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SURFACE PHENOMENA IN HIGH EXPLOSIVES

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SURFACE PHENOMENA IN HIGH EXPLOSIVES

It is the purpose of this paper to discuss, in summary form, the experimental work dealing with the chemistry of surfaces, which has to date been performed by the experimental group at S-Site. Details and a more complete listing of data can be found in the monthly progress reports. Much of this material appears in the Technical Series.

Because of their significance in bomb design, the greater part of the work was performed with Baratols and Cyclotols. This report will consist, therefore, almost entirely of a discussion of these two classes of explosives. The properties which are of greatest interest to us manifest themselves in the liquid state. Most of the measurements have been performed with the slurry. Determinations of viscosity and rates of shear have been very useful.

The report is divided into four parts as follows:

A. Cyclotol Slurries

B. Baratol Slurries

C. Particle Size in Baratols

D. Present and Future Program

Instruments

Viscosity and rate-stress determination. There are, obviously, a variety of instruments suitable for viscosity measurements of H.E. slurries, but for the sake of speed and convenience, a Stormer Viscosimeter, modified and calibrated by E.R.L. at Bruceton, Pennsylvania, was chosen. The modified feature is the substitution for the cylinder of a two-bladed propeller with a pitch so chosen as to cause a slight lift of the slurry and thus prevent segregation during a determination (See Plate I). The container, a tapered copper beaker, is immersed in a steam heated oil bath. The method used in determining

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viscosity is to interpolate to 90°C from a wider range (5° to 6°C). The most recent adaptation has been the use of a constant temperature bath. Unless otherwise indicated, all viscosity values were taken at 90°C.

Calibration of the modified Stormer Viscosimeter is accomplished against a series of oils, the viscosities of which have been determined by absolute methods with efflux type viscosimeters.

Particle Size Determination. For routine measurements in the sub-sieve range, a Fischer Sub-Sieve Sizer is used. Though this method is quite rapid, it is admittedly inaccurate and offers results, the significance of which are difficult to interpret.

For slower, but more accurate work, especially for research purposes, particle size distributions have been derived by direct measurement from photomicrographs.

A. CYCLOTOL SLURRIES (TNT-RDX).

The experiments performed with Cyclotols will be discussed briefly in chronological order. Since many lines of experimentation originated because of immediate need rather than as a logical research development, no attempt is made to show the relationship of one topic to another.

Temperature Coefficient of Viscosity. Determination of viscosity over the range 101°C to 79°C for Composition B-2 indicated a linear increase in viscosity of about 7.0% per degree drop ($-\frac{\Delta\eta}{\eta} = 0.070$ degree $^{-1}$.). Since such a determination is quite time consuming and because of the possibility that a portion of the rise in viscosity may be due merely to agitation of the slurry for a long period (duration of the run), the determinations were repeated with a number of samples, treated identically but measured at different tempera-

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tures. This method eliminated the effect of prolonged stirring of any one sample and showed an increase of 4.5% in viscosity per degree drop in temperature $\left(- \frac{\Delta\eta}{\eta} = 0.045 \text{ deg}^{-1} \right)$.

Effect of Time of Agitation. The previous experiments indicated the fact that the rise in viscosity, due to agitation, was appreciable. Quantitative determinations were made using 3-gallon quantities of Composition B and applying both hand stirring and mechanical stirring. The results of these measurements are plotted in Fig. 1. It is obvious that mechanical stirring is far more effective than hand stirring in raising the viscosity. It should also be observed that when agitation ceases, the viscosity immediately ceases to rise or even shows a tendency to drop. These facts would indicate that the increase in viscosity is due to dispersion of deflocculation or to mechanical grinding of the RDX particles with a consequent increase of surface area to be wet by the TNT and that this process is, of course, accelerated by mechanical agitation as compared to hand stirring. This was borne out subsequently with particle size studies of Cyclotols and will be discussed in a latter portion of this report.

Use of Additives. A variety of surface-active agents were added to Composition B in an endeavor to decrease viscosity and to improve the pouring properties of such slurries. Though low magnitude effects were observed with wax, octyl alcohol, and stearoxyacetic acid, this is due probably to a "lubrication" rather than to surface forces. The similarity of RDX and TNT from the chemical point of view suggests that a high degree of wetting can be accomplished without the use of wetting agents and even that the wetting can not be improved.

Effect of Additives on TNT. Half-second Nitrocellulose: The Stormer Viscosimeter is not suitable for absolute viscosity determinations in

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the low viscosity range of TNT. However, relative results of some significance can be achieved:

	Viscosity
TNT	0.10 poises
TNT + 2 1/2% N.C.	0.15 poises
TNT + 5 % N.C.	0.23 poises

The addition of Cellulose Acetate Butyrate to TNT causes a high increase in viscosity as follows:

	Viscosity
TNT	0.1 poises
TNT + 2% C.A.B.	1.6
3% "	2.1
4% "	2.5
5% "	3.6
10% "	16.4

Blending of Commercial Composition B. Assuming that the viscosity of Cyclotols depends primarily on the particle size and distribution of the dispersed phase, the effect of blending Composition B samples of different viscosities and of correspondingly different particle size distributions was determined. At that period several lots of unpourable Composition B were available, having viscosity values as high as 80 poises. These lots were incorporated, in varying proportions, with normal Lots of Composition B and the viscisities of such mixtures were determined. As will be shown, the particle size distribution for the two types of slurries differ widely, the high viscosity slurry containing a very much higher percentage of "fines" than the normal

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Composition B. The blending experiments show a remarkable lack of rise in viscosity with blend composition until a value is reached where the high viscosity Composition B exceeds 50%, by weight, of the mixture. Below that point the viscosity does not increase appreciably above that of the low viscosity slurry. This phenomenon may be the solution to the problem of disposing of unpourable Lots of Composition B. The explanation may lie in the fact that the surface area of RDX is very greatly decreased in the preparation of a blend as compared to the surface area present in a high viscosity slurry. The results are plotted in Fig. 2.

Particle Size of RDX as Related to Viscosity of Cyclotols. As a consequence of the previous observations, the problem arose of accurately determining the particle size of RDX in Cyclotols and of correlating this with viscosity. For highest accuracy, a microscopic method was developed. It was found that a high temperature method whereby RDX particles could be observed suspended in molten TNT was not possible due to the similarity of the indices of refraction of the two substances. Instead, an extraction method was used. The procedure used was to dissolve the TNT from a small sample of Composition B with a saturated solution of RDX in choloroform. The RDX remaining after solution of the TNT is dispersed by agitation and allowed to settle through the choloroform on to a shallow glass dish. The particles are then observed and photographed through the layer of liquid (For details see Progress Report for January, 1945.) It was first determined photographically that there is no change in size or shape of RDX crystals upon prolonged contact with a saturated chloroform solution of RDX. As a scale, a stage micrometer was photographed under identical magnification as were the particles, and measurements were made from this scale. Since, upon settling, the long axis of the RDX crystals are assumed to be distributed haphazardly in all angles, and since a minimum of

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200 particles were measured on each plate, the average diameter of a particle was taken as the distance between 2 vertical tangents.

From the particle-size distribution curves of a number of preparations it is apparent that in the range studied, viscosity of the melt decreases linearly with increase of particle size, of RDX. Fig. 3-a and Plate II.

A study was made also of the previously mentioned increase in viscosity with agitation. Fig. 3-B shows the particle size distribution for a melt freshly prepared and also for the same melt after an hour of mechanical agitation. It is obvious that the agitation has caused a pronounced decrease in particle size. Though it is not known whether this effect is due to a dispersion of agglomerates or to a crystal breakdown, the net result is the same in either case.

Fig. 4 is a representation of the RDX particle size distribution for several Composition B samples of varying viscosities. These curves are plotted cumulatively. The figure indicates that for all slurries, whether high or low in viscosity, the vast majority of the particles fall into one region and are of an order of magnitude greater than 30 microns. The greatest variations in viscosity seem to be due to the particles in the range below 30 microns. This would appear likely from a surface point of view. A composite of these data were prepared, which was intended as a specification for fluid Composition B. It combines all the curves of Fig. 4 in the upper regions and defines the upper limit for fine particles to yield an ideal melt. (For details see Progress Report, January, 1945.)

At this stage, a series of experiments was performed in an attempt to synthesize several samples of Composition B according to the Specification arrived at above.

Four convenient size fractions were prepared by wet-sieving a sample of

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whole RDX as follows:

Sieve Fraction		Arithmetic Mean of Sieve Openings (microns)	Measured Mean (Photomicrographs)	by % Weight
Through	On			
60	100	200	158.4	16.5
100	200	112	103.5	54.2
200	325	59	63.3	13.3
325	---	44	30.1	16.1

By reference to Figure IV and through a conversion from a number to weight basis, the Specification calls for the following ratio:

60/100 mesh	7.0
100/200	2.2
200/325	0.7
Through 325	0.1
	10.0

The procedure followed in preparing a melt was to incorporate RDX, wet with 10% water (to duplicate ordnance procedure) to molten TNT, and to stir the slurry at 90°C for 3 hours. The resulting viscosities were not in keeping with those expected in that no appreciable rise in viscosity was obtained until the ratio of the finest fraction reached a value of 1.5 to 2.0, whereas it was expected to rise at a value of 0.1. This result was due probably to our lack of complete knowledge of ordnance procedure. We know, for instance, that dispersion of the RDX will depend upon time of cooking, water content, temperature, batch size, rate and type of agitation, rate of incorporation, etc. Our method was developed with no knowledge of the above factors in ordnance procedure. Nevertheless, the relative results were excellent as can be seen in Fig. 5. This graph indicates the results of a series of experiments designed to determine the contribution of various RDX grists when added to a more course fraction (through 50 on 100). This fraction constitutes a large proportion of

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RDX in commercial, low viscosity Composition B. From the curves, two facts are apparent: (1) The effectiveness of any sieve fraction in increasing viscosity is indicated by the slope of the curve, the finer fractions having the greater slopes, and (2) the point at which the viscosity begins to increase rapidly (that point at which the curve leaves the base line) also depends directly upon the particle size. This latter phenomenon probably can be explained by assuming that it is due to the greater ability of fine particles in filling voids left by the 50/100 sieve cut than of equal weights of more course particles. Fig. 5 offers sufficient information for an accurate determination of the per cent of fines of any known particle size required, when combined with a 50/100 sieve fraction, to give a desired viscosity.

<u>Temperature Cycling of Composition B.</u> In an attempt to duplicate ordnance pellet production, all laboratory-prepared Composition B samples were poured out and allowed to freeze once and then remelted before the viscosity was determined. Because a distinct lowering in viscosity was noted during this process, a further study was made. Various samples of Composition B, both laboratory prepared and commercial, were alternately melted and frozen and the viscosity determined after each cycle. The results were as follows:

No. of Cycles	60-40 Cyclotol Lab. Prepared	Comp. B-2 (Holston) Lot 1-687	Comp. B-2 (Holston) Lot 1-684	Comp. B-2 (Holston) Lot 1-684
0-Initial	25.7 Poises	13.4 poises	36.0 poises	33.7 poises
1	15.6	9.4	23.5	16.2
2	10.8	7.5	18.3	15.0
3	9.2	6.5	16.6	12.6
4	9.0	6.3	14.5	10.8
5			14.0	10.2
6			12.9	8.8

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These data are plotted in Fig. 6.

The above results seem to indicate the fact that the phenomenon is due solely to recrystallization. RDX is known to be 4-5% soluble in TNT at 90°C. The above process consists merely of a series of high and low temperature cycles. At the higher melt temperatures the RDX will dissolve to the extent of its solubility. It is obvious that due to higher surface energy the smaller particles will dissolve at a higher rate than the large particles. Upon cooling, the dissolved RDX crystallizes out, not in the small amount of free TNT matrix present but rather upon the larger RDX nuclei. The overall effect, therefore, of this process would be the elimination of fines and a general increase in particle size with attendant decrease in viscosity. It was found that temperature cycling in the liquid state, without the freezing-out process has a similar effect but is not as pronounced.

Rates of Segregation. A logical consequence of particle size study was the determination of relative rates of segregation of the solid component of cyclotol slurries. The experiments were performed over a wide variety of melts containing both relatively pure RDX grist fractions and mixtures of various fractions. A study of the contribution towards settling of 183-second N.C. was also carried out. The procedure was as follows: The sample was poured to an 11" height into a glass tube (15 mm OD) and kept by means of a constant temperature bath at 85°C for two hours. At the end of that period the supernatant TNT layer was measured and the tube allowed to freeze. The glass was then broken from the H.E., and four samples uniformly spaced along the length of the H.E. cylinder were analyzed for composition. From the analytical data the degree of segragation, calculated as percentage spread, was determined. Analysis indicates the fact that the segregation phenomenon can be divided into two phases as follows: (See Progress Reports, May and June, 1945.)

