, wet film weight, and samples sprayed are tabulated. If a space in the column under a sample number is blank, it signifies that the sample did not receive that particular spraying. Sprayings of low weight were of little interest on the porous board Sample 3, whereas heavy sprayings were of no interest on the dense cellophane and greaseproof paper (Samples 1 and 2) and of less interest on the densest board (Sample 4). In the sprayings of Lacquers 2 to 6, Samples 1 and 2 were not used because they seemed to offer no problem.

In the sprayings of Lacquers R and 1, the hood exhaust fan was turned off immediately after spraying, the drum was stopped, and the film-weight plates removed for weighing to follow evaporation loss. By mistake, the exhaust fan was not operating during the spraying 1-2, which is the one exception. For Lacquers 2 to 6, the fan was left on and the drum allowed to rotate until the films had set up.

Specular reflection of light from the sprayed surfaces was taken as a criterion of complete coverage or flooding--that is, a smooth lacquer surface meant that the surface of the sheet had been completely covered and that a continuous wet film existed. Actually, continuity might exist on rough samples before specular reflection is obtained. For the sprayings of Lacquers R and 1, an f in Table XV indicates that the corresponding sample was flooded. An x signifies only that the sample was sprayed, and for Lacquers R and 1 that flooding was not observed.

TABLE XV.

## DATA ON SPRAYINGS

Spraying	Room Temperature ° C.	Drum Speed sec./rev.	Dry Weight mg./sq.cm.	Wet Weight mg./sq.cm.	Samples Sprayed				
					1	2	3	4	5
R-1	20	5.5	1.2	5.1	f	f	x	f	x
R-2	25	11.0	2.5	10.6	f	f	x	f	f
R-3	25	16.6	3.7	15.7	-	-	f	f	f
1-1	25	10.7	0.41	5.8	-	-	f	f	f
1-2	25	9.0	0.35	4.9	f	f	x	f	f
1-3	25	6.7	0.26	3.6	f	f	x	f	f
1-4	25	5.6	0.24	3.4	f	f	x	f	f
1-5	25	4.5	0.17	2.4	f	f	x	f	x
1-6	25	3.7	0.14	2.0	x	x	x	x	x
1-7	25	3.0	0.11	1.5	x	x	x	x	x
1-8	25	40	1.54	21.6			f		f
1-9	25	35	1.25	17.5			f		f
1-10	25	30	1.06	14.8			f		f
1-11	25	25	0.88	12.3			f		f
1-12	25	20	0.70	9.8			f	f	f
1-13	25	15	0.50	7.0			f	f	f
1-14	25	10	0.36	5.0			x	f	f
1-15	25	5	0.17	2.4				x	x
2-1	25	5	0.11	2.5			x	x	x
2-2	25	10	0.20	4.7			x	x	x
2-3	25.5	15	0.34	7.9			x	x	x
2-4	25	20	0.47	11.1			x	x	x
2-5	25	30	0.62	14.6			x	x	x
2-6	24.5	40	0.94	22.0			x	x	x
3-1	25	5	0.21	2.9			x	x	x
3-2	25	10	0.43	6.1			x	x	x
3-3	24.5	15	0.61	8.6			x	x	x
3-4	25	20	0.84	11.9			x	x	x
3-5	24.5	30	1.22	17.3			x	x	x
3-6	25	40	1.66	23.5			x	x	x
4-1	25	5	0.25	2.8			x	x	x
4-2	25	10	0.49	5.6			x	x	x
4-3	25	15	0.74	8.4			x	x	x
4-4	25	20	0.99	11.2			x	x	x
4-5	25	25	1.30	14.7			x	x	x
4-6	25	30	1.50	17.0			x	x	x
5-1	25	5	0.63	3.7			x	x	x
5-2	25	10	1.18	6.9			x	x	x
5-3	25	15	1.89	11.1			x	x	x
5-4	25	20	2.49	14.6			x	x	x
5-5	25	25	3.09	18.1			x	x	x
5-6	25	30	3.70	21.6			x	x	x

TABLE XV (Continued)

DATA ON SPRAYINGS

Spraying	Room Temperature ° C.	Drum Speed sec./rev.	Dry Weight mg./sq.cm.	Wet Weight mg./sq.cm.	Samples Sprayed				
					1	2	3	4	5
6-1	25	5	0.91	4.1		x	x	x	
6-2	25	10	1.86	8.4		x	x	x	
6-3	25	15	2.74	12.3		x	x	x	
6-4	25	20	3.67	16.5		x	x	x	
6-5	25	25	4.58	20.6		x	x	x	
6-6	25	30	5.50	24.8		x	x	x	

Flooding was not as carefully observed in sprayings of Lacquers 2 to 6, and its absence or presence is not indicated in the table.

