A QUANTITATIVE INVESTIGATION OF THE HOMOGENISING OF SMALL GLASS MELTS BY STIRRING

A Thesis Presented By
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of the
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II REVIEW OF THE EARLIER WORK

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SUMMARY

The homogenising process in glass was studied by mixing two different glasses, placed in a known initial distribution. The initial orientation was to have a horizontal interface between the two glasses because usually the inhomogeneities lie in parallel horizontal layers in a crucible containing glass unstirred by convection or a mechanical stirrer.

The homogeneity was measured quantitatively using an etching and interferometery technique developed in this work. The degree of homogeneity was defined in terms of the intensity of segregation, which varies from one in a fully segregated system to zero in a fully mixed system. Mixing was studied using three different simple stirrers.

The intensity of segregation was plotted against number of revolutions of the stirrer. From these graphs it can be seen that the value of intensity of segregation calculated from the etching data has a quantitative significance for following the process of homogenisination.

The flow patterns observed in thin sections of the glass melts were completely different from those observed in room temperature model experiments. This was because the glasses mixed were of different viscosities and densities, while the model had used liquids of equal viscosity and density.

The stirrers studied were not very efficient mixing devices but they were designed to compare results in glasses with the previous room temperature model experiments rather than to be most efficient. The disc stirrer was a convenient standard for comparison of the performance of other stirrers. The addition of a blade to the disc helped in

in breaking up the interface between the two layers. The complex disc stirrer was only efficient when the lower disc was above the liquid-liquid interface. Although no stirrer was extremely efficient, all produced more homogeneous glass than were obtained from unstirred melts.

CHAPTER I

INTODUCTION

1 NATURE OF GLASS AND THE MELTING PROCESS

(i) Definition and composition

Most inorganic elements and compounds melt to form liquids having a viscosity about the same as that of water. When liquids of this type are cooled, rapid crystallisation occurs and the liquid can only be supercooled to a small extent. However, there are some materials which melt to form very viscous liquids. If such a liquid is maintained for sometime at a temperature a little below the freezing point it will only crystallise slowly, but if, instead of holding the temperature constant, the liquid is cooled continuously, crystallisation may or may not occur depending on the rate of cooling. At a higher rate of cooling it is possible to reduce the temperature without crystallisation. The viscosity of the liquid increases steadily as the temperature is reduced until eventually it is so high that the material is apparently solid. This solid material is called glass.

Most glasses are complex mixtures of several oxides. These oxides can be divided into two groups; simple glass forming oxides and modifying oxides. The oxides belonging to the former group, which can form glasses themselves, are SiO_2, GeO_2, B_2O_3, P_2O_5 and As_2O_3. The majority of glasses are composed of these glass formers together with two or more modifiers such as Na_2O, K_2O, CaO, MgO, BaO, PbO and Al_2O_3. The complexity of the mixture is evident from the following examples of compositions of some commercial glasses.

Glasses	SiO_2	Al_2O_3	B_2O_3	SO_3	CaO	BaO	MgO	Na_2O	K_2O	PbO
Plate glass	72·0	0·5	-	0·5	13·0	-	-	13·20	-	-
Pyrex glass	81·0	2·0	12·0	-	-	-	-	4·50	-	-
Lead glass	66·0	0·9	0·6	-	0·7	0·5	-	6·00	9·50	15·50

The process of "melting" is very complex and it depends upon the substances present in the batch. Different phenomena occur in the "melting" process such as dehydration, decomposition, dissociation and chemical reactions. To illustrate the complexity of the "melting" process, consider a simple soda-lime-silica glass in which the raw materials are soda (Na_2Co_3), limestone ($CaCo_3$), and sand (SiO_2). If heated separately to about 1400°C Na_2Co_3 melts but does not decompose, $CaCo_3$ decomposes to CaO + Co_2 without melting. The resultant CaO has a very high melting point of 2580°C, a temperature which is never attained in glass melting tank furnaces. Sand (SiO_2) is unchanged except for the $\alpha - \beta$ quartz transformation at 573°C and the fact that the quartz will very slowly begin to change to its stable high temperature form (cristobalite). When the mixture is heated rapidly, there is some solid state reaction which includes the formation of a little Na_2O - SiO_2 liquid of eutectic composition, but the first important step is the melting of Na_2Co_3 at 851°C which flows around the other grains and begins to dissolve $CaCo_3$ to form the double carbonate $Na_2Co_3.CaCo_3$ and to react with silica forming mostly a composition close to $Na_2O.2SiO_2$. Some of the lime also begins to decompose and be incorporated into the fluid liquid phase which tends to rundown. The double carbonate with sodium carbonate melts and begins to react rapidly at 812^{c}C so that the melt formed by reaction with Na_2Co_3 at 851°C will also begin to react with SiO_2 forming a soda-lime-silica melt (not of the final intended composition). At the same time the evolution of Co_2 causes stirring and frothing of the whole mass. After a time the very rapid gas evolution stops and a melt full of both gas bubbles and partly dissolved silica grains remains.