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a. Segregation downward of the complete RDX component to leave a supernatant TNT layer and

b. Differential segregation within the concentrated RDX column.

Neither of the above processes is, necessarily, a function of the other; in fact, the two are generally in inverse proportion. In the case of slurries which yield, upon segregation, a large, clear supernatant the "spread" in the RDX region is generally quite low and vice versa.

Naturally, this effect is accentuated by the use of course RDX grists rather than fines. The same is true for particles of homogeneous size. These results are apparently due to a "stacking" process. When the particles are uniform in diameter, there can be expected little settling gradient among them, and there is, therefore, a likelihood that they settle and "stack" at the same rate, giving a uniform composition in the RDX area and a large supernatant. Commercial Composition B shows a similar tendency due to the fact that the average particle size is quite high. Yet in commercial Composition B there is the additional shortcoming of a greater degree of segregation in the RDX layer due undoubtedly to the wide range of particle size distribution in the RDX.

Concerning segregation as effected by viscosity, this topic will be discussed more comprehensively in Part II. It should be noted here that it was found that an increase in viscosity of a slurry by an increase in RDX content does not eliminate the high supernatant. It was decided, in attempting to decrease settling, to raise the viscosity of the liquid TNT matrix instead. For this purpose small quantities of 183-second nitrocellulose were incorporated. The improvement wrought by this procedure was quite marked,: the supernatant was decreased from 15 to 20 mm for commercial Composition B to 1 to 2 mm for the same material plus about 0.1% 183-second N.C.

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Until this point these data were recorded for 2-hour settling periods. Since, however, several casting procedures called for maintaining fluid portions of H.E. in the mold for as high as 20 hours, and because it would be of interest to look into the "stacking" process, a series of slurries was kept in the molten condition until complete stacking occurred. Fig. 7 indicates the correlation between absolute viscosity and rate of segregation where the viscosity variation is accomplished by several mechanisms.

Three facts are obvious:

1. The time necessary for stacking to be accomplished is directly proportional to the viscosity of the slurry provided that the viscosity gradient is derived by changes in one variable (such as NC content, composition or particle size).

2. The height of the stacked layer of RDX is proportional to the initial height of the poured melt (curves Va and Vb).

3. As pointed out, viscosity variations for Composition B arise through several mechanisms. In many instances a common viscosity figure is the only similarity between two melts. Indicative of this are curves B (65-35 cyclotol, $\eta = 31.2$ poises) and III (60-40 cyclotol, $\eta = 38.5$ poises). While the viscosities of the two are in the same range, the former nevertheless stacks far more rapidly and to a greater degree than the latter. The slurries containing the nitrocellulose also exhibit superior pouring properties, having the more "sticky consistancy" characteristic of the Baratols. This subject of pouring properties will be more fully discussed in part B of this report.

Further information concerning effects of 183 sec NC on cyclotols with particular reference to law percentage of RDX and detonation velocity will be found in Group X-2 Progress Reports for May and July 1946.

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Application of Settling Data to Casting Procedure. In view of casting and machining procedures, the segregation results were not alarming. In fact, a high degree of segregation has been found advantageous in certain instances; special procedures have been adopted to exploit fully this effect. In the instance of the Composition B inner charge, a method of "Overcasting" has been developed whereby the mold walls are extended well above the spherical contour taking the place of the more narrow risers used previously. No attempt is made to increase the viscosity; the RDX is free to segregate. When the casting is removed, the supernatant TNT layer is simply removed in the process of machining to the desired contour. Most of the casting now consists of homogeneous "stacked" cyclotol. In the case, however, of the Composition B lens overcast, such a machining process is not feasible, and the casting must be poured to the contour. In such an instance, a segregation inhibiting agent would be useful.

In order to test the benifits of 183-second nitrocellulose as applied to castings, an inner charge of commercial Composition B was cast containing 0.1 183-second N.C. An identical casting minus the NC was prepared as a control. The nitrocellulose improved the "spread" by about a factor of 4:

	Composition B	Composition B + 0.1% 183 sec. NC
Density Spread (g/cc)	0.04	0.009
Composition Spread (%)	26.0	7.0

Thusfar, some hindrance has been encountered in the presence of cracks where nitrocellulose is used. However, there appears to be an excellent possibility for the development of a casting technique for such explosives.

Water Inclusion. The problem of water impurities and moisture content are of relatively minor importance where cyclotols are concerned. Since, however, small quantities of water are of prime consideration in Baratols, some mention

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should be made, by way of contrast, of its effect upon cyclotols.

Superficially, the influence of water upon cyclotols is to decrease greatly the viscosity. Quantities of about 5% H_2O have caused a viscosity lowering by a factor of approximately 1/3. The components of cyclotol are, however, quite similar chemically, and as opposed to the water soluble barium nitrate of Baratols, no appreciable attraction is expected between the water and either the TNT or RDX. This is borne out in the melt. In a cyclotol slurry containing water, the latter separates out completely and tends to coat (wet) all foreign substances towards which water exercises an appreciable adhesive force. For instance, a metal stirrer or glass rod inserted into such a Cyclotol will, when removed, contain a film of water rather than Cyclotol. It is practically impossible to "dip out" any quantity of slurry using a glass or metal rod. In all such instances, the rod appears to attract preferentially a film of water. It is, therefore, justified to assume that the apparent viscosity of such a slurry is, rather than a true value, something due to lubrication or slippage. Offhand it appears impossible to measure viscosity under such circumstances without radically altering the method. In any type of determination, whether the measurement is accomplished with a shearing propellor or an orifice or falling body, the above shortcoming will be present. A method is being planned for determining the true viscosity of water-Cyclotol slurries.

B. BARATOL SLURRIES (TNT-$Ba(NO_3)_2$).

Shear and Pouring Properties. It is known that Baratols, when properly prepared, exhibit pouring properties that are superior to those of Cyclotols, regardless of absolute viscosity values. A Cyclotol will acquire poor pouring qualities at viscosities above 40 poises and will become unpourable at viscosities of 70 to 80 poises. On the other hand, it was observed that Baratols will have a high degree of pourability at extremely high viscosities (200 to 300 poises). The difference lies in the "sticky consistency" of the Baratols.

A short discussion of general dispersion properties would be of value at this point since the various classes of Baratols which are prepared for research purposes represent virtually all categories of Dispersions and Flocculations. Little mention has been made of these properties until this point as it will be more helpful to compare the Rheology of the Cyclotols and the various Baratols.

Various finely subdivided materials exhibit vastly different rheological characteristics when incorporated into small amounts of liquids in which they are fairly insoluble. This has been found to be the cast for $Ba(NO_3)_2$ and for RDX. It is known, for instance, that far more $Ba(NO_3)_2$ can be incorporated into TNT (containing a small quantity of nitrocellulose) than can RDX and, also, that where no nitrocellulose is present, a relatively small quantity of $Ba(NO_3)_2$ can be incorporated to yield a fluid melt. Slurries of such concentrations can be studied qualitatively, as in the pigment industry, by a variety of more or less subjective methods. Our own procedure has been to adapt a Stormer Viscosimeter for the determination of rate-stress information. This instrument enables one to determine the response, as rate of shear, to a range of torsional forces. A plot of shear rate against driving force reveals to us the nature of the liquid. Slurries can be divided into three main classes as follows:

1. Those in which the solid component is in a very highly dispersed state.
2. Those in which dispersion is poor. This type of slurry is often referred to as a "flocculated" suspension.

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3. Those in which the dispersion state is intermediate between the above two.

The degree of dispersion of finely divided solid particles in a liquid matrix depends upon the affinity or, more correctly, upon the adhesive forces at the liquid solid interface. The rheological properties of a slurry can be defined as a resultant of three surface forces:

1. The adhesive force exerted between liquid and solid (F_{ls}).
2. The cohesive force between solid particles (F_{ss}).
3. The cohesive force or consistency of the liquid medium.

Where F_{ls} exceeds F_{ss}, we find a strong adhesion of the liquid to the solid particles. In such a case, the angle of contact is zero, or very nearly so. The molecular orientation at the interface is such that F_{ss} becomes negligible, there is little interference amongst the solid particles which are highly dispersed, and complete freedom of flow or shear is allowed. Such a slurry has the property of a "true viscous" or "Newtonian" liquid. It is characterized by a linear rate-stress curve which passes through the origin. (See Fig. 8 - 1,2.) In such liquids an infinitesimal stress increment causes a corresponding infinitesimal shear.

If, on the other hand, F_{ss} exceeds F_{ls}, we have an example of poor wetting. The contact angle in such a case is large; a liquid film is not firmly held. In this case it requires a larger quantity of liquid to "wet" the solid than in the case of a dominant F_{ls}. In a dilute suspension of this type there would be a tendency toward flocculation and increased rate of precipitation of the solid aggregates. In slurries of extremely high concentration of which Baratols and Cyclotols are an example, the tendency instead is for the setting up of a structure maintained by the cohesive forces between the solid particles. The magnitude of the strength of this structure is indicated by the "yield value"

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as determined with the viscosimeter. This factor represents the minimum force required to cause fluid flow for a particular slurry. (See Fig. 8 --3,4.)

Further mention will be made of these properties. It should be mentioned here again that micropulverized $Ba(NO_3)_2$ cannot be incorporated into TNT without the use of a wetting agent. This is not surprising in view of the differences, chemically, between $Ba(NO_3)_2$ and TNT. Nitrocellulose serves very effectively as a wetting agent for this system. Such agents generally have a highly polar group and a non polar group which orient the molecule in the proper direction at the interface between liquid and solid.

Temperature Cycling. In conjunction with general Baratol preparation it was observed that freezing of a Baratol containing 0.1% stearoxyacetic acid followed by remelting causes a very extreme rise in viscosity, often to a point beyond the range of our instrument. The Baratol under this treatment loses the small degree of translucency which it normally has and acquires a more pale color. Microscopic examination of thin films of such melts revealed the presence of numerous small gas bubbles. See Plate III. (For details see Progress Report for June, 1945.) This phenomenon is lacking in Baratols which do not contain stearoxyacetic acid. The mechanism is, as yet, uncertain. Whether the phenomenon can be explained as a "stirring in" of air or, more likely, as a release of adsorbed air from the $Ba(NO_3)_2$ is not known. As can be seen from Plate III, there is a distinct correlation between air content and density of the cast H.E. The presence of such air in a melt may well cause a density gradient due to upward segregation of the bubbles. It should be pointed out that melts containing considerable quantities of air acquire very high yield values. It is also well known that stearoxyacetic acid tends to stabilize air in a Baratol melt.

Variation of Nitrocellulose Content. In order to increase the detonation rate of Baratol to the extrapolated value for Baratol 70 and still

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prevent excessive settling, a series of experiments was inaugurated whereby the nitrocellulose content was varied. It is known that a pourable Baratol could not be prepared without the incorporation of nitrocellulose. Since the expectation for a 70% Baratol with the usual 0.1% nitrocellulose was a prohibitively low viscosity (at least from the point of viewof settling), we expected a sharp rise in viscosity upon lowering of the nitrocellulose content from 0.1% toward 0%. The first series of runs was made with pure cotton linters nitrocellulose; the second series contained nitrocellulose of Lot #5257, of which there is some doubt but which we believe consists of 90% wood pulp nitrocellulose and 10% cotton linters nitrocellulose. Figure 9 indicates the effect of varying quantities of two types of nitrocellulose upon 70% Baratol. It should be noted that a minimum in viscosity is obtained for approximately 0.04- 0.05% nitrocellulose.

It should be emphasized that, though equal viscosity values may be derived on both sides of the minimum point (i.e., for nitrocellulose values below and above 0.05%), the properties of a slurry having a low nitrocellulose content are vastly different from one of equal viscosity but having a high nitrocellulose composition. Melts having an insufficiency of nitrocellulose exhibit poor pouring properties and high yield values, the latter being inverse to the nitrocellulose content. On the other hand, slurries containing an excess of nitrocellulose can be classed as "Newtonian." Examination of the data leads us to conclude that the phases indicated by the two branches of the curves in Fig. 9 represent two completely different phenomena. The low nitrocellulose branch can be explained on the basis of surface action. Since viscosity and yield values decrease upon the addition of nitrocellulose until the 0.05% value is reached, we believe that complete wetting is not accomplished until that point is reached. On the other hand, wetting has been accomplished in the high nitro-

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cellulose branch of the curve. There, the viscosity rise is proportional to the nitrocellulose content. There is probably no surface action here; the viscosity of the TNT matrix is simply increased by the nitrocellulose with a resulting increase in viscosity of the melt. These data were collected for $Ba(NO_3)_2$ of 9 μ to 10μ average diameters (Sub Sieve Size). It must be pointed out that the curve would be displaced, depending upon the particle size and distribution, since variations in these factors yield large variations in total surface area.