An initial film weight of about 2.5 to 15 mg. per sq. cm., depending upon the roughness or porosity of the samples and the viscosity of the sprayed lacquer, was found necessary for complete flooding. Similar behavior was observed with Lacquers 2 to 6.

In every spraying, with the possible exception of the lightest with an initial wet film weight of 1.5 mg. per sq. cm., the tin film-weight plates were flooded, although the cellophane sample may not have been. The difference in behavior on tin and cellophane, which is essentially as smooth and almost as impervious, may be attributed to a slightly smaller contact angle on the former, to the warming of the cold lacquer droplets by the higher heat capacity and better thermal conductivity of the tin plate, or to a greater kinetic effect as the droplets impinge on the solid metal surface. The first two are probably the most important.

Although the films on greaseproof paper and cellophane were never really tested for continuity, there is every reason to believe that, when the surface is once wet and flooded, the film is not broken during drying on these dense, essentially nonabsorbant materials. After drying, visual inspection showed a smooth or hazy surface for the cellophane, depending upon whether or not flooding took place. Examination under a low-power microscope revealed the statistical nature of spray pattern. In going from light to heavy sprayings, the lacquer appears in spots corresponding to the original droplets, after which irregular splotches of varying size are observed as some of the droplets strike near enough to coalesce on the surface; the splotches then fuse, leaving an occasional bare spot; finally, with complete flooding, a continuous film is formed.

Observations during the sprayings permit surmises concerning the mechanism by which bubbles are formed in sprayed films. For light sprayings, bubbles were not observed on the film-weight plates, the cellophane, or the smooth boards, but always occurred on the roughest, most porous board (Sample 3). The conclusion is drawn that these bubbles arise from air trapped in the voids of the sample. In the heaviest sprayings, bubbles occurred on all the samples and on the film-weight plates. It is believed that these are the result of air carried into the film by impinging spray droplets, just as air is carried below the surface when a stone is dropped into water. It is considered improbable that bubbles are formed by the grouping of the spray droplets with inclusion of air during their flight or at the moment of striking the surface.

In general, the bubbles appearing in the initial films broke and the lacquer leveled during drying. In any event, a bubble does not constitute a departure from continuity in the film; even though leveling should not occur, if one side is broken the other half remains.

In measuring the viscosities of the evaporated lacquer samples, differences of several per cent were found if balls of various size were used in the determination. At the high viscosities, these differences were not considered significant in so far as necessary accuracy was concerned; however, the results threw some doubt on the theory of the entire method of viscosity measurement. A further comparison of the balls in a sucrose solution of high viscosity checked the original calibrations. In explanation of the anomalous behavior of the lacquers, a non-Newtonian nature is postulated. A comparison of drum speeds during spraying and of film weights bears out the hypothesis. Average values of the spraying rate, i.e., the ratio (dry film weight x 100)/(time of rotation x percentage of nonvolatile), for all the lacquers are given in Table XVI.

TABLE XVI

COMPARISON OF SPRAYING RATE OF LACQUERS

Lacquer	Spraying Rate*
R	1.28
1	0.74
2	0.72
3	0.84
4	0.83
5	0.99
6	1.12

\* The unit is (dry film weight x 100)/(time of rotation x percentage of nonvolatile matter).

The spraying rate values are in agreement with postulates that the lacquers are dilatant, that dilatancy increases with molecular size (viscosity type of nitrocellulose), and that shearing rates were greater in spraying than they were in the viscosity measurements. The postulates are further established by the observation that, the larger the ball used in determination of viscosity, the greater was the value obtained.

#### TESTS ON DRY FILMS

Observations of the phenomena of spraying have supplied some insight into the mechanism of continuous film formation. Tests on the dried films permit further conjecture.

