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AERO DOPES AND VARNISHES

By H. T. S. Britton

From "The Industrial Chemist," March, 1927

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Washington
July, 1927



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By H. T. S. Britton.

During the earlier period of the war, and before the problem of procuring solvents and diluents in the vast quantities demanded by the rapid increase in aircraft construction had become acute, it was customary to apply five or more coats of dope, the last one or two of which were sometimes pigmented, and then to finish off with a coating of a transparent oil varnish. The first coat was brushed on with a specially diluted dope, containing about 6 grams of cellulose acetate per 100 cm³ of solvent mixture, whereas the subsequent coats were applied with a full-strength dope containing about 9 grams of cellulose acetate in every 100 cm³ of solvent mixture. In order that the amount of dried dope film did not greatly exceed 2 ounces per square yard, a cellulose acetate giving a lower viscosity dope was used. The idea of using a dilute first coat dope was to ensure thorough penetration of the dope into the fibers of the linen fabric. This doping scheme was, however, very extravagant in solvents and ultimately gave way to a scheme, advanced by the Air Ministry, of three coats, not including protective coatings, in which full-strength dope was used for every coat, the concentration of cellulose acetate being kept about the same as in the earlier

* From "The Industrial Chemist," March, 1927.

schemes, but a cellulose acetate was used which gave more viscous solutions, whose viscosities were about 40-50 per cent of glycerol at 25°C.

Before proceeding to discuss the preparation of dope solutions, it will be necessary to consider some of the essential properties which should be possessed by a dope film, deposited in and on the surface of an aero fabric. The first is that it should tauten the fabric and maintain it in a "drum-tight" condition. Needless to say, flabbiness of the fabric on aero parts may interfere very considerably with the safety and efficiency of an airplane. Secondly, it should withstand weathering, with its changes, often sudden, from hot to cold and from wet to dry. Thirdly, it should protect the fabric from deleterious light effects.

The brushing on of a cellulose acetate solution on to a fabric, which has been evenly attached to a wooden framework, will on drying produce a taut cellulose acetate film in the meshes of the fabric. This film will become brittle when the last traces of solvent have passed off. Brittleness can, however, to a great extent be avoided by the inclusion in the dope of a solvent of cellulose acetate whose volatility is very low, i.e., one with a high boiling point, and which consequently remains in the dried dope film. In the early days of dope manufacture tetrachlorethane was used as a solvent and this gave a tough film, and one which withstood the effects of dry weather

fairly well. Its low volatility enabled much of it to be retained on drying. This solvent, acting as it did as a "softener," proved unsatisfactory in wet warm weather through the development of hydrochloric acid which destroyed the fabric and probably the cellulose acetate as well; at any rate, the surface soon became a network of cracks and especially if the planes were pressed with the finger. This, coupled with the poisonous effects of tetrachlorethane on the dope operatives in promoting a type of jaundice which, in some cases, resulted in death, led to its early abandonment. It was found at the Royal Aircraft Establishment (Advisory Committee for Aeronautics, Reports and Memoranda No. 498, 1915, published in 1919) that benzyl alcohol could be used with greater success than tetrachlorethane. Its high boiling point, 200-213° C., and its solvent property, caused it to be retained in the dope film for a considerable time under ordinary weather conditions, though its volatility became apparent when it was incorporated in dopes which were used on airplanes in Egypt, where the temperature changes were greater. The superiority of benzyl alcohol over tetrachlorethane in acetyl dopes may be seen from the results of weathering tests after exposure for 50 days. In the case of tetrachlorethane dope, the loss in tensile strength was 32 lb. per inch width of fabric, whereas in the case of the benzyl alcohol dope the loss was only 12 lb. per inch. The addition of too much benzyl alcohol to a dope gives rise to an appreciable reduction in its tautening

property. It has also a marked effect on its viscosity, as the following figures will show, which illustrate its effect on a typical dope, containing 8.5 grams of cellulose acetate in 100 cm³.

Table I.