Effect of Stearoxyacetic Acid. Hitherto, stearoxyacetic acid had been reported as a viscosity-lowering agent for Baratols. All Baratols tested, however, contained the customary 0.1% nitrocellulose. In view of results with varied nitrocellulose content, the phenomenon was studied further. Here again the average particle size of $Ba(NO_3)_2$ was from 9 to 10 microns.

It was discovered that small quantities of stearoxyacetic acid lower the viscosity only when the nitrocellulose content exceeds 0.05%. At values
)5% nitrocellulose the viscosity is increased with addition of stear-
acid. This increase is inverse to the nitrocellulose content. At
ellulose content of 0.002% the stearoxyacetic acid (0.1%) raises the
y by 600%. The properties of melts containing stearoxyacetic acid
e those of melts deficient in nitrocellulose; they have appreciable
alues, depending upon stearoxyacetic acid content and time of incorpora-
Reference to Figure 9 might give some clue to this phenomenon. It is believed that stearoxyacetic acid displaces the nitrocellulose or counteracts its effect. Whether this is due to a chemical reaction or merely to a physical displacement is not, at present, known. From Fig. 9 it is obvious that the viscosity is somewhat higher with 0.1% nitrocellulose than at the point of complete wetting. If, as we believe, stearoxyacetic acid displaces the nitrocellulose, then it is not surprising to find that small quantit[redacted]

PLATE IV
$Ba(NO_3)_2$ Micropulverized
(Average diameter = 10μ)

stearoxyacetic acid cause an initial viscosity lowering. The effect there is a removal of nitrocellulose that is in excess of 0.05%. However, if stearoxyacetic acid is added to a Baratol containing less than the required 0.05% nitrocellulose, the viscosity and yield values rise radically due to the fact that wetting is now incomplete. It was found, too, that these changes are dependent upon the quantity of stearoxyacetic acid added. For instance, 0.2% stearoxyacetic acid will go beyond the minimum point and raise the viscosity and yield value of a slurry containing 0.1% N.C., Experiments designed at discovering the nitrocellulose-stearoxyacetic acid relationships are planned. Here again the average particle size and distribution is a controlling factor.

Rate of Stirring; Scaling. In order to avoid discrepancies between large "Production" melts and laboratory-scale melts, a series of experiments was designed to study the effects on Baratols of stirring and scaling. In studying stirring rate, an attempt was made to keep all factors constant, though this is a difficult task. Several series of melts were prepared in 3-gallon kettles. The $Ba(NO_3)_2$ was blended in a Hobart Mixer in order to insure identical particle size distributions in all the melts. Identical type stirrers were used; temperature was controlled. A strobatac was utilized for adjustment of speed. The stirring rate was varied from melt to melt between 90 RPM to 360 RPM in 4 equal intervals. It is noteworthy that these rates represent the very extremes in stirring rate for a 3-gallon system. The lowest rate was just sufficient to prevent segregation while the highest rate was adjusted to give maximum stirring, yet not reach the "whipping" stage.

The results indicate the fact that there is no appreciable viscosity difference in Baratol 73A (no stearoxyacetic acid) but that the viscosity and yield value of Baratol 73 (0.1% stearoxyacetic acid) rises rapidly with stirring rate and duration. The method that has been adopted to eliminate this decrease in pourability is to add the stearoxyacetic acid after the melt has been

[redacted]

[redacted]

prepared and only 10 to 15 minutes before the pouring.

The scaling experiments were performed in a similar manner. Here the $Ba(NO_3)_2$ was again blended, but the batch size varied from 150 gms to 120 lbs. Stirring rate was kept constant. Very little difference in viscosity was observed after 2 hours:

Batch Size	Melt	Viscosity (poises)
200 gms.	73A	38.2
15 lbs.	73A	36.2
30 lbs.	73A	35.3
120 lbs.	73A	34.0
150 gms.	73	24.7
15 lbs.	73	21.4
30 lbs.	73	23.1
120 lbs.	73	21.9

It may be concluded from these results that various engineering considerations concerning agitation of H.E. melts are superfluous at least from the point of view of dispersion, since any changes in agitation by varying propeller pitch, depth of immersion, angle, etc., fall easily within the limits worked with in the experiments. A type of stirring which would decrease air inclusion would be advantageous, since SAA apparently stabilizes air in the melt.

Effect of Average Particle Size. A series of experimental grinds was prepared by micropulverizing $Ba(NO_3)_2$ to batches varying in average particle size from 5 to 13µ. These had normal distributions; unlike the sieved RDX used in previous similar experiments. For 10 samples in this range there was found to be a linear relationship between viscosity and average particle diameter (as measured with the Fisher-Sub-Sieve-Sizer). The variation is, of course, inverse, viscosity varying 25 poises with a 1 micron variation in average particle diameter.

[redacted]

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$Ba(NO_3)_2$ Composition. A study was made of the variation in viscosity of Baratols with changing percentage of $Ba(NO_3)_2$. It was found that there is no appreciable rise in viscosity until a composition of 60% $Ba(NO_3)_2$ is reached. Thereafter the viscosity rises extremely rapidly (see Fig. 10). This is obviously dependent upon the ratio between the solid and liquid volumes. At lower concentrations the $Ba(NO_3)_2$ exists as a dilute suspension. Only at 60% is its volume sufficient to cause enough interference to particle motion to raise the viscosity.

Water Inclusion. Baratols react toward water in a manner opposed to the Cyclotols. With Baratols there occurs a very sharp decrease in pourability and, with the addition of 0.1% H_2O, a complete gellation, This is not surprising in view of the surface properties of the materials involved. Water would be expected to have extremely high attractive powers toward $Ba(NO_3)_2$ as evidenced by the solubility of $Ba(NO_3)_2$ in water. This is decidedly higher than the adhesive force between the TNT and $Ba(NO_3)_2$, even with the added surface active agent, nitrocellulose. Hence, we would expect the water to be preferentially adsorbed by the $Ba(NO_3)_2$, thus displacing the TNT. Apparently, 0.1% H_2O is sufficient to coat the $Ba(NO_3)_2$ surface. Since, however, this system lacks a continuous water matrix (i.e., water filled voids), it does not act as a liquid slurry but rather as a "packed" mass. If, to such a "gel" a high excess of water is added, the TNT separates out as a distinct layer, leaving a "slurry" of $Ba(NO_3)_2$ in a water solution of $Ba(NO_3)_2$.

It has been found that prolonged heating of a slurry containing small quantities of water will lower the viscosity and tend to bring it to normal. This is caused by a boiling off of the water.

C. PARTICLE SIZE DETERMINATIONS

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[redacted]

It has been mentioned that a Fisher-Sub-Sieve-Sizer is used for particle size determination of pulverized material in the sub-sieve range. This instrument has been found none too adequate. A superior method would be the application of photomicrographs, but this is both time-consuming and inconvenient. Since, also, the particle size distribution is micropulverized $Ba(NO_3)_2$ is very large (1.0-150.0 μ) (see Plate IV), poor resolution is attained at higher magnification due to the limitation in depth to the focal plane. The Sub-Sieve-Sizer is in essence a permeability measuring instrument. Gas, at constant pressure, is forced through a packed sample (density weight packed to 100). The resistance of the sample is registered on a flowmeter arm against a specifically prepared chart which reads directly in microns. The instrument must be calibrated against standard materials. It is significant to note, in view of the Los Alamos altitude, that the instrument must be calibrated here and not shipped already calibrated from sea level, since the pressure differential across the sample will vary with variation in the low side. The Sub-Sieve-Sizer gives an "average particle size." Such a figure is of little value in slurry work since it gives small indication of distribution and surface. Furthermore, the "standard material" recommended by Bruceton for calibration is an aluminum powder having an "average" of 20.6 μ but having also a very wide distribution and peculiar particle shape (Plate V). As a method of standardization, samples are required for which the particle size is very accurately known. Such samples were produced by a variation of the method of Sollner (Ind. and Eng. Chem. Anal, Ed., 2, 48-9, 1929). This consists of pulverizing glass tubing (Ball Mill) and then allowing the powdered material (dry) to be carried as part of the oxygen supply through a blast burner. (See Progress Reports for March and April, 1946.) The particles are, of course, melted in the flame, which results in their assuming spherical shape. These spheres were collected

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in water. Narrow cuts (to 1 μ) were separated by sedimentation according to calculation from Stokes Law. Such fractions varying from approximately 3 μ to 20 μ were used for calibration. Microscopic checks were made (Plate V)

At present, a colorimetric method is being developed for the determination of specific surface. It is based upon adsorption of soluble colored materials from a solvent to the pulverized material. Changes in optical density are measured by means of a Beckmann Spectrophotometer.

In using such a method it is desirable to find a soluble, colored substance which is strongly adsorbed upon the pulverized dispersed material in question. A variety of organic dyes are possible. We have chosen, however, dilute solutions of Iodine in $C\,Cl_4$ since the chemical literature contains a discussion of the mechanism for this adsorption. It is possible, with the use of various fractions of the microscopic glass spheres, previously prepared, and for which the specific surface is very accurately known, to test and calibrate this method. Since Iodine is adsorbed also on the $Ba(NO_3)_2$, a method may exist for directly determining specific surface of $Ba(NO_3)_2$.

If, however, the adsorption mechanism is not similar for glass and $Ba(NO_3)_2$ (i.e. equal surfaces of glass and $Ba(NO_3)_2$ will adsorb different quantities of Iodine), the relationship of the two mechanisms may be readily determined by the use of one sample of nitrate whose surface is accurately known. (Air separated, and carefully photomicrographed and measured).

D. WORK IN PROGRESS; PLANS.

Several additional experiments are in progress. Of primary importance is an attempt to find a measure of the elasticity and tensile strength of a liquid stream. The problem arose due to various considerations of pouring A.E. slurries from a kettle into the riser of a mold. Of the numerous melts which have been prepared and studied, a number are conspicuous for their peculiar qualities. That property of very poor pourability or complete unpourability

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despite low or moderate viscosity values was observed first in melts which contain low nitrocellulose contents or high stearoxyacetic acid contents. This situation could be accentuated to a point where a slurry could be prepared at will which would be as low in viscosity as 15 poises but which, nevertheless, would not flow from a stirring rod. Rather, such slurries would break off piece by piece rather than flow in a continuous stream. This as previously observed is characteristic of melts having high yield values as opposed to Newtonian fluids. Viscosity variations (even where the liquids are "Newtonian") may occur due to a variety of factors such as composition, particle size of the solid component, temperature, surface active agents, etc. We know that segregation and pouring properties of such slurries may be vastly different, though the absolute viscosities are identical. The method developed by the writer may give some measurement of the property in question. In principle, it consists of allowing the slurry to flow through a standard orifice and drop through the air. Depending upon the "elasticity" or the cohesive properties of the liquid, the falling stream will remain unbroken for a specific length and then become discontinuous. A high speed photographic method utilizing a gas-filled discharge tube has been developed to measure the distance through which the falling stream remains unbroken. The container for the molten slurry is steam heated. Caution will be taken to record data for a standardized hydrostatic head. It is expected that melts will be prepared over a range of viscosities by adjusting all variables. Data will then be accumulated to show differences in the cohesive properties of various slurries having identical viscosities. It is of interest to note that the method may be used as an indication of the tensile strength of a liquid column. This system may be compared to a tensile strength testing apparatus. Since the orifice is standardized, the initial cross sections of the samples (in this case a liquid cylinder) can be considered constant. Instead of a mechanical force acting to separate the sample, we have here the force of

[redacted]

[redacted]

gravity. Since this force is constant where the force exerted in a testing device is variable, the length to which the column extends itself before breaking will here by the indication of tensile strength (see Plate VI).

The method may be of use in determining "yield value" in hydrostatic units rather than gram units as determined with the viscosimeter. Preliminary experiments indicate that when a quantity of "plastic" slurry is run through the device, it flows until the hydrostatic head drops to a limiting height. At that point, the flow ceases. The remaining fluid height may be considered the "yield value" since it must be exceeded in order to induce flow. This is a much more convenient figure than the viscosimeter value, since yield value is the controlling factor in "feed" during casting processes. Here, where the riser either contains a sufficient or insufficient height of slurry to "feed", the hydrostatic units would be ideal. With the aid of our set-up a conversion factor may be derived between "Stormer" yield values and hydrostatic head yield values.