The results of turpentine tests are given in Table XVII, and the data on the modified Bekk viscosity measurements in Table XVIII. A comparison of the two methods, based on the data for the sprayings R-2 and 1-1 to 7 on board Samples 4 and 6, has been made on page 34.

Although the Bekk test proved superior to the turpentine test, neither was completely satisfactory. Plots of Bekk values against film weight would yield "shotgun" diagrams which could be interpreted only in terms of trends; these may be found also by careful inspection of the data. It is incorrect to attribute the poor performance entirely to the tests, because they are fairly reproducible on any one spraying.

It was considered possible that very thin films across the



TABLE XVII  
RESULTS OF TURPENTINE TESTS

Spraying	Dry Weight mg./sq.cm.	Penetration Time for Different Boards, sec.		
		3	4	6
R-2	2.5	19.4	>1,500	900
R-3	3.7	35.2	-	1,500
1-1	0.41	15.7	> 720	49.8
1-2	0.35	16.8	786	31.0
1-3	0.26	15.5	329	26.9
1-4	0.24	15.6	91	28.0
1-5	0.17	15.9	130	27.5
1-6	0.14	15.4	100	24.0
1-7	0.11	14.5	102	24.8

interstices of the samples might exist, which would be broken by the pressure of testing. However, the same porosity values were obtained when the samples were tested first with pressure differences of 125 to 120, followed by 250 to 240, and then by 500 to 480 mm. of mercury.

Examination of the data of Table XVIII in comparison with those of Table XV shows that initial flooding does not guarantee continuous dry films on porous samples. As film weight was increased for any particular board sample and lacquer, the Bakk time (which is inversely related to porosity) was found to increase at a rapidly accelerated rate. This increase in time of fall, or decrease of porosity, can be pictured as taking place as the pores (first the smallest and finally the largest) are progressively plugged as the weight of film is increased.

TABLE XVIII

RESULTS OF MODIFIED BREK POROSITY TEST

Spraying	Dry Weight mg./sq.cm.	Time of Fall for Various Boards, sec.		
		3	4	6

Average of Three Measurements

R-2	2.5	-	continuous	-
1-1	0.41	2.3	1,710	14.3
1-2	0.35	2.3	580	13.3
1-3	0.26	1.9	69	7.7
1-4	0.24	1.9	53	11.8
1-5	0.17	1.5	60	9.3
1-6	0.14	1.7	53	7.8
1-7	0.11	1.5	47	8.0
1-8	1.54	4.9	-	250
1-9	1.25	3.5	-	290
1-10	1.06	4.1	-	340
1-11	0.88	2.5	-	80
1-12	0.70	2.6	11,500	29
1-13	0.50	2.4	7,700	19
1-14	0.36	1.8	200	31
1-15	0.17	-	170	8

Average of Four Measurements

		Film	Blank	Film	Blank	Film	Blank
2-1	0.11	1.6	1.6	41	14.6	6.7	6.0
2-2	0.20	1.8	1.8	50	15.1	8.0	6.0
2-3	0.34	2.0	1.7	51	11.3	8.9	6.1
2-4	0.47	2.2	1.8	600	18.3	22.8	7.1
2-5	0.62	2.5	1.6	1,030	16.0	24.7	8.3
2-6	0.94	3.1	1.8	1,000	10.9	51	6.1
3-1	0.21	1.8	-	110	16.0	12.0	9.5
3-2	0.43	2.2	1.6	121	15.0	14.5	7.2
3-3	0.61	2.2	1.8	105	14.0	30.4	8.3
3-4	0.84	3.3	2.1	2,000	15.6	52	8.3
3-5	1.22	3.8	2.0	3,400	13.0	36	7.0
3-6	1.66	4.8	2.0	4,500	10.5	300	7.0

TABLE XVIII (Continued)