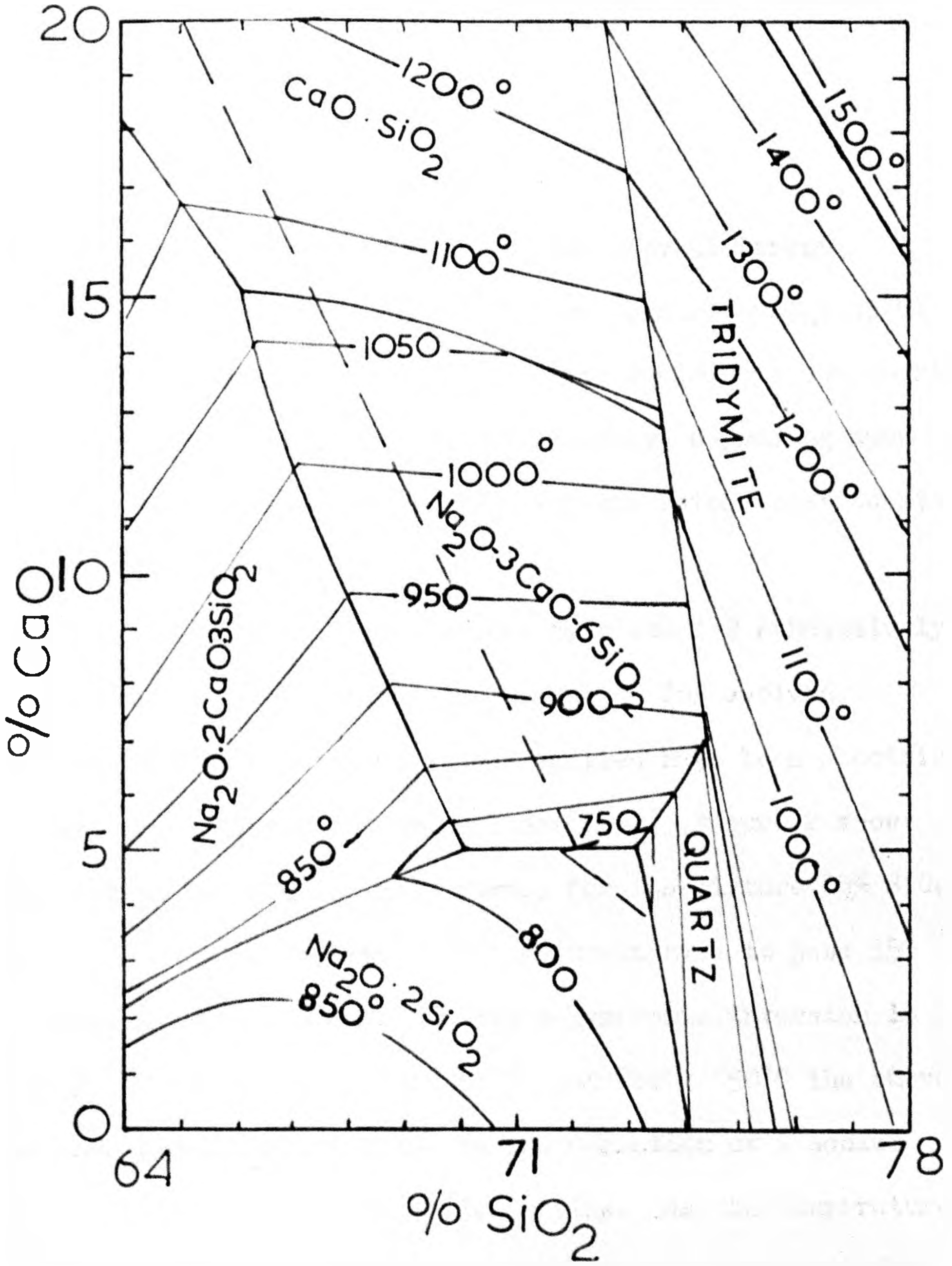
"Melting" is considered complete when all the silica has dissolved and the melt is batch-free but still contains gas bubbles. When the melt has become batch-free it is usually very inhomogeneous. During "melting", liquid richer in Na_2O and CaO than the finally intended composition runs to the bottom and a sort of froth floatation process carries silica grains upwards to form silica rich layer on the surface of the melt.

It is well known that glass formation involves both solid and liquid state reactions. Although glass is not in equilibrium, studying the appropriate phase diagram often gives useful information about glass melting reactions. Morey and Bowen[1] determined the phase diagram of the part of Na_2O-CaO-SiO_2 system in which glasses are formed. The phase diagram is shown in Figure 1. In this system the lowest eutectic is at 725°C and the chemical composition of that melt is 21% Na_2O, 5% CaO, 74% SiO_2.

On slowly heating a mixture of Na_2Co_3, $CaCo_3$ and SiO_2 there would be a considerable increase in reaction rate at this temperature. At higher temperatures other reactions occur such as the formation of sodium metasilicate or sodium disilicate or the formation of the eutectic melt between $Na_2O.2SiO_2$ and SiO_2 at 790°C. The peaks seen at various temperatures on differential thermal analysis curves can often be correctly interpreted from the relevant phase diagrams.

Phase diagrams cannot, however, give any information about the kinetics of these processes, especially the dissolving of

FIG. 1



PART OF THE SYSTEM

Na_2O-CaO-SiO_2

(AFTER MOREY)

residual sand grains which is a diffusion controlled process.