Benzyl Alcohol cm ³	Viscosity at 25° (Glycerol = 100)
0	65.1
2	53.2
5	48.5
10	42.8
15	37.1

As is well known, linen and cotton fabrics undergo variations in dimensions in wet and dry weather, and even though the fabric may have been covered with dope, yet these changes still go on, though perhaps not to so great an extent. Similar effects are observed in hot and cold weather. Thus, doped fabrics on airplanes will undergo great changes in tautness, and in the case of moist, cold weather may become so flabby as to incapacitate the airplane. The great difference in temperature between the daytime and night in Egypt caused the tautness to suffer extreme variations, and this had weakening effects on the structural parts of the airplane. Benzyl alcohol in the dope used did not give the best results, for it tended to promote a tautness which was directly dependent on the weather. Dopes, however, which contained triacetin (glycerol triacetate), though not giving quite such a high degree of tautness, gave a coating which underwent less variation. This is remarkable, for it has a lower

boiling-point, 169-172°C., than benzyl alcohol.

Another agent which was found to plasticize the dope film was triphenyl phosphate - a crystalline solid melting between 45-48° C., and having a sufficient, though slight, solvent action to prevent it from crystallizing out in the dope film, and thereby to cause its disintegration. Tricresyl phosphate, which is widely used as a plasticizer in the kinema film industry, does not appear to have found favor in this country as far as dope was concerned, probably because of its tendency to cause "whiteness" through its lower solvent action for the particular quality of cellulose acetate used in dope. Triphenyl phosphate does not alter the tensile strength of a dope film, but permits it to undergo greater elongation before being ruptured. This was proved, as shown in Table II, by preparing a series of dope films by brushing several coats, each succeeding coat at right angles to the previous one, of dope containing varying proportions of triphenyl phosphate to cellulose acetate on to squares of plate glass and afterwards stripping off and ascertaining the tensile strength of strips cut from them 1 inch in width, 7 inches of film being placed between the jaws of the airplane.

Table II.

Weight of film per sq. yd. (oz.)	Triphenyl phosphate Cellulose acetate	Cellulose acetate per sq. yd. (oz.)	Percentage elongation (approx.)	Tensile strength lb./in.
4.42	0	4.42	7	32.4
4.92	0.1	4.50	9	33.8
5.64	0.25	4.51	11	34.0
6.90	0.50	4.60	15	36.9

The proportion of triphenyl phosphate to cellulose acetate which is usually found in dopes is about 1:6. Thus the formula of the Air Ministry for acetyl-cellulose dope required 15 lb. of triphenyl phosphate for every 85 lb. of cellulose acetate in 100 gallons of solvent mixture, 2 gallons of which is benzyl alcohol. The 98 gallons, instead of being composed entirely of one of the better solvents, such as acetone or methyl acetate, as was the case in some of the earlier dopes, were to contain, according to the Air Ministry specification, 45 gallons of one of these solvents in dopes for use in summer months, and 50 gallons for use in winter months. The remaining 53 gallons (summer months) and 48 gallons (winter months) were made up of liquids which have by themselves practically no solvent powers, though they may materially improve the solvent capacity of the mixture as a whole, and are known as "diluent." This diluent mixture was made up of 26.5 gallons each of alcohol and of benzol for summer dopes, but for winter dopes the benzol preponderates, there being 28 gallons of it to 20 gallons of alcohol. Ethyl

formate was sometimes used as a solvent and took the place volume for volume of acetone. In ethyl acetate both the Rhone and Spondon cellulose acetates appear to be insoluble, although the addition of alcohol permits of solution taking place. It has been suggested that it may be used to replace one-third of the acetone. Methyl-ethyl ketone, although not an ideal solvent for cellulose acetate, has an advantage in that it has a higher boiling point than acetone, and has therefore a somewhat reduced volatility, was occasionally used to replace one-fifth of the volume of acetone. Another solvent sometimes used is that technically known as "methyl acetone," which is principally a mixture of methyl alcohol, methyl acetate, and acetone. If it contained no non-volatile material and was free from acidity, it could be used as a substitute for both solvent and alcohol in the diluent mixture, the methyl acetate and acetone replacing pure acetone and the methyl alcohol replacing an equal volume of ethyl alcohol.