## RESULTS OF MODIFIED BEKK POROSITY TEST

Spraying	Dry Weight mg./sq.cm.	Time of Fall for Various Boards, sec.			Average of Four Measurements		
		3	4	6			
Average of Four Measurements							
		Film	Blank	Film	Blank	Film	Blank
4-1	0.25	1.8	2.0	47	8.5	9.9	5.6
4-2	0.49	2.3	1.6	113	11.2	15.0	6.4
4-3	0.74	3.2	1.8	128	11.5	23.1	7.4
4-4	0.99	3.0	1.8	2,040	10.5	54	10.0
4-5	1.30	3.2	1.8	1,300	12.5	55	6.5
4-6	1.50	4.5	1.7	48,000	11.1	137	6.5
5-1	0.63	2.4	1.9	315	10.1	25.5	7.2
5-2	1.18	3.0	1.8	650	12.2	40	7.0
5-3	1.89	4.5	1.3	550	10.5	186	7.4
5-4	2.49	5.4	1.8	cont.*	13.5	410	8.0
5-5	3.09	6.6	1.8	cont.*	8.4	cont.*	7.8
5-6	3.70	11.5	1.8	cont.*	11.5	cont.*	8.4
6-1	0.91	2.0	1.6	460	6.7	31	6.6
6-2	1.86	4.3	1.7	1,500	8.7	214	5.3
6-3	2.74	5.5	1.7	cont.*	11.4	870	6.3
6-4	3.67	9.0	1.7	-	-	cont.*	5.7
6-5	4.58	20.4	1.6	-	-	cont.*	5.9
6-6	5.50	93	1.9	-	-	-	-

\* No fall was observed, and these samples are considered to be continuous.

Under the conditions of these experiments, the rate of drying was held constant and a film twice as thick would have about twice the time to penetrate into the sheet before setting up. If drying time for films of different weight were held constant--for example, by changes in solvent formulation--the decrease in porosity with increase in film weight could be expected to occur even more rapidly.

From the study of dry films, a number of conclusions can be drawn concerning the effects of the board properties. The porosities

of the board samples are of primary importance. The Back time for the same film weight is greater and increases more rapidly with increase in film weight for the denser boards than for the more porous ones-- that is, in the order of 4, 6, 3. Immervious films were formed at lower film weights on Board 4 than on 6, and none at all on Board 3 with the weights of film studied.

The porosity measurements made on the masked portions of the same samples in the sprayings of lacquers 2 to 6 show a wide variation in the individual boards, and offer some explanation for the unsatisfactory results in testing. These values, corresponding to the time of fall from 380 to 360 mm. of mercury, are tabulated (together with the film tests) under the heading Blank in Table XVIII.

Microscopic examination of the films on cellophane has already been mentioned under the discussion of spraying and flooding. Similar observations of the films on the greaseproof paper showed the effect of roughness. Unlike the cellophane, the films were not uniform, but thin at raised portions (such as a fiber lying above the average sheet surface) and thick in the recesses at the edge of such a fiber. A similar effect could be observed even for the wet films in the case of projecting fibers on Board 3. All in all, the effect of roughness would seem to be, first, to increase the effective area of a sheet and, second, to decrease the uniformity of the film. It may be considered of secondary importance as compared with porosity.

As a result of the tests, certain conclusions may be drawn about the lacquers. Contrary to expectations based on the consideration of the similarity of physical properties as a function of time in the series

of Lacquers 2 to 6, the porosity of the sprayed sheets or the continuity of the films was a function of dry film weight within the rather considerable experimental error. That is, for the same wet film weight, the effectiveness of the lacquers was nearly proportional to their concentrations. However, in view of the fact that approximately the same wet film weight was required for flooding, it is still reasonable to expect that, at higher initial wet film viscosities, the physical properties and not the concentrations of the drying films would be the deciding factor.

From Figure 9, it may be seen that Lacquer 1 differs from the series 2 to 6 in having a higher initial viscosity, as well as a correspondingly greater viscosity during drying. A comparison of the film test data on Boards 4 and 6 shows that, at the same dry film weight, Lacquer 1 is more effective. The viscosity difference is not great enough to have an effect for Board 3 (the most porous sample).

As mentioned in the foregoing section, the interfacial tensions of a number of liquids against 95 per cent glycerin were determined to permit a better interpretation of the measurements on the lacquers. Although no special precautions were taken to purify the materials used, the results are reported in Table XIX, since it is believed that they are not available elsewhere.

The value for chloroform may be too low, because it was the only one in which the time of drop formation seemed to make much difference. The presence of a surface active impurity is suggested. The value for butyl acetate is certainly low, because of the alcohol content

TABLE XIX

INTERFACIAL TENSIONS OF VARIOUS LIQUIDS AGAINST GLYCERIN AT 25° C.