A second experiment is aimed at quantitatively determining the adhesion tension and contact angle between TNT and the suspended solid. The apparatus in use is the Bartell Cell. The method consists essentially of measurements of pressure on a liquid exerted in opposing the capillarity of a packed solid material in the cell. The method is based upon the fundamental capillary equation:

$$S = \frac{rdgh}{2} = \frac{rPg}{2}$$

where;
S — Surface tension
P — Pressure in gms/cm^2
g — gravitational constant
d — liquid density
h — height of capillary rise
r = capillary radius

For finite contact angles the equation is as follows:

$$S_1 = \frac{Prg}{2\cos\theta_{s1}}$$

where θ — contact angle
S_1 — liquid surface tension

[redacted]

Subscript s is solid
l is liquid
r — pore radius of packed material

The first step is the determination of pore radius by using a liquid having a zero contact angle. After this value has been determined, it can be used for determining θ for other liquids. Knowing θ, the adhesion tension can be determined by substitution in the following equation:

$$A_{sl} = S_s - S_{sl} = S_l \cos \theta_{sl}$$

where: A_{sl} = Adhesion tension between solid and liquid
S_s — Solid surface tension
S_{sl} = Interfacial tension
S_l — liquid surface tension

For finite contact angles the equation for the use of the Bartell Cell can be expressed as:

$$A_{sl} = \frac{Prg}{2}$$

References: Colloid Symposium Annual 7, 139 (1930)
Ind. Eng. Chem. 19, 1277 (1927)
Ind. Eng. Chem. 21, 1102 (1929)
J. Phys. Chem. 37, 543 (1933)
J. Phys. Chem. 32, 1553 (1929)

Since surface tension is an essential variable in the equations for the Bartell Cell, it was necessary to find a suitable method for determining surface tension of liquid TNT and TNT-nitrocellulose combinations. Considerable effort was put forth in testing the "bubble pressure" method and the Du Nuoy Tensiometer. Despite careful temperature control of the melted TNT, little reproducibility was obtained for TNT containing nitrocellulose. Only for pure TNT was there found to be any reproducibility. It is suspected that here, as in the case of all systems containing wetting agents, an orientation must occur at all liquid-solid, liquid-gas interfaces. Such orientations are functions of time. Since both the Bubble Pressure Method and the Tensiometer

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Method are dynamic determinations, the system is in a state of flux during a run, and as a result, there is a loss of reproducibility. A third method has been decided upon--the Pendant Drop Method (Andreas, Hanser, Tucker, J. Phys. Chem. 42, 1001, (1938)) Here, a drop of liquid is allowed to hang pendant from the tip of a capillary. Photographs are taken, using a parallel light source and from geometric considerations, the surface tension can be determined very accurately. The advantage of this method is that it may be considered "static," and the drop size is not critical. Furthermore, a time study may be made of the effect upon surface tension of slow changes in orientation till equilibrium is reached.

There are a variety of additional experiments planned, which will appear from time to time in the monthly reports.

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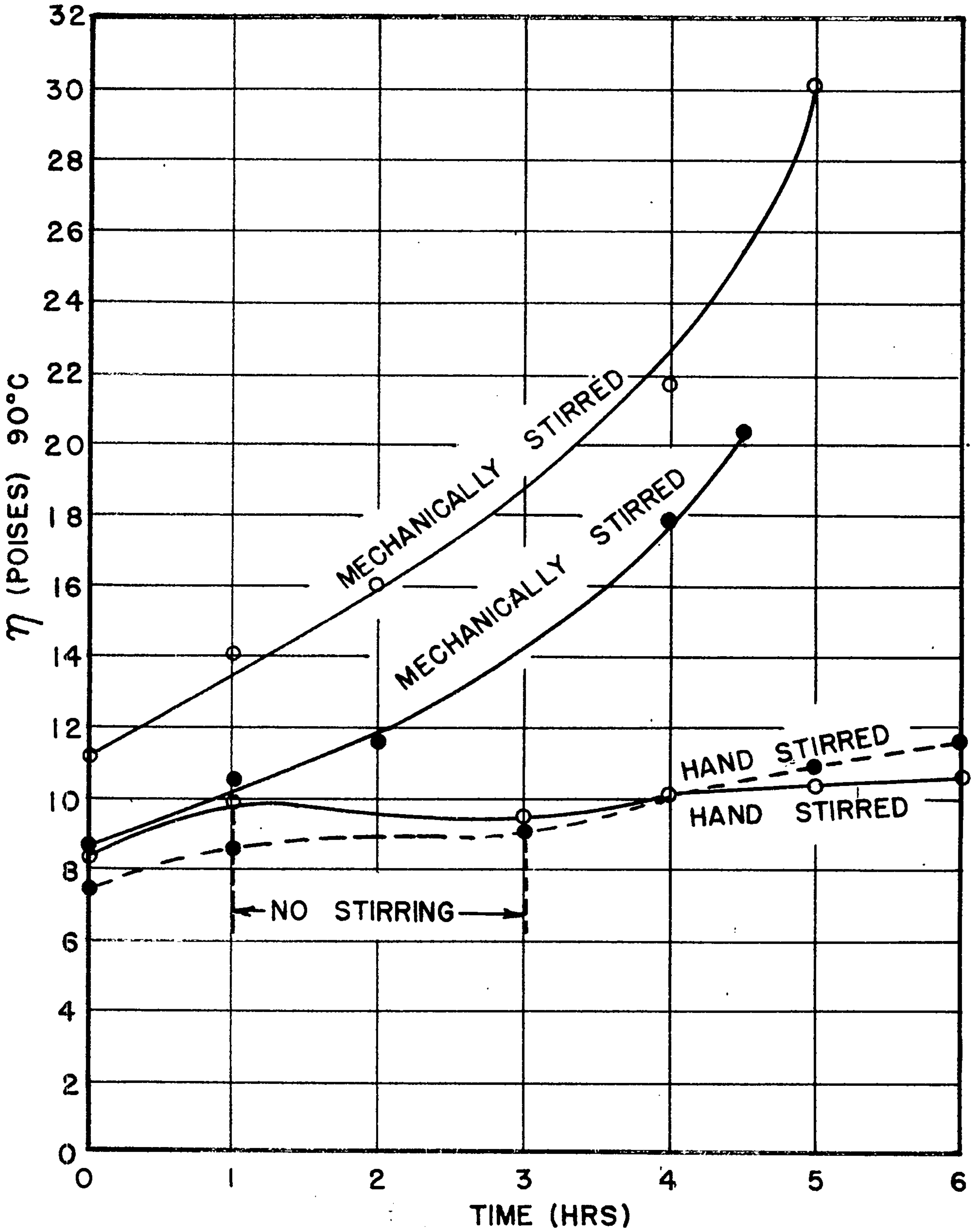
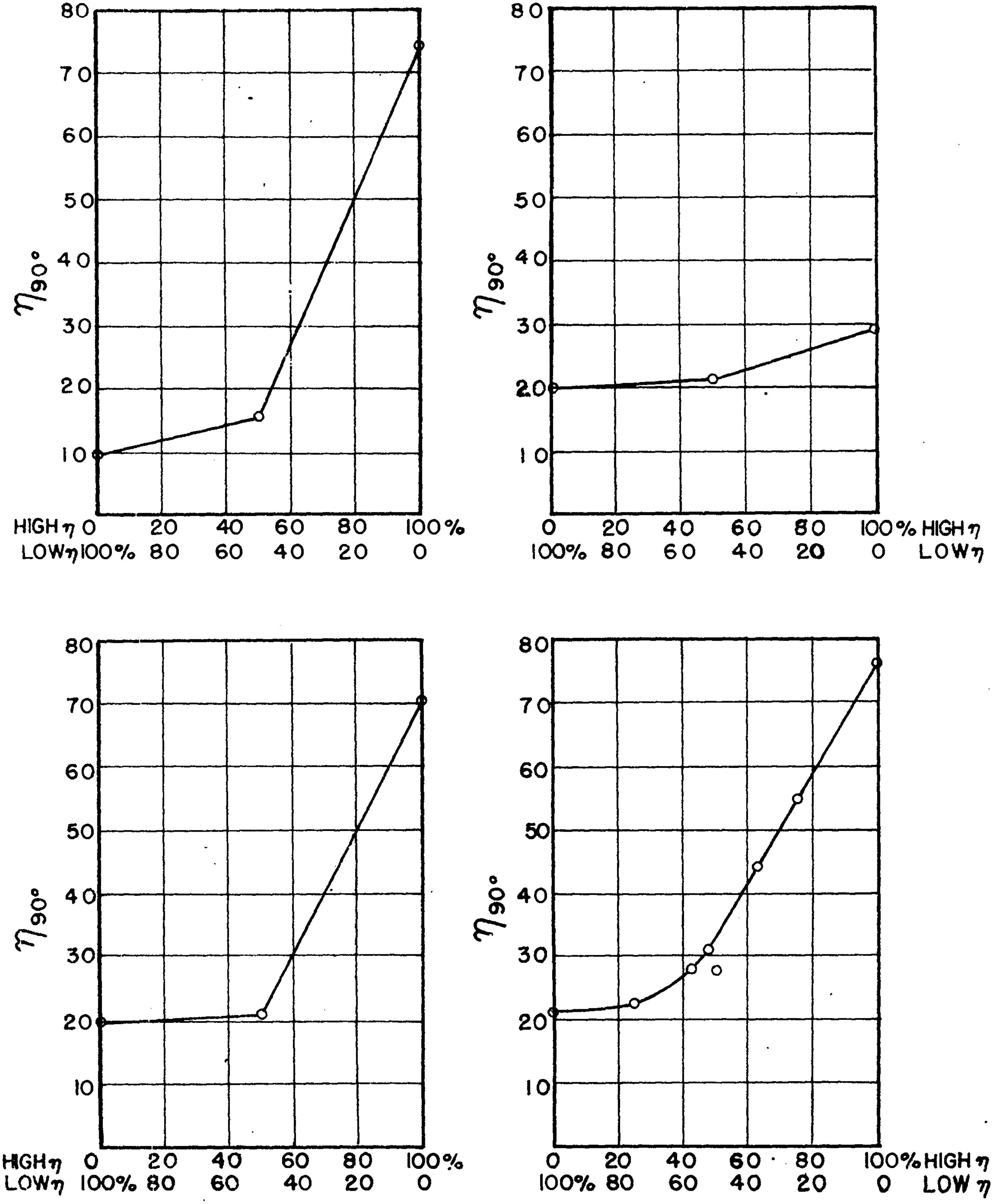
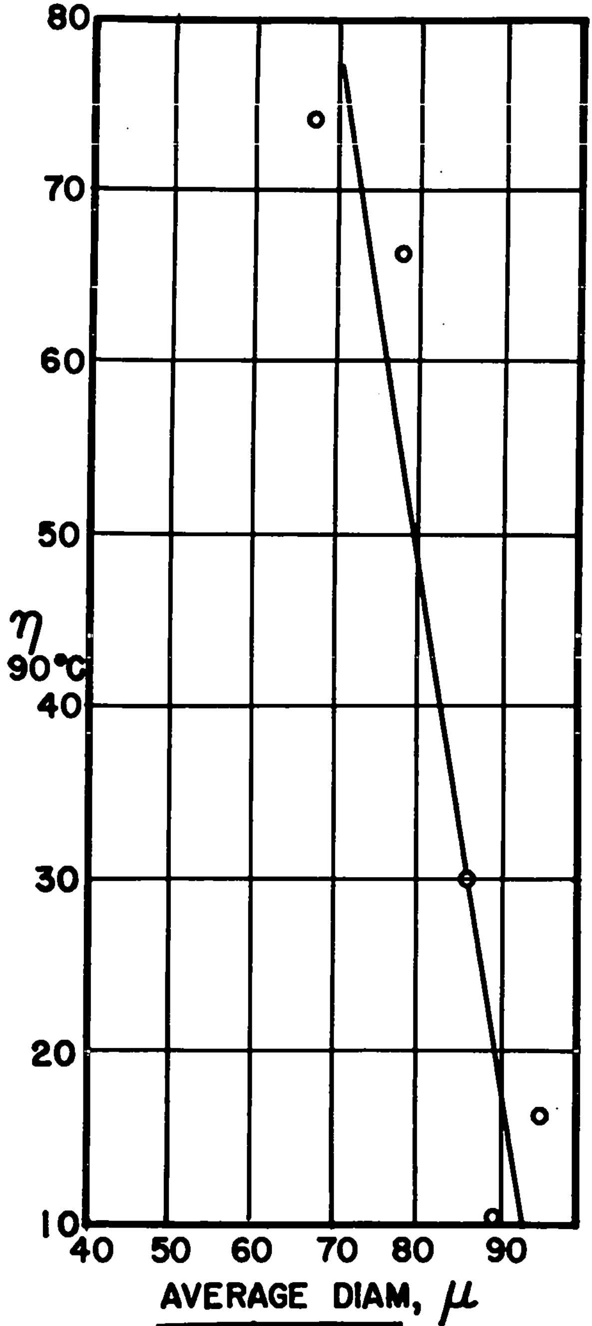