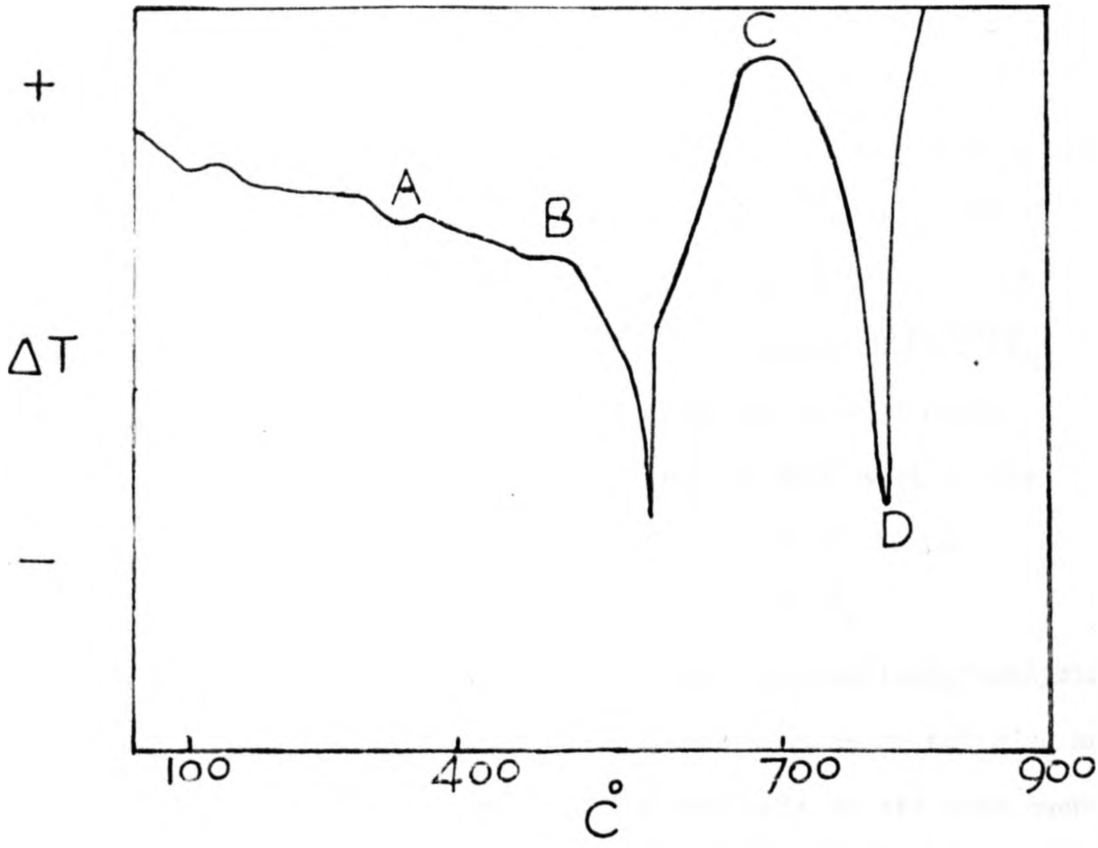
Phase diagrams also give useful information about the probable products of crystallisation when glass melts are slowly cooled but discussion of nucleation and crystal growth is outside the scope of the present review.

(ii) Reactions in the molten batch

It may be seen from the Figure 1 that many different compositions in the sodium-calcium-silicate ternery system might be of interest and the reactions between the individual components upon heating could exhibit considerable variety, depending upon the stability and the proportions in which the batch constituents are mixed.

The reactions in the batches have been studied exhaustively by Kröger et al[2], by determining the amount of Co_2 evolved thermogravimeterically. Other methods applied have been electrical measurements and differential thermal analysis. Figure 2 shows the differential thermal analysis curve, for the mixture 85% SiO_2 and 15% Na_2Co_3[2(a)]. Both materials have grain size to pass 350 B.S.S. Peaks A and B indicate the two polymorphic inversion in Na_2Co_3 at 340°C and 470°C respectively. At about 550°C the curve shows an endothermic reaction due to the formation of a sodium meta silicate layer around the silica grains. As the temperature rises, sodium disilicate is formed, shown by the exothermic Peak C at 700°C. Peak D indicates the melting of sodium disilicate as a eutectic with silica at 790°C. A glassy matrix is formed immediately after the endothermic peak at 790°C.

FIG. 2



(AFTER WILBURN)