U.S.P. Glycerin:  $d_{25}^{25}$  1.24871  
94.85% (10)

Liquid	Density, 25° C. (reduced to vacuo)		Interfacial Tension dynes/cm.
	Phase A*	Phase B*	
Dioxane	1.0440	1.1994	1.5
Acetone	0.8101	1.2299	3.5
Cyclohexanone	0.9509	1.2296	4.1
Tri- <i>o</i> -cresyl phosphate	1.1549	1.2446	5.7
Butyl acetate (technical)	0.8716	1.2425	7.7
Ethyl acetate	0.8975	1.2418	9.2
Chloroform	1.4758	1.2470	10.8
Ethyl ether	0.711	1.2393	11.6
Dibutyl phthalate	1.0426	1.2445	15.7
Benzene	0.8718	1.2431	18.3
Velsicol Solvent No. 1	0.8146	1.2443	19.8
Toluol	0.7353	1.2446	20.8
Carbon tetrachloride	1.5833	1.2450	21.3
Petroleum ether (boiling range 30-60° C.)	0.628	1.2448	23.2

\* Phase A is the liquid of the first column saturated with glycerin;  
Phase B is glycerin saturated with the other liquid.

of the technical grade. Also, materials such as dioxane and acetone probably would have given higher values had they been dried.

In general, the materials are ranked in the same order by interfacial tension against glycerin as they would be against water, the values for the former being about half those for the latter. However, there are inversions. For example, acetone and dioxane are miscible with water; therefore, they have zero or negative interfacial tensions against water, but positive values against glycerin. In like manner, glycerin is miscible with the higher alcohols, whereas water is not.

From the results for petroleum ether and benzene, it is seen that glycerin, like water, has a higher interfacial tension against aliphatic than against aromatic hydrocarbons. Trolucil and Velsicol Solvent No. 1 are petroleum thinners, primarily aliphatic but with a certain portion of aromatic compounds. The interfacial tensions of these two solvents lie between those for benzene and petroleum ether, as might be expected. This suggests that an interfacial tension measurement might serve as a rapid method of estimating the aromatic content of such solvents. It also might be possible to correlate this value with the dilution ratios ordinarily used as criteria of tolerance in lacquer formulation.

## MECHANISM OF FILM FORMATION

It might be worth while at this point to give a summary of the conclusions and hypotheses concerning the mechanism of film formation, which have been drawn from the experimental data, as well as from those of The Institute of Paper Chemistry (3), Hollabaugh (4), Doolittle (6), and Stewart and Hook (7).

For the purpose of this discussion, the coating operation may be divided into two phases. The first is the initial film formation or flooding of the paper; the second is the preservation of the continuity of the film during drying.

In the first phase, it is essential that the coating material wet the paper evenly and completely. A smooth paper surface, small contact angle, and low lacquer viscosity are desirable. Because of the statistical nature of the spray pattern, at any set viscosity a certain minimum weight of sprayed material must be exceeded to flood the surface. The initial wet film viscosity may be controlled somewhat by a variation of the spraying conditions and the volatility of the solvent. The process of flooding is essentially complete in the spraying operation; little, if any, spreading occurs afterward.

Coincident with and following the initial film formation, forces set to ~~work~~ which thin out and may even break the film. The driving forces for the changes are surface effects and decrease in film volume. These forces are less effective in liquids with a high viscosity and are more effective with long drying times. The films thin out



at points or projections and thicken in recesses. The film penetrates the voids of the sheet and, if sufficiently fluid, it is eventually drawn into the smallest capillaries and breaks in the large capillaries which have been depleted in part of their liquid content. If good wetting is maintained, it is inconceivable that, once coated, the lacquer would completely draw away from the fibers, whether they be projecting as fuzz or at the boundary of a large pore. However, particularly in the case of fuzz, the films may be so thin and weak that they are easily broken by mechanical action after drying.

Bubbles in the initial film may arise from air trapped in surface voids for rough paper, or as the result of the splash of impinging droplets on the partially formed films. In addition, bubbles may be produced in the second phase, if air is trapped in pockets of the sheet as the lacquer penetrates.

For comparable drying times, a different optimum initial viscosity is to be expected for boards of varying porosity and roughness; the latter is of secondary interest. With increase in porosity or drying time, the initial viscosity should also be increased.