FIG. 1
Affect Of Time Of Agitation
On Comp. B

FIG. 2


$\eta_{90°}$
80
70
60
50
40
30
20
10
HIGH η 0 20 40 60 80 100%
LOW η 100% 80 60 40 20 0
0 20 40 60 80 100% HIGH η
100% 80 60 40 20 0 LOW η



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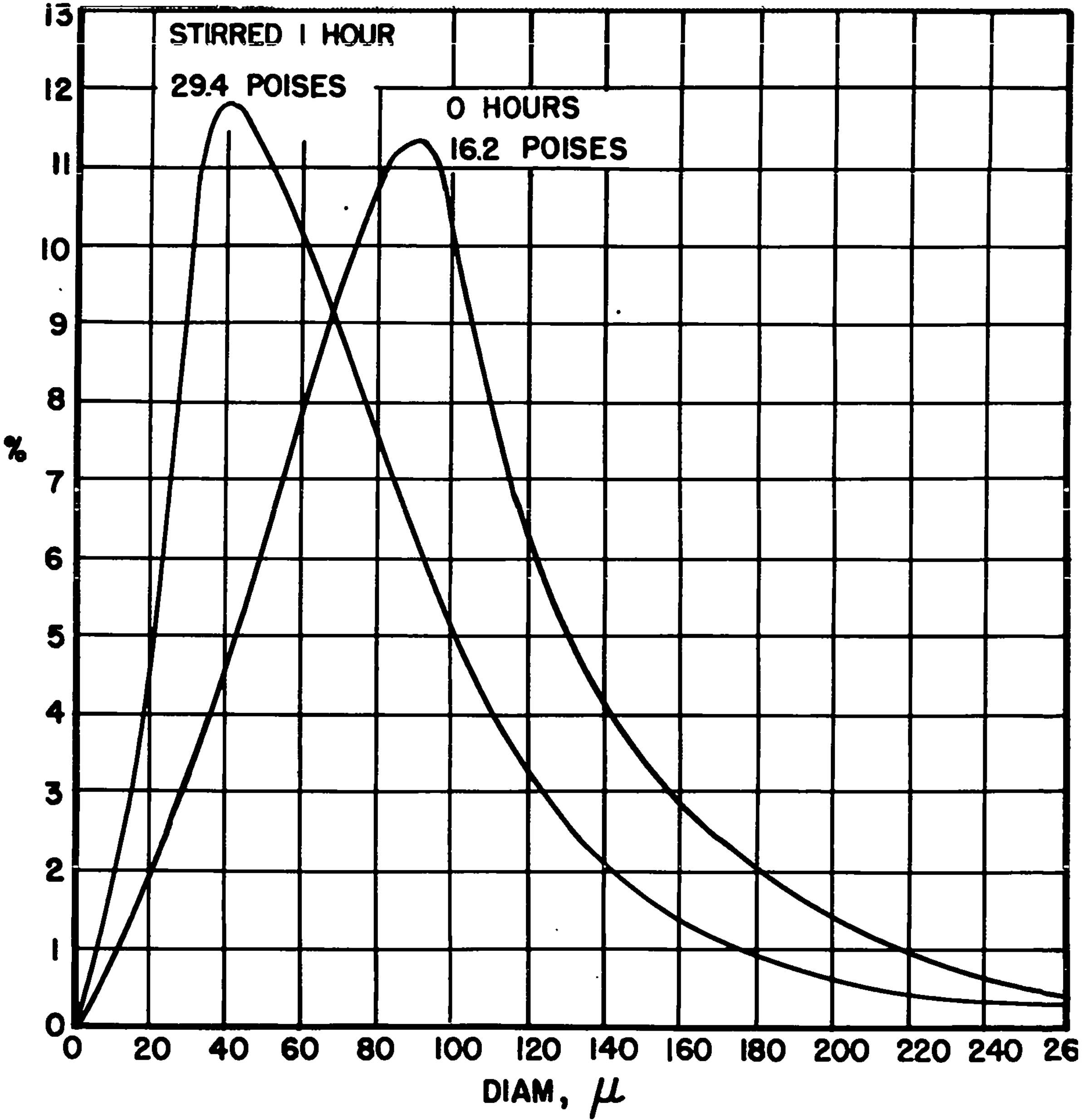


[redacted]

FIG. 4

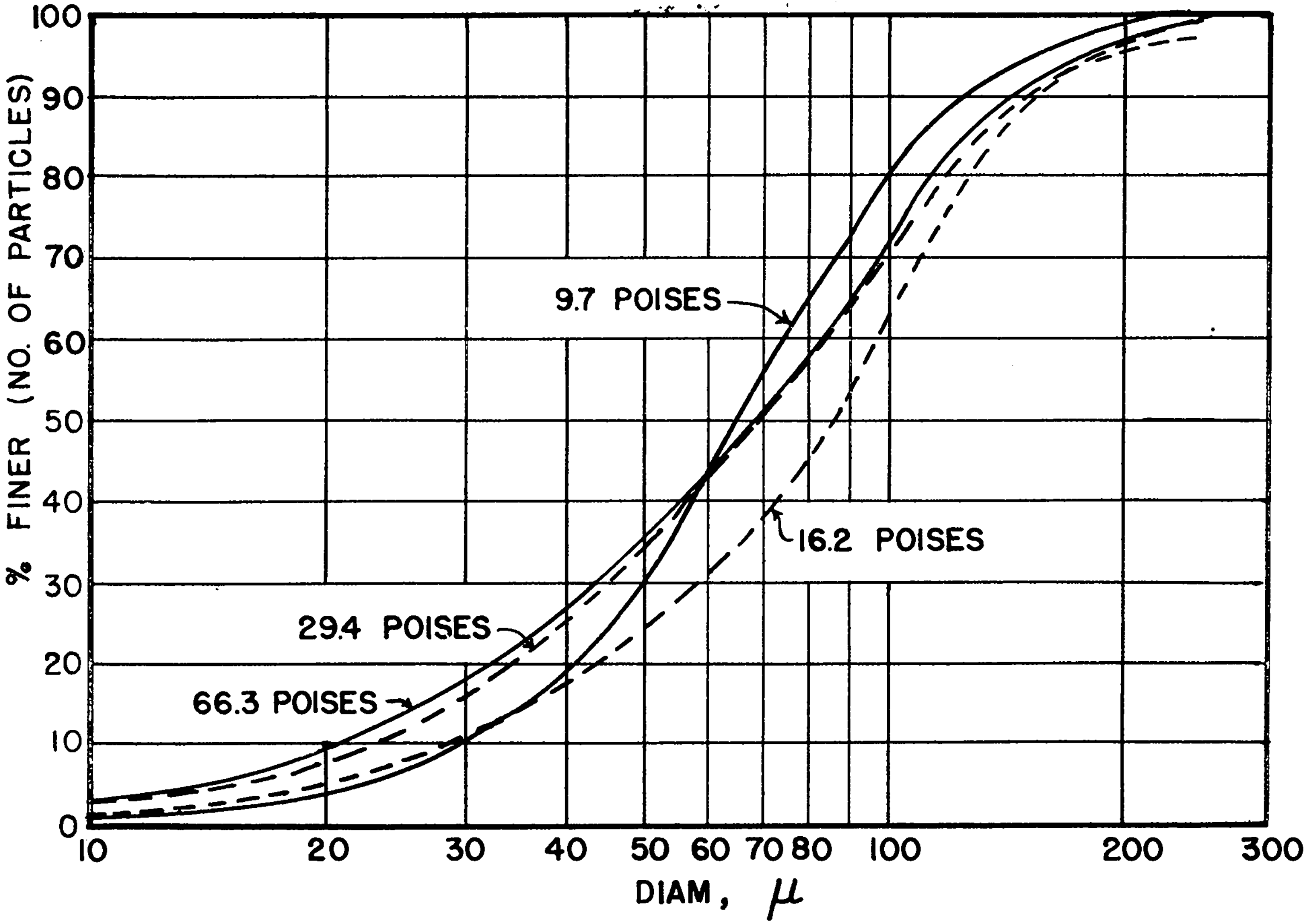
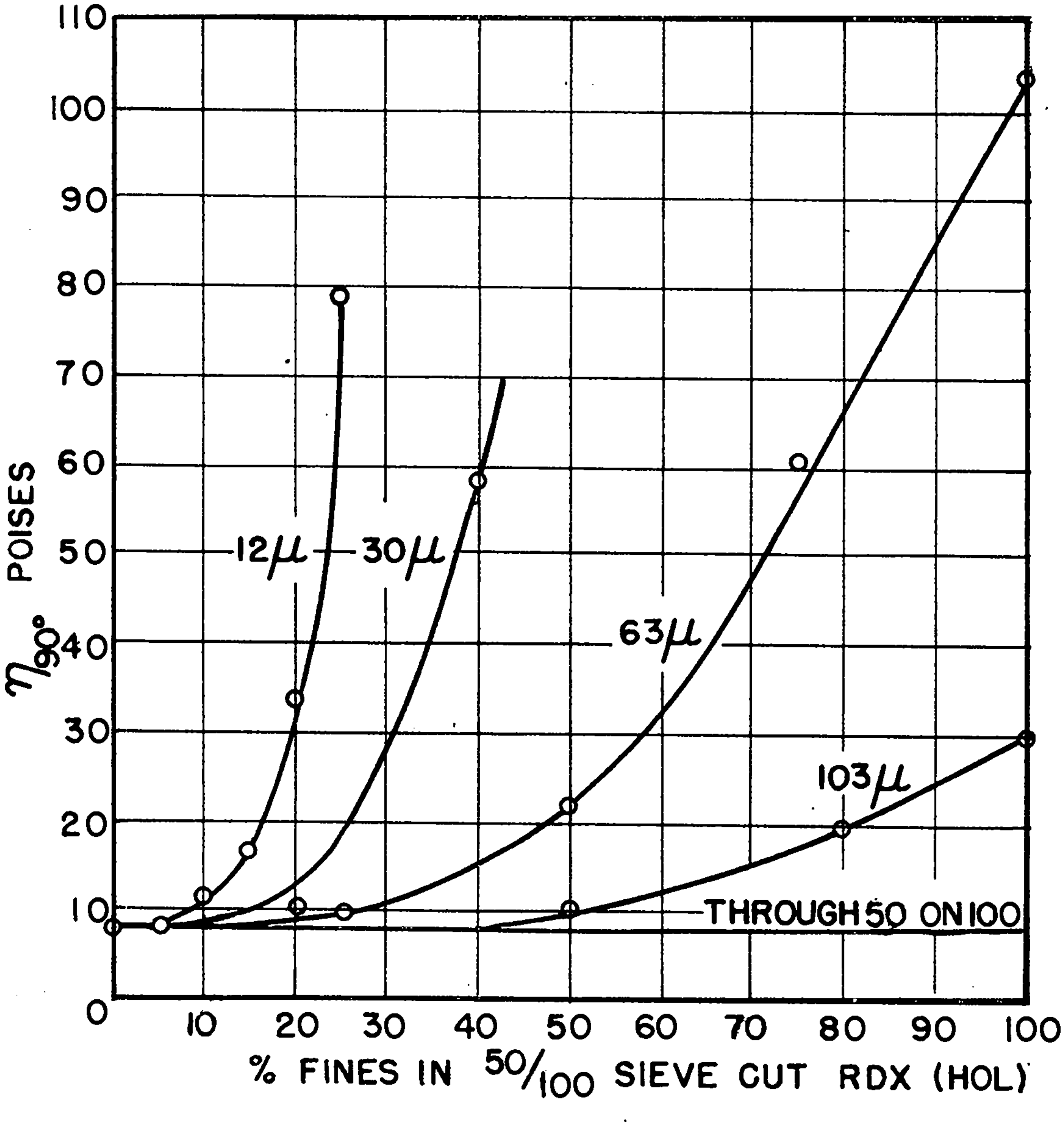
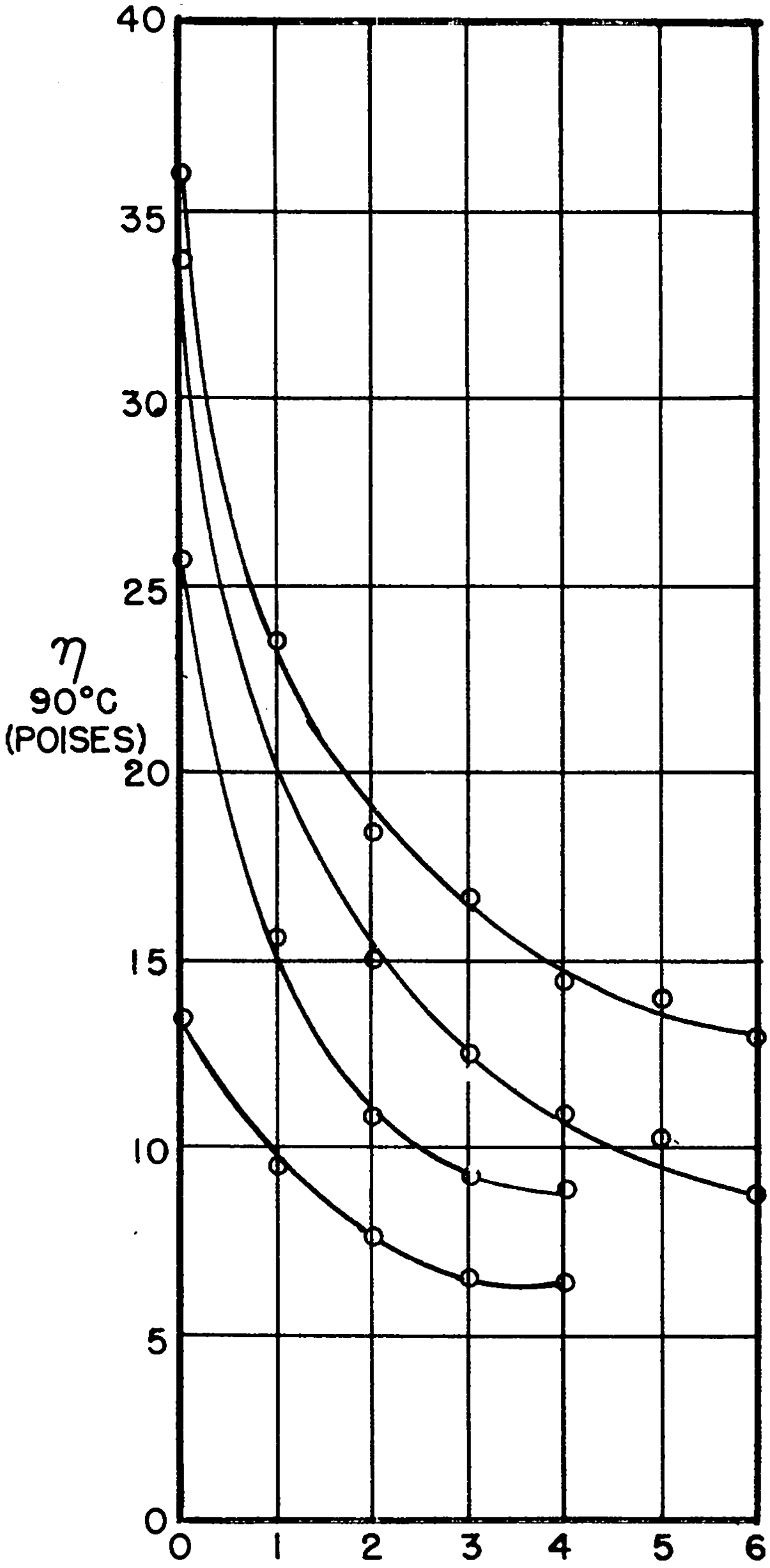