At first sight the composition of the mixture of solvents and diluents may appear somewhat fantastic. It will be noticed that the solvents, acetone, methyl acetate, etc., have lower boiling points than the two diluents used, and are consequently more volatile. A serious trouble in the doping of airplanes is that technically known as "whiteness." If dope is brushed on to airplanes in a humid atmosphere it will often be found that the dope surface on drying contains white patches or streaks, giving

an opaque film and a rough surface. It is, in fact, cellulose acetate which has been precipitated from colloidal solution instead of drying to a continuous transparent gel. These patches are readily penetrated by water, becoming on weathering a network of cracks and, moreover, reduces considerably the tensile strength of the fabric. The cause of this "whiteness" is often due to the precipitating action of water, though too large an amount of alcohol or benzol will do the same thing. To avoid this trouble arising from the dope itself, every precaution should be made to use only those materials which contain no water or only such quantities which will have no such deleterious effect on the dried film. The trouble usually arises through insufficient precautions being taken to control the humidity of the doping shops, which can be done by suitable control of their ventilation and heating, for a doped surface on drying tends to become cold through the extraction from it of the latent heats of vaporization of the liquids, and its temperature may therefore fall below the dew-point, with the result that water condenses on the surface and precipitates some of the cellulose acetate in the form of "whiteness."

As mentioned before, both alcohol and benzol, when used alone as diluents in conjunction with either acetone or methyl acetate as solvent, behave to varying extents as precipitants; using alcohol alone, the dope itself is opaque and white, whereas with all benzol a part of the cellulose acetate remains in

clear solution and a part fails to dissolve. With equal volumes of the two diluents a clear solution is produced and nearly so with a 1 : 3 mixture, but not with a 3 : 1 mixture. The solvent influence of benzol appears to be greater than that of alcohol. Those dopes which were clear had greater viscosities and gave films of greater tensile strength. Furthermore, the dope film deposited on fabric when dried under suitable conditions showed no "whiteness" in the case of dopes containing 1 : 1 and 1 : 3 alcohol-benzol mixtures. These proportions represent the limiting proportions of alcohol and benzol which can be safely included in dopes.

Dopes manufactured in accordance with the summer formula contained diluents in the quantity and proportions which only just prevented the formation of "whiteness" and therefore did not allow of any absorption of water, whereas the extra solvent and greater proportion of benzol to alcohol in the winter dope rendered possible a greater absorption of water before "whiteness" was produced under good doping conditions. Thus, it was found that summer dopes, prepared from materials which had satisfied the Air Ministry specifications, could absorb moisture to the extent of about 0.5 per cent, but if the ingredients happened to be anhydrous about 3 per cent could be absorbed. If one-fifth of the solvent, however, were methyl ethyl ketone, the dope permitted of still less water absorption. The winter dope did not produce "whiteness" until 6 per cent of water, using anhydrous

constituents, and 4 per cent, using approved materials, had been absorbed.

The manufacture of acetyl dopes is not a matter of great difficulty. Any type of mixing machine may be used, whether it be a revolving barrel or a metal or wooden cylindrical vat containing baffle plates and rotating paddles. The cellulose acetate often requires much time for complete solution, through the formation of gelatinous layers on the surfaces of lumps of the acetate which thereby impede the penetration of the solvent. This can sometimes be prevented by agitating the cellulose acetate with the diluents in order to get the material well disintegrated before introducing the solvent. If, on the other hand, it is attempted to get the cellulose acetate to dissolve first in the solvent, before adding the diluents, the resulting extremely viscous solution will exert an excessive and perhaps disastrous strain on the paddles.

The temperature of a dope shop should be between 70° and 75° F. and care should be taken to keep the humidity of the atmosphere at a minimum. The fabric should be quite dry and should contain the least possible quantity of dressing, the only lubricants permitted in sizing the warps of the linen fabric being pure tallow, pure palm oil, or pure Japan wax. If any unsaponifiable matter be used, such as paraffin wax, the dope will not adhere satisfactorily to the fabric, but will give a "bubbly" surface. Another point of importance is that the dope on being

brought from storage shall have ample time to attain to the temperature of the room. If the dope be cold the viscosity will be much too great, and if too warm, too small. Fig. 1 shows the considerable change in the viscosity of a dope with temperature, and shows that a dope at 10° C. has a viscosity of about double that at 25° C. The application of dope at too high a temperature will also cause the coating to contain so many small bubbles that the continuity of the dope film will be impaired.

Dopes used for covering airships are generally applied mechanically by a scraping motion to the fabric before it is attached, for which a highly concentrated, and therefore highly viscous, dope is used. As the dope is to function mainly as a waterproofing agent, a larger proportion of plasticizers, such as triphenyl phosphate, is included.