A low contact angle and high surface tension favor not only flooding but also penetration and later unevenness. In the absence of variation of these properties in the present study, it can only be said that good wetting (small contact angle) is essential to flooding; for corresponding contact angles, the rate of spreading, drawing away, and penetration should be proportional to surface tension. Considering the relatively small possible range of variation of surface tension, it

may be expected to play a distinctly secondary role as compared with viscosity, and a more or less equivalent one to drying time.

## PRACTICAL SIGNIFICANCE

Many of the conclusions of this work have been recognized consciously or unconsciously and applied in practice. However, it may be desirable to review the important factors and some of the methods which may be used to obtain the objective of a light-weight impervious film. In general, the same remarks apply to the coating of a container or a flat sheet.

First, the distinction between continuous and impervious must be recognized. That is, the coating material must be chosen to fit the requirements of resistance in any particular use.

Second, the difference in the nature of paper as compared with metal or other dense material must be considered, as well as the purpose of the film. Ordinary painting practice cannot be bodily transposed to the problem of coating paper to render it impervious.

It is desirable that the paper be uniform, relatively non-porous, and smooth. Uniformity with respect to formation and density must be controlled on the paper machine. The absence of shives or other coarse particles is desirable. Their presence depends upon the selection and treatment of the stock. Nonuniformity may arise, in the forming of a container, as the result of scoring, or even bending if the structure of the sheet is greatly disturbed. In the final analysis, the coating must be sufficiently heavy to seal the most porous spots.

Low porosity may be obtained by hydration of the pulp to give a dense sheet of close structure. Starch treatment or coating may be

expected to be of value. Calendering, although it may increase density, does not seem to be highly effective.

Smoothness may be attained by calendering, but is partly determined by selection of the stock and paper machine variables.

The paper surface must be wetted by the coating material. In the case of nonaqueous coating materials of low or medium viscosity, good wetting may be expected and sizing of the sheet does not appear to be of importance. Although this study was not concerned with aqueous coating materials, wetting agents or alcohol should improve wetting, in which case sizing would probably be of importance.

It is true that poor wetting reduces penetration, but it also may be the cause of uncoated areas.

A low surface tension is desirable. In the case of lacquers, this is dependent upon the formulation, particularly of the vehicle. A small variation would seem to be possible. In general, for aqueous coatings, surface tension is reduced by the same agents which promote wetting.

For smooth, nonporous papers, a low viscosity of the coating material may be used to advantage to promote the formation of a continuous wet film of low weight. The concentration of the coating material should have little effect on the continuity of the final film.

In the case of a more porous paper, a higher viscosity must be employed. A correspondingly heavier wet film must be applied if it

is to be continuous. If the viscosity is low enough so that considerable penetration and impregnation occur, the effectiveness of the coating material increases with increase of concentration.

Materials of high viscosity may be applied by using special spraying equipment designed for viscous materials. Heating may be employed to reduce viscosity during spraying. Emulsions in which the dispersed phase is a lacquer of high viscosity have also been used.

An ideal coating material would be one which could be applied at a fairly low viscosity, but which would quickly reach a much higher one. It would be desirable that the high viscosity be reached before a great reduction in film volume occurs.

A coating which exhibits a very rapid increase in viscosity for a small change in concentration would be a step in this direction. The use of solvents of high volatility, as well as accelerated drying by air currents or heating, is to be recommended.

The effects of multiple coatings have not been investigated in this study. However, with materials such as lacquers, lifting occurs if one coat is applied over another. That is, the second coat softens the first, and the two may be said to fuse. If the first coat is dry, one effect of lifting would be a rapid increase in the viscosity of the second coat. Thus, it is perfectly reasonable to expect that two coats may be more effective than one of the same total weight.

## SUMMARY

The desirability of a better understanding of the mechanism of film formation in the proofing of paper or paperboard by a method which may be used for finished containers has been mentioned.

Spray-coating, using nitrocellulose lacquers as the coating material, was adopted for study.

The problem was resolved into the following divisions: (1) standardisation of spraying conditions; (2) variation of the formulations and properties of the lacquers; (3) measurement of these properties; (4) a study of spray-coating with the lacquers of cellophane, a grease-proof paper, and three paperboards of different porosities; and (5) measurement of the continuity of the dried films.