100
90
80
70
60
50
40
30
20
10
0
% FINER (NO. OF PARTICLES)
10
20
30
40
50
60
70
80
100
200
300
DIAM, μ
9.7 POISES
16.2 POISES
29.4 POISES
66.3 POISES

FIG. 5



$\eta_{90°}$ POISES
0
10
20
30
40
50
60
70
80
90
100
110
10
20
30
40
50
60
70
80
90
100
% FINES IN 50/100 SIEVE CUT RDX (HOL)
12μ
30μ
63μ
103μ
THROUGH 50 ON 100

FIG. 6



Temperature Cycling
Of Comp. B

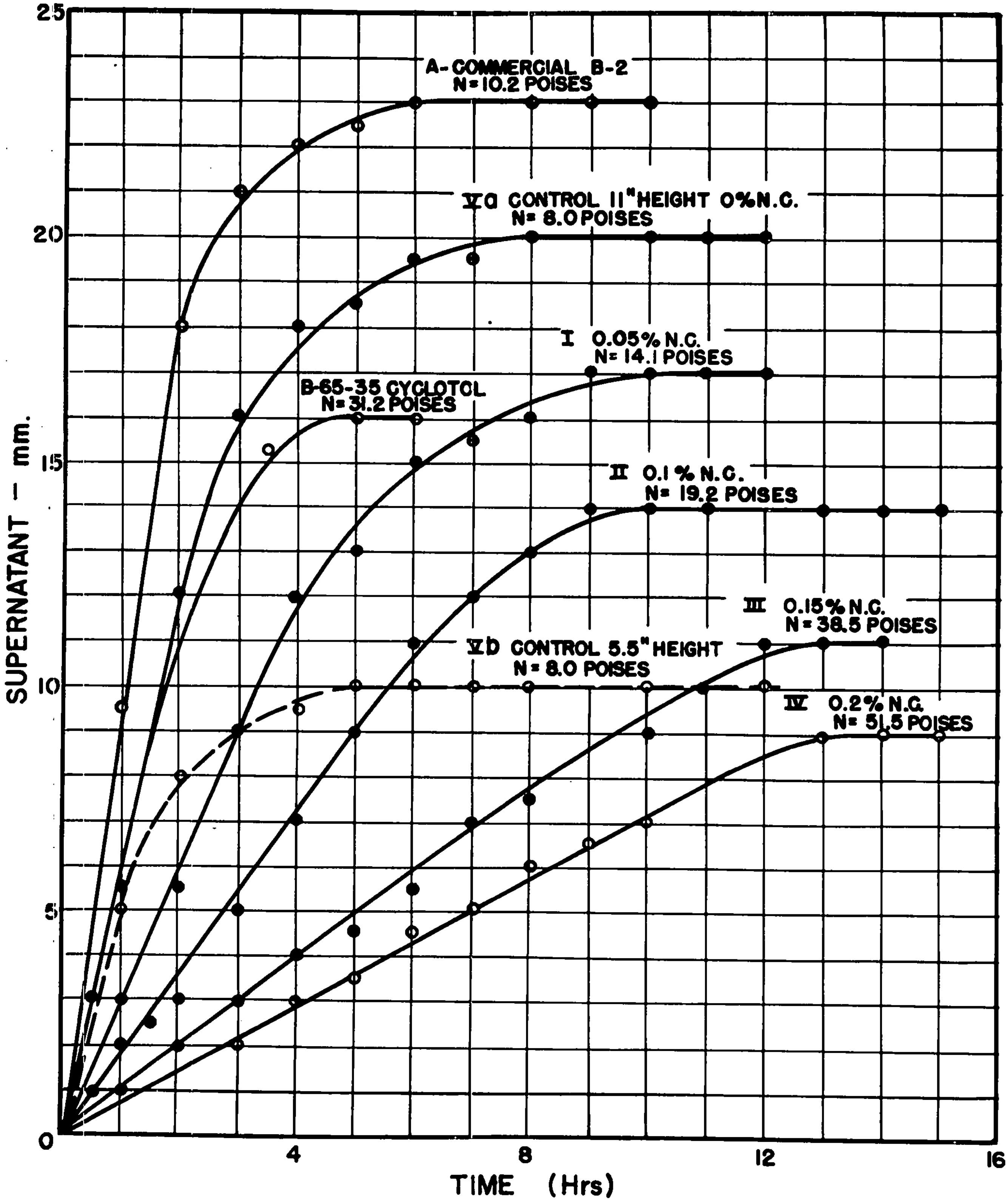
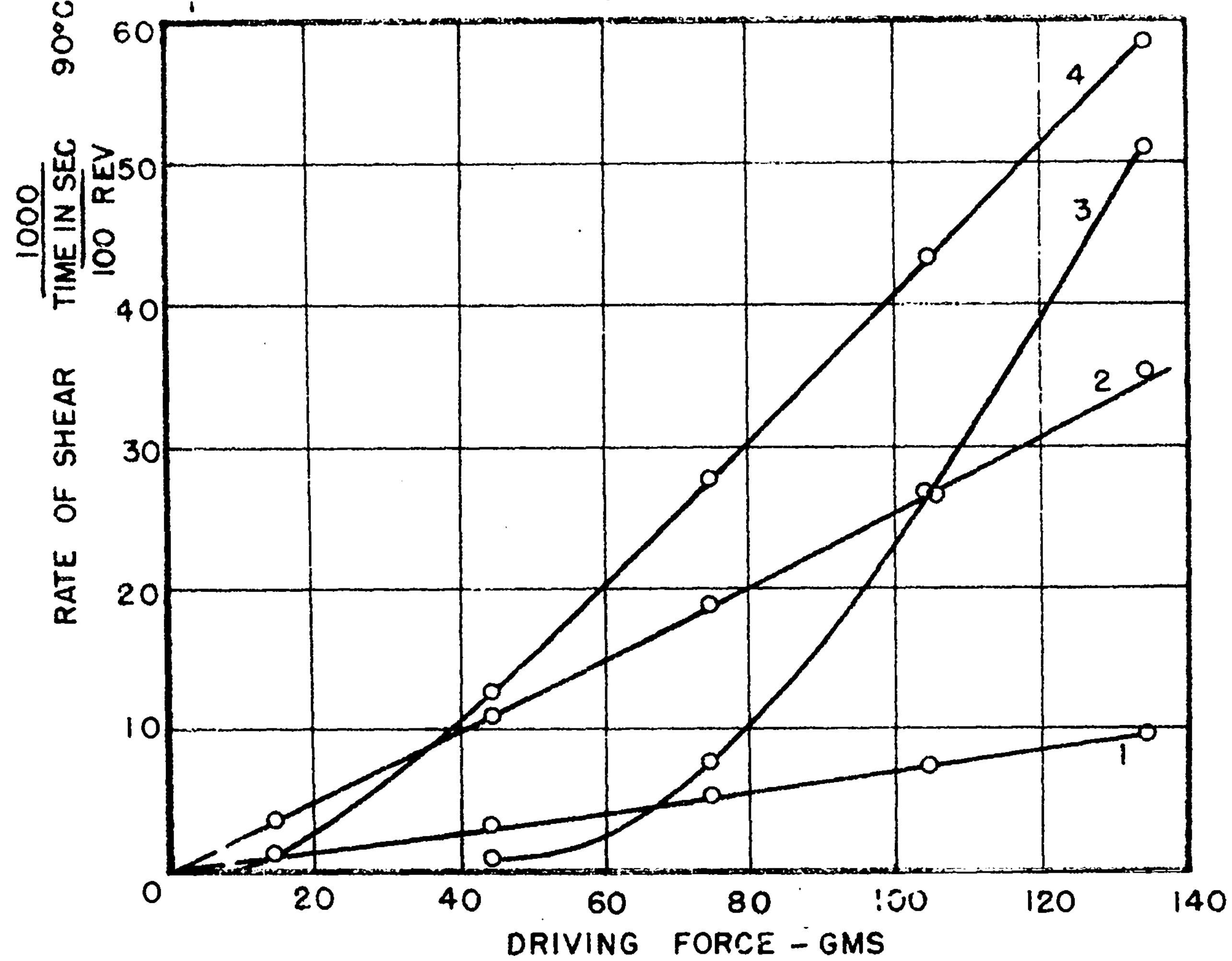

A-COMMERCIAL B-2
N=10.2 POISES
Va CONTROL 11" HEIGHT 0% N.C.
N=8.0 POISES
I 0.05% N.C.
N=14.1 POISES
B-65-35 CYCLOTOL
N=31.2 POISES
II 0.1% N.C.
N=19.2 POISES
III 0.15% N.C.
N=38.5 POISES
Vb CONTROL 5.5" HEIGHT
N=8.0 POISES
IV 0.2% N.C.
N=51.5 POISES
SUPERNATANT - mm.
TIME (Hrs)
0
5
10
15
20
25
4
8
12
16

Fig. 7

FIG. 8



1- 73% Ba (No 3)2 0.1% N.C.
2- 70% Ba (No 3)2 0.1% N.C.
4- 71% Ba (No 3)2 0.1% N.C. 0.1% Steroxyacetic Acid
3- 69% Ba (No 3)2 0.03% N.C. 0.2% Steroxyacetic Acid