The dope film which has been applied to the fabric of an airplane may give initially the necessary tautness and waterproofing, but after some time both the dope film and the fabric will begin to deteriorate. The softening agent, either benzyl alcohol or triacetin, will slowly evaporate from the dope film leaving it brittle, and in time the adhering film will tend to strip off from the fabric. This evaporation can, however, be prevented to a great extent by the application to the doped surface of a coat of suitable varnish. Linseed oil-rosin varnish affords satisfactory protection in winter weather, but in warmer weather the chemical action that goes on in the drying oil hard-

ens the varnish coat, so much so that it may peel off, bringing the dope film with it. Tung-oil (Chinese wood oil) rosin varnish gives better results in all weathers. Perhaps the best covering yet found is a nitrocellulose varnish, the outcome of research at the Royal Aircraft Establishment, and known as V.114. This varnish is rendered extremely supple by the inclusion of a good deal of castor oil. The following formula makes 100 gallons:

Nitrocellulose syrup	250 lb.
Amyl acetate	17½ gal.
Castor oil	90 lb.
Methylated spirit (66 per cent over-proof)	21½ gal.

The nitrocellulose syrup contained 20 per cent by weight of dry nitrocellulose, not more than 10 per cent by weight of alcohol, and not less than 70 per cent by weight of either butyl or amyl acetate. V.114 proved most serviceable when used on the undersides of airplanes, but when used on the upper surfaces deterioration of the fabric still occurred. This is forcibly illustrated in Table III by some measurements of the tensile strengths of doped and doped and varnished (V.114) fabrics after exposure to the weather for varying periods (vide Advisory Committee for Aeronautics, Reports and Memoranda No. 498).

Table III

Tensile strengths in lb. of strips 1 inch wide.
(a) In winter months:

Days exposed	0	10	20
Dope	103	93	91
Dope + V.114	104	98	97

(b) After 52 days' exposure in summer.

Dope alone	39
Dope + V.114	41
Dope + P.C.10	91

It will be seen that the deterioration did not take place at a great rate in winter, but in summer-time the loss in tensile strength of the doped fabric covered with V.114 after 52 days was only slightly less than that of the doped fabric alone. The cause of this remarkable loss was traced to the ultra-violet radiations, and thus accounted for the deterioration taking place only in the sunny months (see also Aston, Advisory Committee for Aeronautics, Reports and Memoranda No. 585). Table IV gives the results of tensile strength experiments, expressed in pounds per inch, of doped fabrics covered with various pigmented varnishes when exposed for different periods.

Table IV.

Days exposed	0	25	50	75
Covering				
Dope	95	66	47	32
Dope + Dyed varnish	95	62	49	32
Dope + Blue pigmented varnish	95	62	53	51
Dope + Khaki pigmented varnish	95	80	76	75

These figures indicate that the greatest protection from the ultra-violet radiations was given by the two pigmented coverings, one of these, the khaki-colored one, was more efficient. This led to an almost general adoption of khaki pigmented varnish coverings for the upper surfaces; sometimes they were pigmented tung oil-rosin varnishes, and more often a nitrocellulose-castor oil varnish of the type of V.114, in which was incorporated the pigments necessary to give a khaki hue. The following is the formula of this varnish, known as P.C.10, to make 100 gallons:

Nitrocellulose syrup	250 lb.
Castor oil	50 "
Methylethylketone or acetone	20 gal.
Butyl or Amyl acetate	15 "
Methylated spirit	15 "
Benzol	15 "

Pigments 74 lb.

e.g.: (Yellow ocher, 40 lb.; Umber, 30 lb.;
Red ocher, 40 oz.; Chinese blue, 25 oz.)

These pigments were thoroughly ground with the castor oil in either a cone or roller mill and then mixed with the nitrocellulose mixture. As shown in Table III, it gives an excellent protection to the fabric.

The tensile strength of doped fabric in the directions of both the warp and the weft are in general a little greater than the sum of the tensile strengths of the fabric and the dope film alone. This may be due to the reinforcement which the adhering dope film gives to each individual fiber, for a piece of doped fabric under tension usually yields in an even break and not with an irregular tear, as is often the case with fabric. Fig. 2 gives an approximate measure of the tensile strength of typical dope films alone, strips of 1 inch in width being used.