FIG. 3

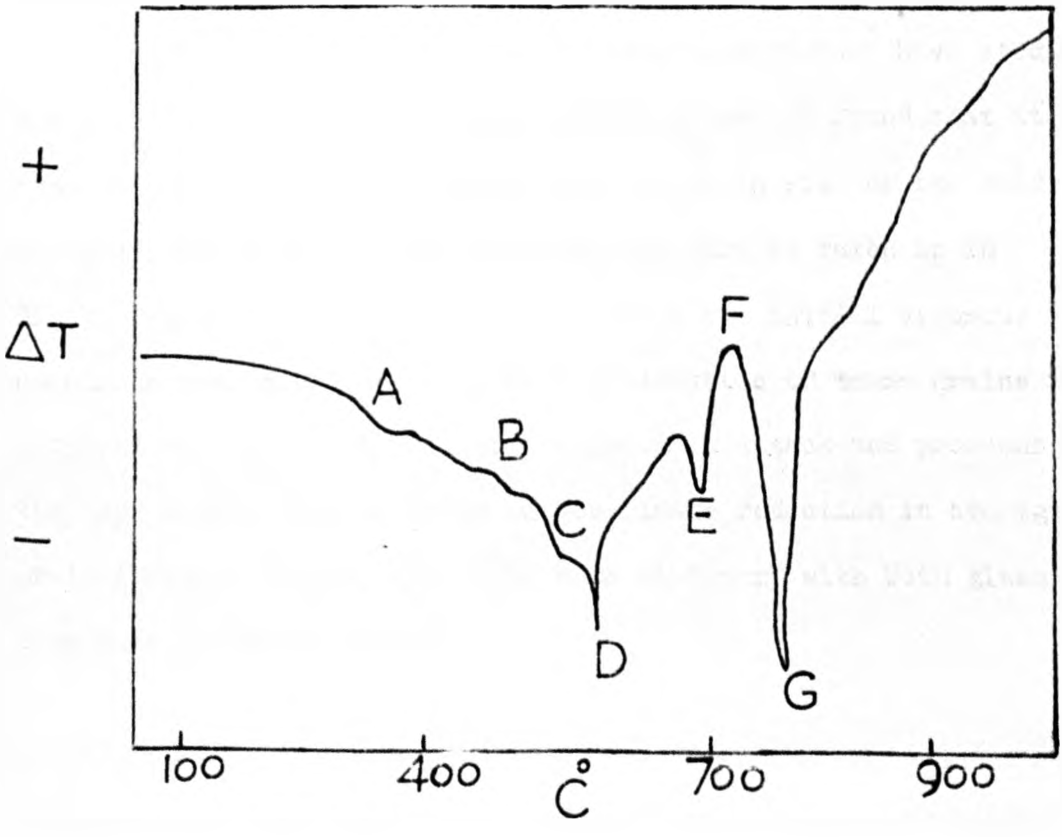


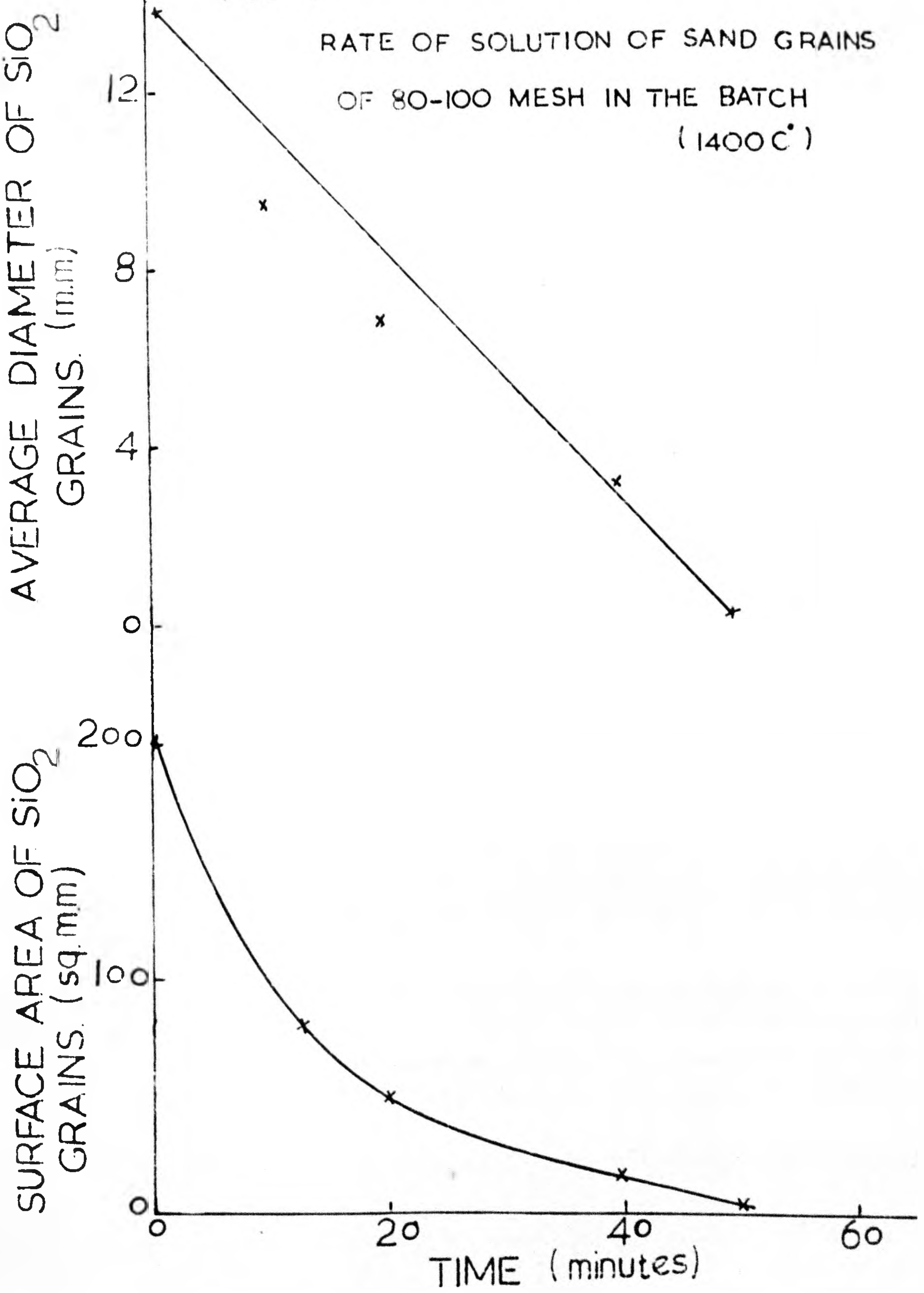
Figure 3 shows the differential thermal analysis curve for the three component system; 85 mole % SiO_2, 14 mole % Na_2Co_3 and 2 mole % NaF. In this diagram peak A and B include the crystalline inversion in Na_2Co_3 at 350 and 470°C. Peak C at 540°C is due to the chemical reaction resulting in the formation of sodium meta silicate. The peak D indicates $\alpha - \beta$ quartz inversion (573°C). The peak E at 680°C is due to chemical reaction between Na_2Co_3 and SiO_2. The exothermic peak at 710°C agrees with that in the two component system and is due to the formation of sodium disilicate. At 760°C a glassy matrix is formed[2(a)].