FIG. 9

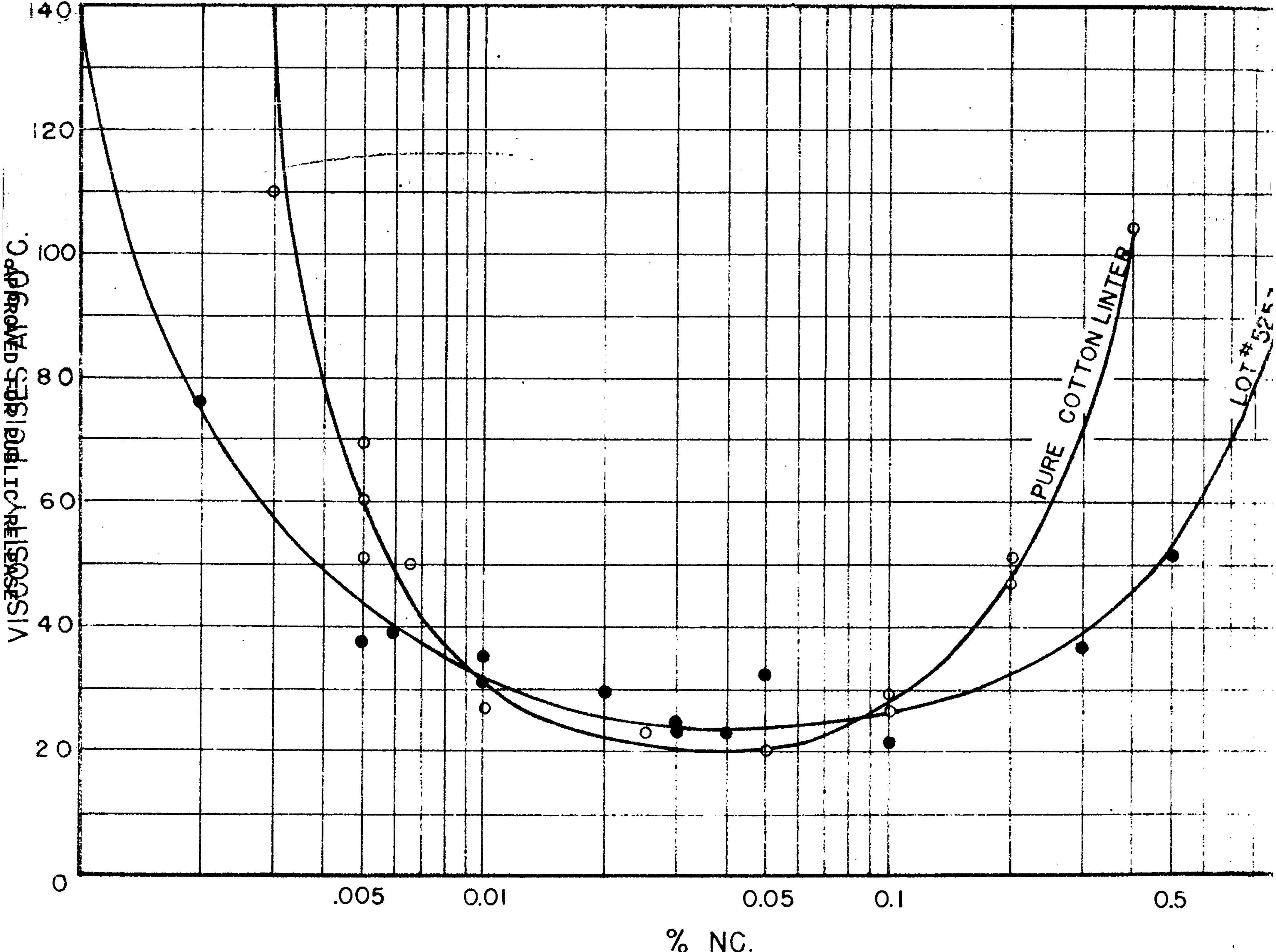
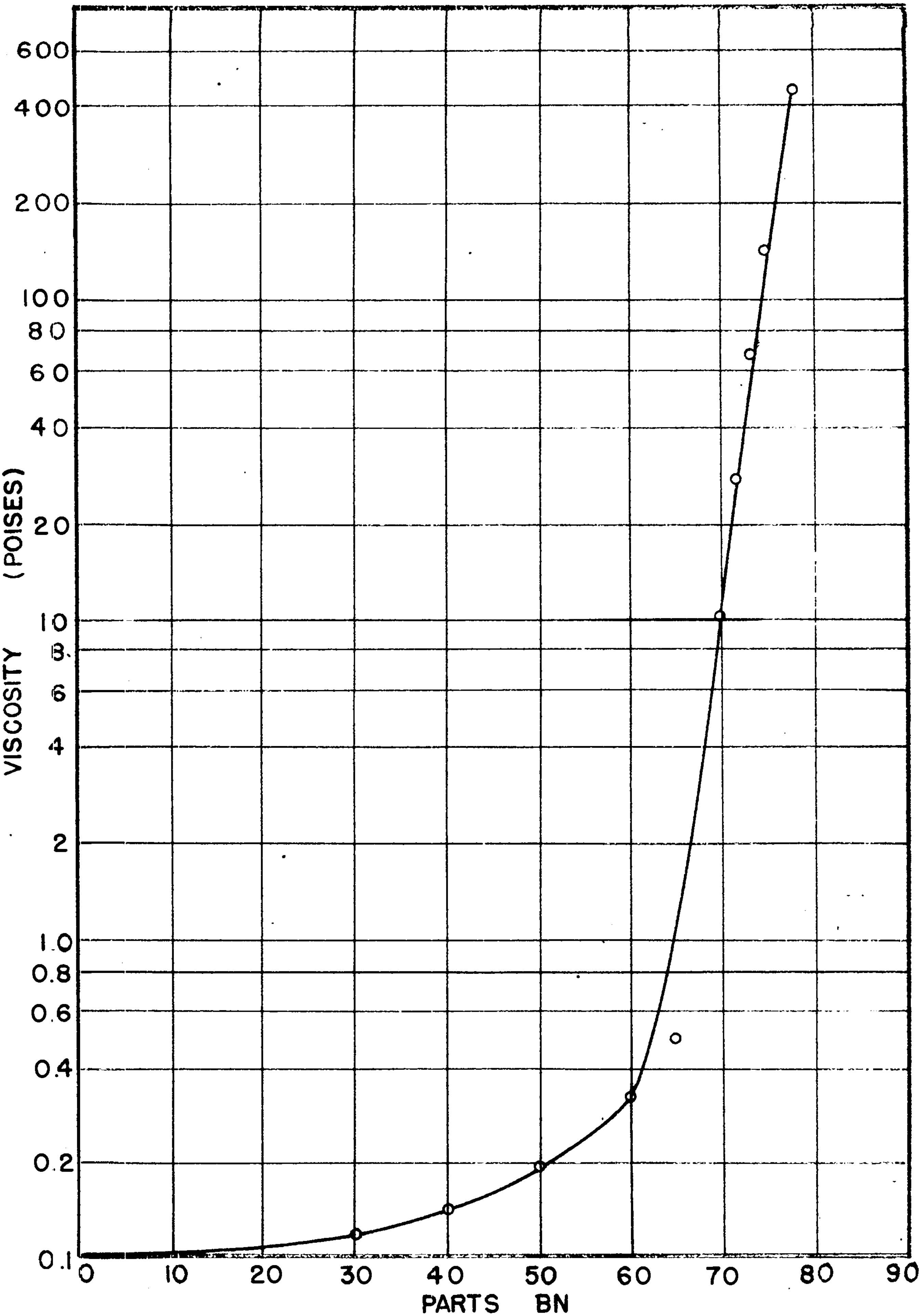
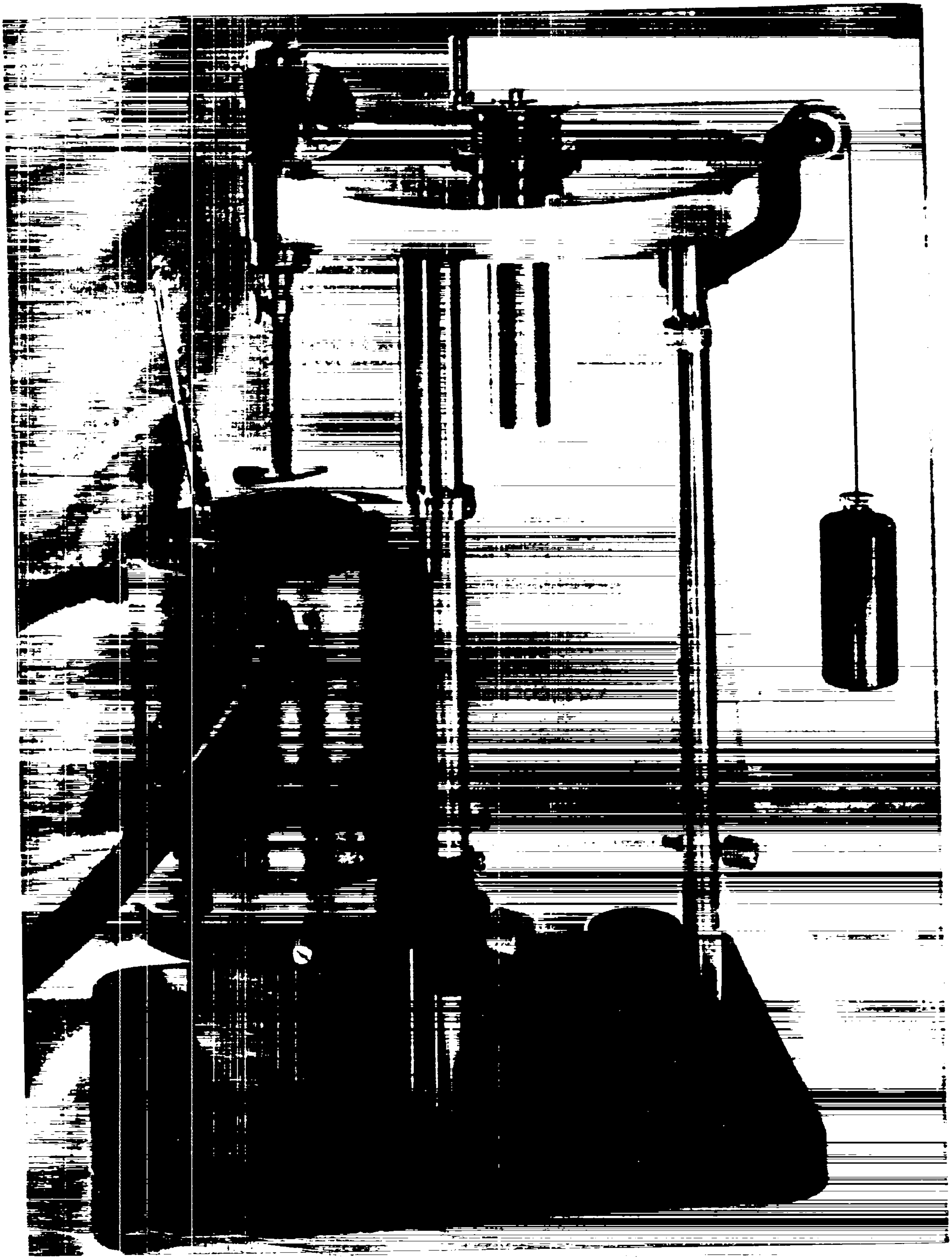