The question of inflammability of doped fabrics is one of great importance. Acetyl-cellulose dope films are almost unflammable, due to the acetate itself and the triphenyl-phosphate. Nitrocellulose dope films, on the other hand, are highly inflammable, though airplane dopes are still being manufactured from pyroxylin in the form of used kinema films. It should be stated that these dopes contain certain ingredients to reduce their inflammability, and it is probable that when airplanes

are in flight neither acetyl- nor nitro-dope film can burn, and the fact that wings have so burned must have been due to saturation with gasoline (Barr, Advisory Committee for Aeronautics, Reports and Memoranda No. 573, 1919), and therefore one of the essential properties of the protective varnish coverings is that they shall be resistant to gasoline and also to hot castor oil, which is used as a lubricant. It is when the airplanes are stationary that the nitro-dopes may exhibit their greater inflammability. Table V gives the ignition temperatures of fabrics covered with various dopes when heated in a muffle furnace and are taken from the paper by Barr, mentioned above.

Table V.

Ignition Temperatures.

Undoped linen	353° C.
Linen doped with acetyl	380° C.
" " " " + P.C.10	375° C.
" " " " + pigmented oil varnish	390° C.
" " " nitro, containing no fireproofing agents	200° C.
" " " proprietary nitro con- taining fireproofing agent (CaCl ₂)	195° C.

The table, despite the necessarily rough method employed, shows that doping with acetyl dope actually increased the ignition point, due, no doubt, to the smaller heat capacity and

there being no open structure. It is significant that the nitro-varnish P.C.10 when applied to an acetyl-doped fabric only lowered the ignition point by a few degrees, and that the pigmented oil varnish raised the ignition temperature, evidently through the formation of a blanket of charred matter. The nitro-doped fabrics inflame at a considerably lower temperature, and the incorporation of calcium chloride had very little influence. It has, however, an effect on the rate of propagation of flame, and so has such substances as finely ground zinc oxide, precipitated chalk, and china clay. The rate of burning of acetyl-doped fabrics is considerably lower, and if any of these substances be inserted in the dope the rate of burning is reduced still further.

Some experiments made by the author give a qualitative idea of the rate of burning of fabric strips, 12 by 1 inch, having different coverings. These strips were hung vertically from a wire, kindled at the bottom, and the time recorded with a stop watch for complete combustion. Three further experiments were performed to see if the rate of burning could be lessened by fireproofing the linen before applying the dope. Fireproofing was effected by immersing the fabric in a solution of ammonium phosphate to which an equivalent amount of aluminum-sulphate solution was afterwards added so as to precipitate gelatinous aluminum phosphate in the fibers. After removing adhering substances by washing, the fabric was dried, attached to a wooden frame, and doped.

The results are given in Table VI.

Table VI.

Linen		18 sec.
" + acetyl dope		25 "
" " " + clear oil varnish . . .		30 "
" " " + k. pigment-oil varnish		31 "
" + nitro dope		12 "
" " " + clear oil varnish . . .		14 "
" " " + k. pigment-oil varnish		16 "
Linen (fireproofed)	Did not	burn.
" " + acetyl dope		30 sec.
" " + k. pigment-oil varnish		42 "

The marked superiority of acetyl dope over nitro dope is evident. The oil varnish impeded burning, but in the case of the nitro-doped fabric the dope film could be seen to be flaring underneath the varnish film. The last set of data show that fireproofing of the fabric did diminish the rate of burning to a small extent, but when it is remembered that the fireproofing rendered the dope film less adherent, it will be gathered that no real advantage can thus be obtained.

It might be imagined that the insertion of insoluble matter in dopes may cause the dope film to become discontinuous and thereby fail to protect the fabric and to diminish the tautness. There is no doubt that hygroscopic substances like calcium chlor-

ide, as was used in a certain proprietary nitro dope, had an undesirable effect on the tautness of the dope fabric in damp weather. Ramsbottom and Thomas (Advisory Committee for Aeronautics, Reports and Memoranda No. 606, 1918) recommended that all coats of dope should be pigmented, for they state that pigmentation enhances the tautening power and reduces the slackening which invariably occurs in a moist atmosphere. This should also reduce the inflammability, and if khaki protect the fabric from ultra-violet radiations. They state that the greater the quantity of pigment up to $1\frac{1}{2}$ lb. per gal., the more efficient will be the dope with respect to tautness. Highly pigmented dopes become brittle on weathering. This, however, can be remedied by the use of additional softening agent, and provided that a suitable cellulose acetate is used no difficulty arises over adhesion of the dope to the fabric.