Differential thermal analysis and thermogravimeteric analysis lead to some understanding of the reactions which occur but give no direct evidence about the homogeneity of the melt or its subsequent refining.

After the vigorous reactions are complete, some sand grains remain incompletely dissolved. On dissolving, these will produce regions or cords rich in silica. Preston and Turner[3] have studied the rate of melting of soda-lime-silica glass and found that at a constant temperature it depends upon the grain size of the sand. At 1400°C about 90% of the total melting time is taken up in dissolving the residual sand grains after the initial vigorous reactions have subsided. The rate of solution of these grains is proportional to the surface area exposed to attack and proceeds at the approximate rate of 0·003 mm per minute reduction in average grain diameter (Figure 4). (The rate will vary with both glass composition and temperature.)

FIG. 4

RATE OF SOLUTION OF SAND GRAINS OF 80-100 MESH IN THE BATCH (1400C°)



(AFTER PRESTON)

The observations of several workers support the notion that the dissolving of the residual sand grains is a diffusion controlled process but only Kreider and Cooper[4] have so far reported experiments to confirm this, although a paper also confirming this has been read by Hlavac[5] but not yet published.

2 ACCIDENTAL INHOMOGENEITIES

It has already been mentioned that the heterogeneous reactions involved in glass melting lead to inhomogeneities. There are also some other important sources of inhomogeneities. All commonly used refractories are attacked by glass and dissolve in it, producing cords rich in Al_2O_3, SiO_2, ZrO_2; sometimes solid crystalline fragments (stones) break away and do not dissolve completely. Stones can also occur when refractory materials in the batch do not dissolve completely. Cords produced by refractory corrosion often lie on or very close to the outer surface of the glass. More randomly oriented silica rich cords may be caused by drips from the crown of the furnace.

Other specific types of inhomogeneity can be caused by evaporation or absorption at the top surface of the melt; alkali, boron, lead, fluorine may easily be lost by volatilisation and water vapour or SO_2 absorbed from the furnace atmosphere. When an excessive amount of fines are used in batch or sometimes, perhaps, batch may be charged in such a way that there is a danger of batch material being entrained by the flames and batch dust may be carried on to the refractories. The alkalies present cause fluxing of these refractories causing drops of corrosion product to fall into the melt and resulting in aluminous or siliceous streaks in the glass.

A general inhomogeneity is often due to some carelessness in the batch mixing. When the batch is to be transferred some distance, demixing of already mixed batch can occur if the dry batch is subjected to vibration or poured from one container to another.

(i) Segregation during melting

The importance of using a well mixed batch and thus by implication the seriousness of any inhomogeneity of the batch has been reported by Poole[6 a]. However, even well mixed batch often tends to segregate during melting. The reason for this segregation is that during the early stages of melting, when batch is heated rapidly, the liquid phase first formed is very fluid and can begin to drain downwards before it reacts. This leaves the upper part of the batch enriched in silica and other less reactive constituents. Also the gases evolved during reaction stir the reacting mass. This might be expected to have a chiefly beneficial effect but a froth floatation effect can also sometimes cause additional segregation by making partly dissolved silica grains rise and float on the surface of the melt.

(ii) Cords formed during dissolving of refractories

Molten glass is very corrosive at high temperatures and so dissolves aluminous material from the surface of refractory pieces in any part of the furnace. In the throat of a tank furnace or the doghouse corners, the effect of attack is much greater due to the relatively rapid movements of glass, giving forced convection conditions for corrosion. Another factor which profoundly influences the rate of solution of the refractories is the temperature of the glass at the interface. When the tank blocks corrode, there is usually enhanced attack at the top of the blocks near the glass surface. This enhanced attack at the top of the block is known as fluxline attack. Many theories have been put forward to explain this profile of attack. Some of these theories are based on the temperature gradients which exist in glass melting tanks. It can be shown that the rate of solution of refractories in molten glass is very much affected by the temperature and it can be seen from Figure 5 that change of temperature from 1200 to 1500°C increases the rate twenty times[6,4].

Kingery[7] has reported that the kinetics of the solution of refractories can be determined by two processes; the rate of reaction at the interface and the diffusion of the solute from the reacting zone. This later effect can be expressed by the Nernst equation,