An apparatus for applying uniform sprayed films was developed. Measurements of concentration, specific gravity, viscosity, surface tension, interfacial tension against both water and 95 per cent glycerin, contact angle against the paper and board samples, and changes of these properties with evaporation, as well as the rate of evaporation and evaporation loss in spraying, were made on the lacquers. The porosity, roughness, density, and wettability of the paper and board samples were determined. The dry films were tested for porosity as a measure of continuity, and also were studied under the microscope. A number of techniques and apparatus were developed or adapted for the measurements.

Comparison of the physical properties of seven lacquers and the results of the tests on the dry films showed that viscosity, rate

of evaporation, and concentration were the most important lacquer variables. The differences in the other variables were too small to play a large part. For the paper or board samples, porosity was the most important property.

A general picture of the mechanism in spray-coating was developed. For purposes of discussion, the coating operation may be divided into two phases. The first is the initial film formation or flooding of the surface; the second is the preservation of the continuity of the film during drying.

In the first phase, it is essential that the coating material wet the paper evenly and completely. A smooth surface, small contact angle, and low viscosity are desirable. Little, if any, spreading occurs after spraying.

Coincident with and following the initial film formation, changes take place which thin out and may even break the film. The driving forces for the changes are surface effects and decrease in film volume. These forces are less effective in liquids with a high viscosity and are favored by slow drying. The coating thins out at points or projections and thickens in recesses. It penetrates the voids of the sheet. If sufficiently fluid, it is eventually drawn into the smaller capillaries and it may break in the larger ones which are depleted, in part, of their liquid content.

Bubbles in the initial film may arise from air trapped in surface voids of rough paper, or as the result of the splash of

impinging droplets on the partially formed films. In addition, bubbles may be produced in the second phase if air is trapped in pockets of the sheet as the lacquer penetrates.

For comparable drying times, the optimum initial viscosity will vary for boards of differing porosity and roughness. With increase in porosity or increase in drying time, the initial viscosity should also be increased.

A low contact angle and high surface tension favor not only flooding but also penetration.

The practical significance with regard to choice of paper and coating material, as well as techniques of application, has been discussed.

A number of other observations were made:

Drying time appeared to be proportional to film weight.

The lacquers were found to be dilatant.

It was observed that nitrocellulose in solution is surface active against glycerin.

A relationship between viscosity and advancing contact angle was observed, but not explained.

In testing the dry films, an air porosity test was found to correlate well with a turpentine penetration test.



The interfacial tensions of fourteen liquids against 95 per cent glycerin were measured.

## CONCLUSIONS

The problem of producing continuous films on paper has been resolved into two phases: formation of the wet film, and preservation of continuity during drying. The properties of both the paper and coating material must be considered. Conclusions concerning film formation are listed below:

1. The porosity of the paper or paperboard is of first importance; roughness is of secondary interest.
2. For each paper, depending upon its roughness and porosity, there is an optimum viscosity at which flooding just occurs and the film is maintained during drying.
3. Wetting is necessary for complete coverage, but does not present a problem for nitrocellulose lacquers.
4. A continuous wet film does not necessarily give a continuous dry film.
5. The viscosity of the lacquers is of prime importance in the formation of the film and its preservation; the first is favored by low values and the latter by high values. Other lacquer variables are of secondary importance.
6. For low viscosities in which considerable penetration occurs, the effectiveness of the lacquers is proportional to their concentrations.
7. In spraying, dry spray need present no problem if the lacquers are properly formulated.
8. Bubbles in sprayed films may result from air trapped in

voids of rough paper and from the splash of impinging spray droplets.

9. Drying time is of considerable importance. Rapid drying favors the preservation of the film.

10. Drying time is proportional to film weight, at least during the early and most important stages.

These conclusions are in agreement with those of other investigators.

Although no great differences were observed in these lacquers, surface tension may be expected to be of comparable importance to drying time.

No correlation of the interfacial tensions of the lacquers against water or glycerin and their contact angles against the paper samples was evident.

Several observations, not related to film formation, have also been made:

1. The nitrocellulose lacquers were dilatant.
2. Nitrocellulose in the lacquer solvents was found to be surface active in the interfacial tension measurements against glycerin.
3. A porosity test on the films was correlated with a turpentine penetration test.

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