In the foregoing, little has been said on nitro dopes. During the war they, with the exception of one proprietary dope, were restricted solely to airplanes for "home service," and it may be that in the future they will be discontinued altogether. The utilization of used stripped kinema films for the manufacture of dope presented some difficulty, on account of the variable composition of the films and the difficulty in selecting only that material which was suitable. This, presumably, will also occur in any attempts which may be made to employ kinema films for the manufacture of lacquers. The difficulties which

arise are due to the fact that (a) both cellulose esters - acetate and nitrate - are now used in film making; (b) the esters used in the manufacture of films give considerably higher viscosities than are suitable for dopes; (c) variable types and quantities of plasticizers are employed, which will necessitate careful investigation before subsequent use and (d) the difficulty of stripping and drying. The high viscosity can to some extent be overcome by making the dope solutions less concentrated, but this would mean that more coats would have to be applied to the fabric with a resulting greater consumption of expensive solvents. On the whole, kinema film was not satisfactory during the war, and resort was made to low-nitrated cotton. The "home service" dopes contained about 10 per cent of nitro-cellulose, 3 per cent of plasticizers such as triphenyl phosphate, and in a few instances camphor, and a small percentage of a "softener," which was usually about 1/4 to 1/2 per cent of castor oil. The usual solvents were employed, namely, acetone, methyl ethyl ketone, amyl and butyl acetone, and as diluents, benzol, methylated spirit, and butyl alcohol.

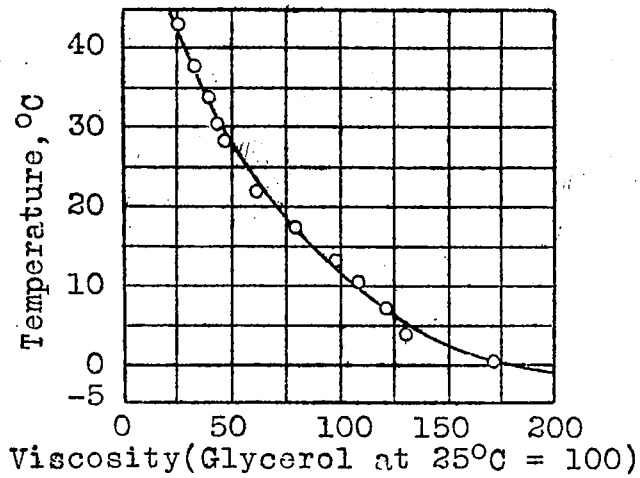


Fig. 1 Change of viscosity of dope with temperature.

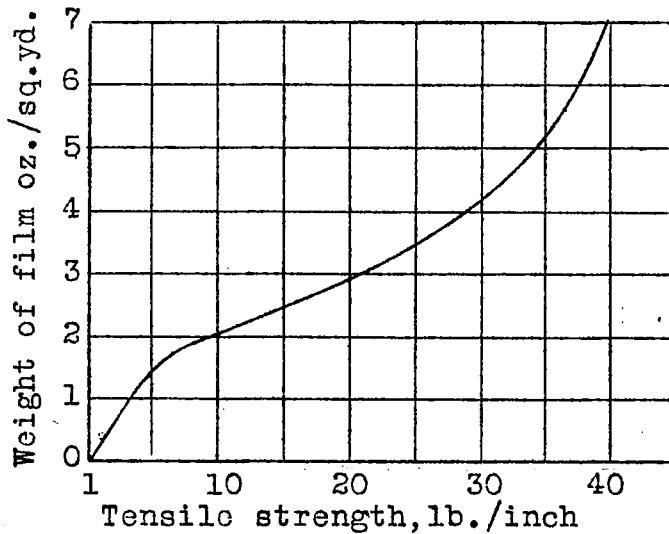


Fig. 2 Graph showing tensile strength of dope films.