$$n/A = K\,(C_s - C) = D/\delta_{eff}\,(C_s - C)$$

where n/A = rate of solution

C = concentration in the bulk fluid

C_s = concentration of the saturated solution

K = rate constant

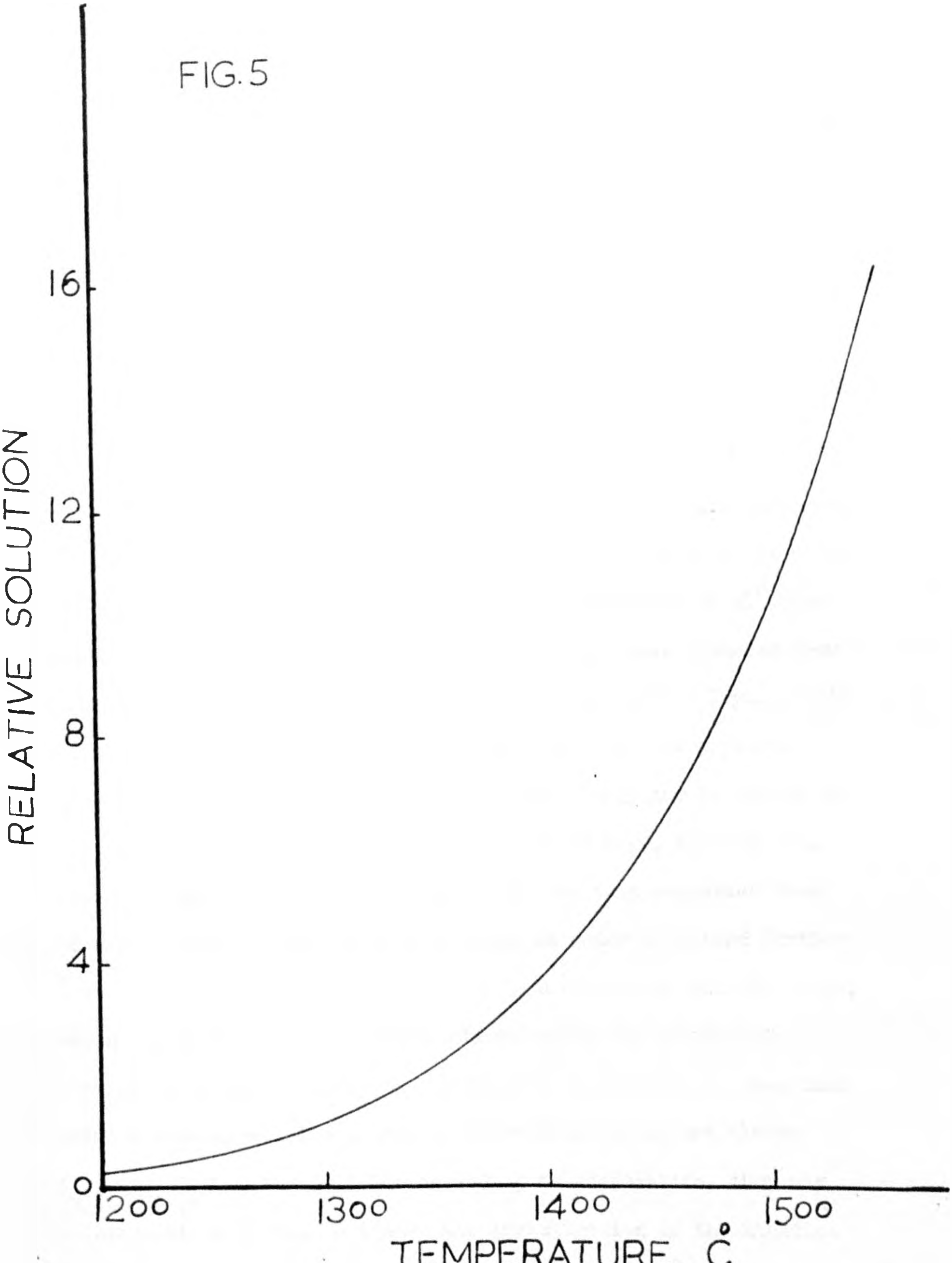
D = diffusion constant

δ_{eff} = effective film thickness for diffusion

This equation shows that rate of solution depends directly on the difference in concentration between the bulk solution and a saturated solution, on the diffusion constant and inversely on the effective boundary thickness.

If the aluminous glass which is formed as a result of corrosion enters the main current of glass, it will give streaks or cords in the finish ware. Usually much of the glass recirculates between melting and working regions a number of times so that the inhomogeneities are widely distributed, greatly attenuated and can be neglected. But if there is excessive solution of material near

FIG. 5



EFFECT OF TEMPERATUR ON DISSOLUTION OF REFRACTORY BLOCK

(AFTER BUSBY)

the forming point, then there is a real danger of developing streaks in the finished product. Cords are also formed when pieces of refractory material are dislodged as stones. The stone would be surrounded by a zone of glass which, inconsequence of its containing dissolved refractory, would be more viscous than the main mass of the glass and would appear as a sac or cord.

(iii) Volatilization

It is a well established fact that loss of volatile components from a melt, especially a laboratory melt of relatively small depth can produce serious inhomogeneity in glass. Kruithof et al[8] have published a qualitative study of this process. Mass transfer from melt to atmosphere can result in heterogeneous surface layers, bulk inhomogeneity and changes in most of the chemical and physical properties of at least the surface layers. Cords may be formed in borosilicate glasses by the volatilisation of Na_2O, K_2O and B_2O_3 leaving a silica rich surface layer. It has been suggested that it may be best to leave this scum alone in order to retard further losses. Often the scum is skimmed off, leaving good quality glass, though in difficult cases heavy inhomogeneity may necessitate partial draining of the tank. Kruithof's[8] work seems to show that surface inhomogeneities caused by volatilisation do not always disperse through the melt but depending on composition, they may either sink or float. A systematic investigation of the kinetics of the process has been made by Oldfield and Wright[9] with particular reference to volatilisation and the formation of silica scum on borosilicate glass. They found the loss of alkali and B_2O_3 from the glasses obeyed a linear relation with the square root of time indicating a diffusion controlled process through the cristobalite surface layer. The loss was accounted for as metaborate in the ratio $5(Na_2O.B_2O_3):1(K_2O.B_2O_3)$. They also concluded that the two mechanism were involved; evaporation from a free melt surface and diffusion through a SiO_2-rich layer which itself varies with time.