140
120
100
80
60
40
20
0
VISCOSITY 20° C.
.005
0.01
0.05
0.1
0.5
% NC.
PURE COTTON LINTER
LOT #525

FIG. 10


VISCOSITY (POISES)
600
400
200
100
80
60
40
20
10
8
6
4
2
1.0
0.8
0.6
0.4
0.2
0.1
0
10
20
30
40
50
60
70
80
90
PARTS BN



Stage Micrometer
0.01 mm
0.10 mm

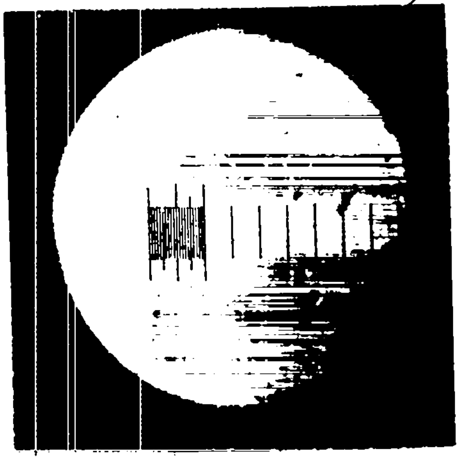
η = 9.7 poises

η = 16.2 poises

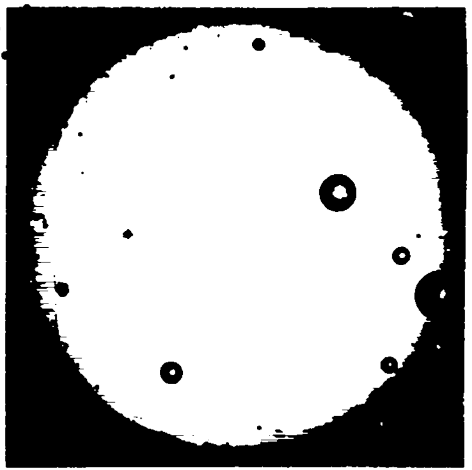
η = 73.8 poises

RDX Extracted from Cyclotols

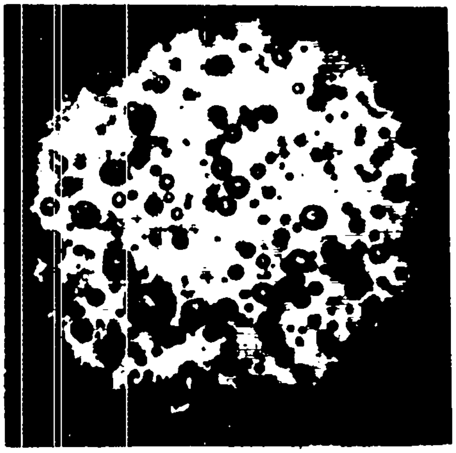
PLATE II



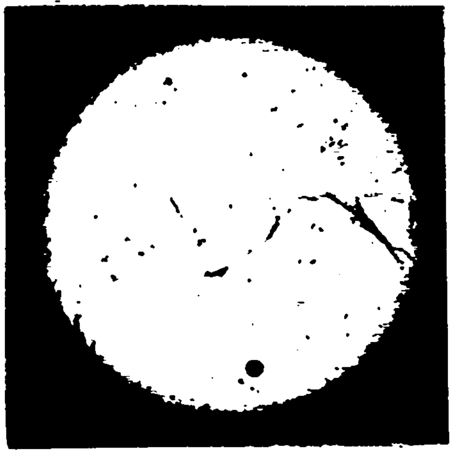
Stage Micrometer
0.10 mm
0.01 mm



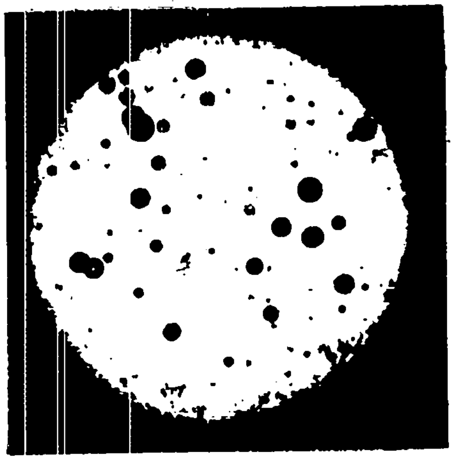
η_{90° = 18.1 poises



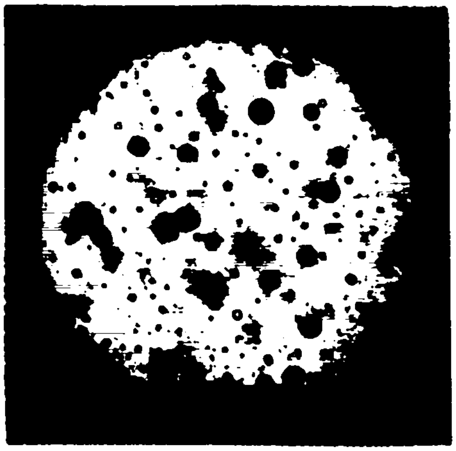
η_{90° = 200 poises
Density = 2.390 gms/cc



η_{90° = 26.9 poises
Density = 2.507 gms/cc

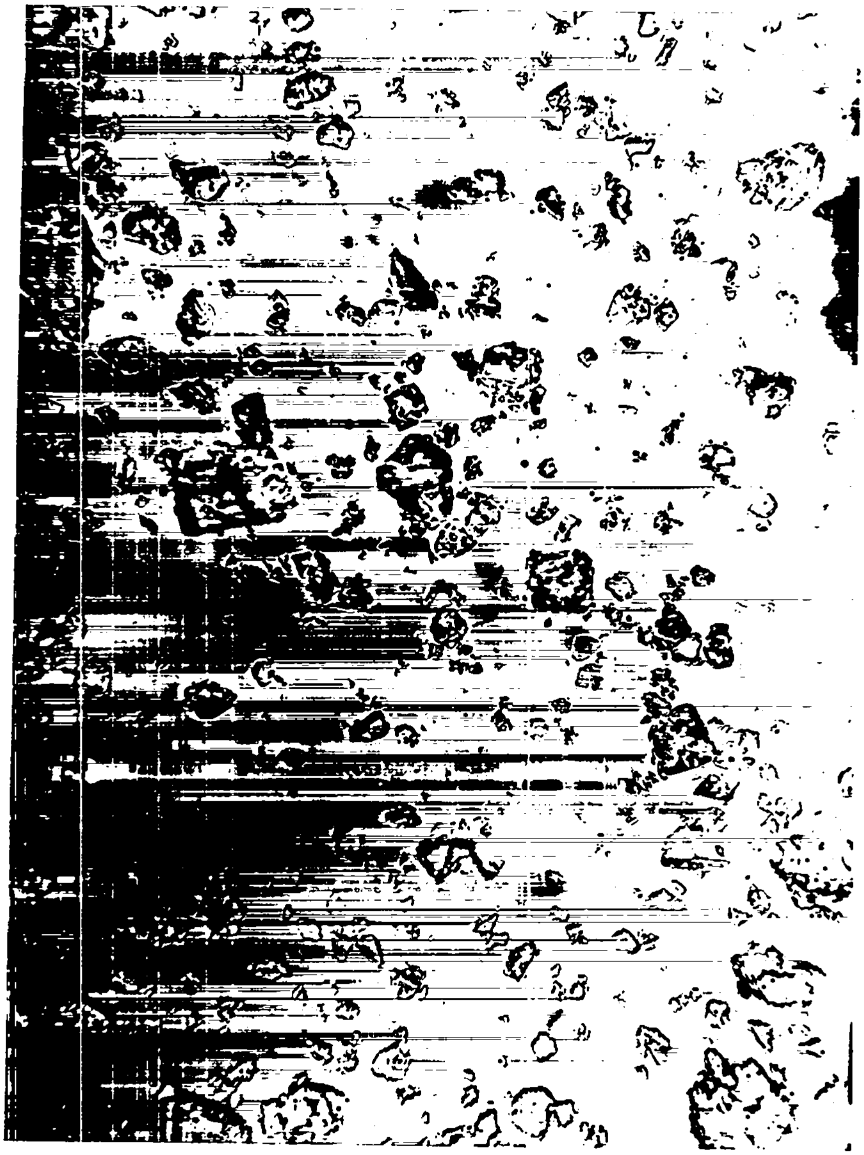


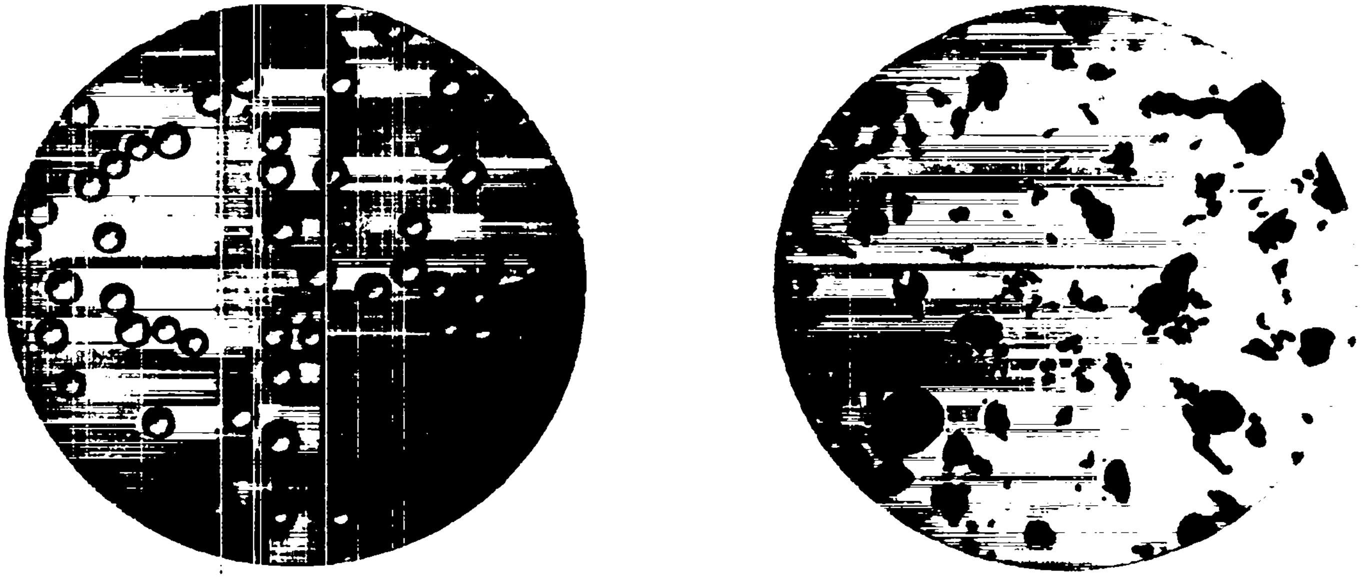
η_{90° = 32.4 poises
Density = 2.489 gms/cc



η_{90° = 36.8 poises
Density = 2.498 gms/cc

PLATE III





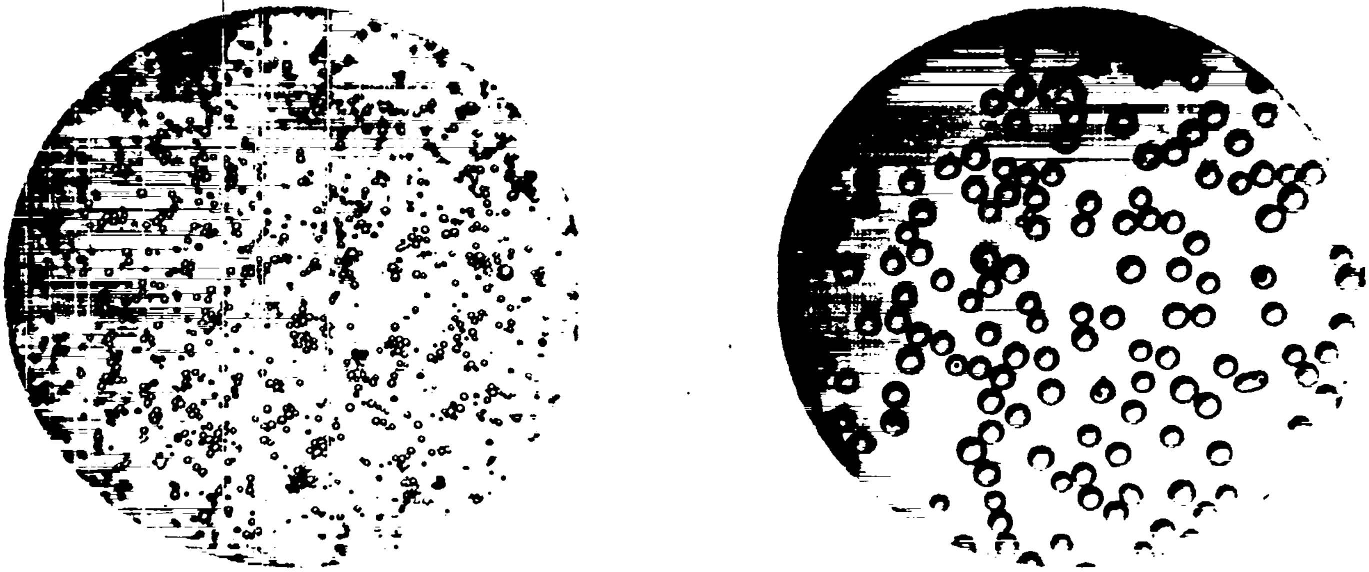
GLASS
21.6 µ

ALUMINUM
20.6 µ

PLATE V

GLASS
3.8 µ

GLASS
15.9 µ




10
20
30
40

UNCLASSIFIED

~~SECRET~~

UNCLASSIFIED