Volatilisation of alkalies from soda-lime-silica system tends to give siliceous cords which leads to higher surface tension and viscosity and lower refractive index. The specific evaporation of alkali is higher in the presence of water vapour, the rate of evaporation increases with the increase in water vapour content[10]. The water enters the melt, where it reacts with Na_2O and is evaporated as NaOH. PbO is easily volatilised from lead glasses giving a large decrease in density with correspondingly large changes in refractive index and viscosity.

3 MECHANISM OF HOMOGENIZING

The final homogenizing of glass or any other inhomogeneous viscous liquid depends upon the diffusion of any inhomogeneity into the bulk of the melt or liquid. The process of diffusion can be accelerated by increasing the surface area of the inhomogeneities and thus reducing the distance over which interdiffusion must take place or by increasing the diffusivity.

Since diffusivity is a physical property of the system, there are only two ways of influencing it; change in temperature or change in composition. Only change in temperature is possible for a particular glass but it will increase the refractory corrosion, losses by volatilisation and cost of running the furnace. It is, therefore, important to examine the possibility of reducing the distances over which diffusion must take place. This may be accomplished by attenuation of the inhomogeneities.

Attenuation of inhomogeneities by laminar flow was first discussed by Spencer and Wiley[11]. They reported that it can be considered as consisting of two processes, increasing the surface area of the interface between the liquids being mixed and distributing that interface through the volume of the material. The first person to consider application of this to glass was Geffcken[12] but the most detailed discussion of this process is due to Cooper[13], who has also considered its application to homogenization of glass in tank furnaces[14]. He has shown that the parameter that measures the local mixing rate in a continuous laminar flow system is $D/\delta^2 u_x$, where D is the appropriate chemical diffusion coefficient, δ is the striation thickness and u_x is the throughput velocity.

Cooper[14] has suggested that the amount of mixing required (H) between two adjacent striations (i & i + 1) can be defined as

$$H_i = \int_{n_i}^{n(i+1)} (N - \bar{N})\, dn = C_1 \Delta N_i \, \delta_i$$

where C_1 is a number depending on the details of concentration distribution, ΔN_i is the intensity of the individual striations and δ_i the striation thickness. The rate of mixing is given by

$$\frac{dH}{dt} = h = \frac{\delta(N - \bar{N})}{\delta t}$$

which leads to

$$\frac{dH}{dt} = C_2 \frac{D \Delta N}{\delta}$$

where C_2 accounts for the details of the concentration distribution and is of the order of 2π, ΔN is the intensity of segregation, D is the chemical diffusion coefficient and δ is the striation thickness.

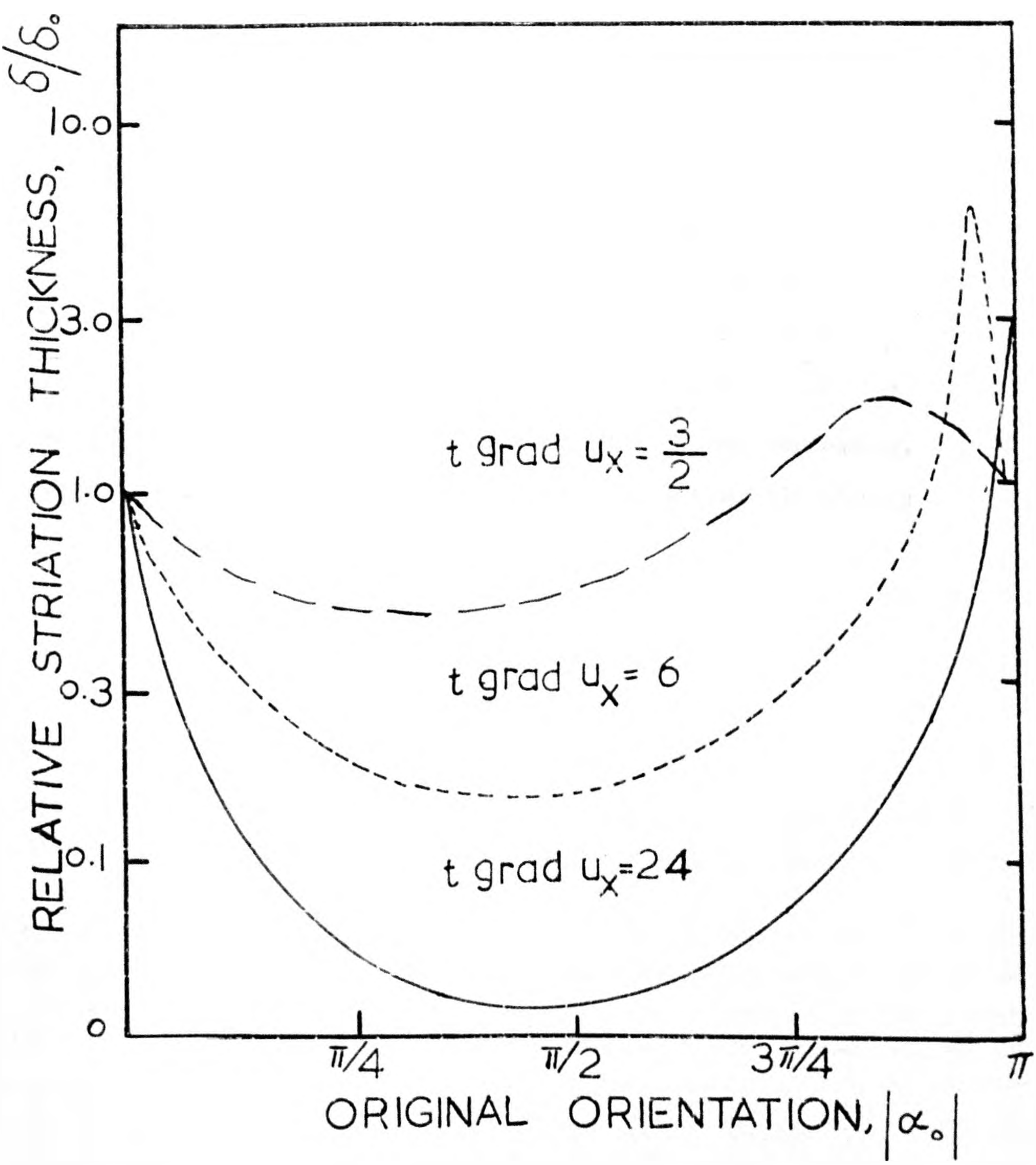
Cooper[14] shows that for parallel sided inhomogeneities originally at angle α_0 to the streamline, the effective striation thickness (δ) at a later time is given by

$$\delta / \delta o = \left\{ 1 + 2t \text{ grad } u_x \operatorname{Cos}\alpha_0 \operatorname{Sin}\alpha_0 + (t \text{ grad } u_x)^2 + \sin^2\alpha_0 \right\}^{-\frac{1}{2}}$$

Figure 6 is a plot of this equation for various values of the total shear (t grad u_x). It is evident from this figure that greater the total amount of shear, the greater the probability of attenuation for any value of α_0.

Because of the complex flow patterns and temperature distributions different elements of glass follow very different paths through the furnace and therefore are subject to very different amounts of attenuation and effective D between entering

FIG.6



DEPENDENCE OF RELATIVE STRIATION THICKNESS ON ORIGINAL ORIENTATION FOR SEVERAL VALUES OF TOTAL SHEAR.

(AFTER COOPER)

and leaving the furnace. Cooper[13] has suggested that in this case a suitable way to compare efficiency of processing of these different elements is to integrate the expression $D/\delta^2 u_x$ which is equivalent to $\frac{Dt}{\delta^2}$, along the whole length of each streamline

$$\int_{x_0}^{x} \frac{D}{\delta^2 u_x}\, dx$$

and this expression should be maximized for every path. For diffusion alone in a parallel slab of thickness 2δ it is a standard result that diffusion is approaching completion when $\frac{Dt}{\delta^2} > 1$, so one would wish to have $\int \frac{D}{\delta^2 u_x}\, dx > 1$ for every path but if much greater than 1, this represents distinct over processing, even though its occurrence would not have the undesirable effects of having $\int \frac{D}{\delta^2 u_x} \ll 1$.

4 REASON FOR INVESTIGATION

It is generally assumed that despite minor evidence of slight heterogeneity, normal commercial glasses made in pots or tanks are substantially uniform in composition. This assumption is rarely tested although inhomogeneities in glass articles due to local composition variations may seriously affect its strength, thermal shock resistance, internal stress distribution and refractive index or other important properties.

Considering the great importance of homogeneity it is surprising that it has by no means exhaustively been studied. Work previously published includes several methods of measurement but most of them give only a qualitative value of homogeneity. Very few attempts have been made to measure the homogeneity of glass quantitatively.

The common practice for obtaining homogeneous glass in the laboratory is to melt, crush and remelt repeatedly until the sample is thought to be homogeneous. This is a very tedious process. If efficient stirrers were developed, the homogenising process could be simplified. Although very little has been done concerning homogenising of the glass melt, some work has been done on mixing and homogeneity of batch. The one exception is making of optical glass where mechanical stirrers are being used because of the very good homogeneity required. The function of the stirrer is to improve homogeneity by attenuation of inhomogeneities, serving to reduce distance and increase areas overwhich interdiffusion can operate. The concentration of the inhomogeneities as well as the details of the flow pattern govern the effectiveness of attenuation.

This work was done for several reasons. The most important are:-

(i) to show that homogeneity of glass can be measured quantitatively.

(ii) to follow the kinetics of mixing for several different simple stirrers.

(iii) to compare results obtained in glasses with those obtained in room temperature models.

It was hoped that the results would increase understanding of the process of mixing glasses or other viscous newtonian liquids and show what dimensionless parameters need to be matched to obtain reliable information from room temperature models. Although these experiments are not directly related to flow and homogenising in tank furnaces, better understanding on laboratory scale may be expected to help understand behaviour of full size pots or tank furnaces.

5 PRINCIPLES OF MEASURING HOMOGENEITY

A homogeneous body is one for which small samples taken from numerous different positions have exactly the same chemical composition or the same value of some other property. To describe this quantitatively the values and accuracy of measurements of the property chosen and also the size of the samples taken must be stated. The minimum reliable description of homogeneity requires two parameters; the scale and the intensity of segregation.

(i) Scale of segregation

If the actual size of the inhomogeneity can be measured, this is the scale that really matters but it is not often accessible. Therefore, the size of the sample usually has to be accepted as the scale. If the samples are very much larger than the inhomogeneities the result will not indicate serious inhomogeneity, even if it exists on a smaller scale. The sample size therefore needs to be very carefully chosen. It is inherent in any method of measurement that as the sample size increases, the variance of the results decreases. This is shown in the figure 7, where I is a function of the variance. The diagram shows how measured value of I depends on sample size. So long as sample size is smaller than the actual size of the inhomogeneities I has its maximum value (Region A). When sample size is much bigger than the size of the inhomogeneities I is very low (Region C). The upper and lower limits of Region B, in which I is sensitive to sample size roughly indicate the size range of the inhomogeneities. Ox could be considered as the sample size for this particular case.

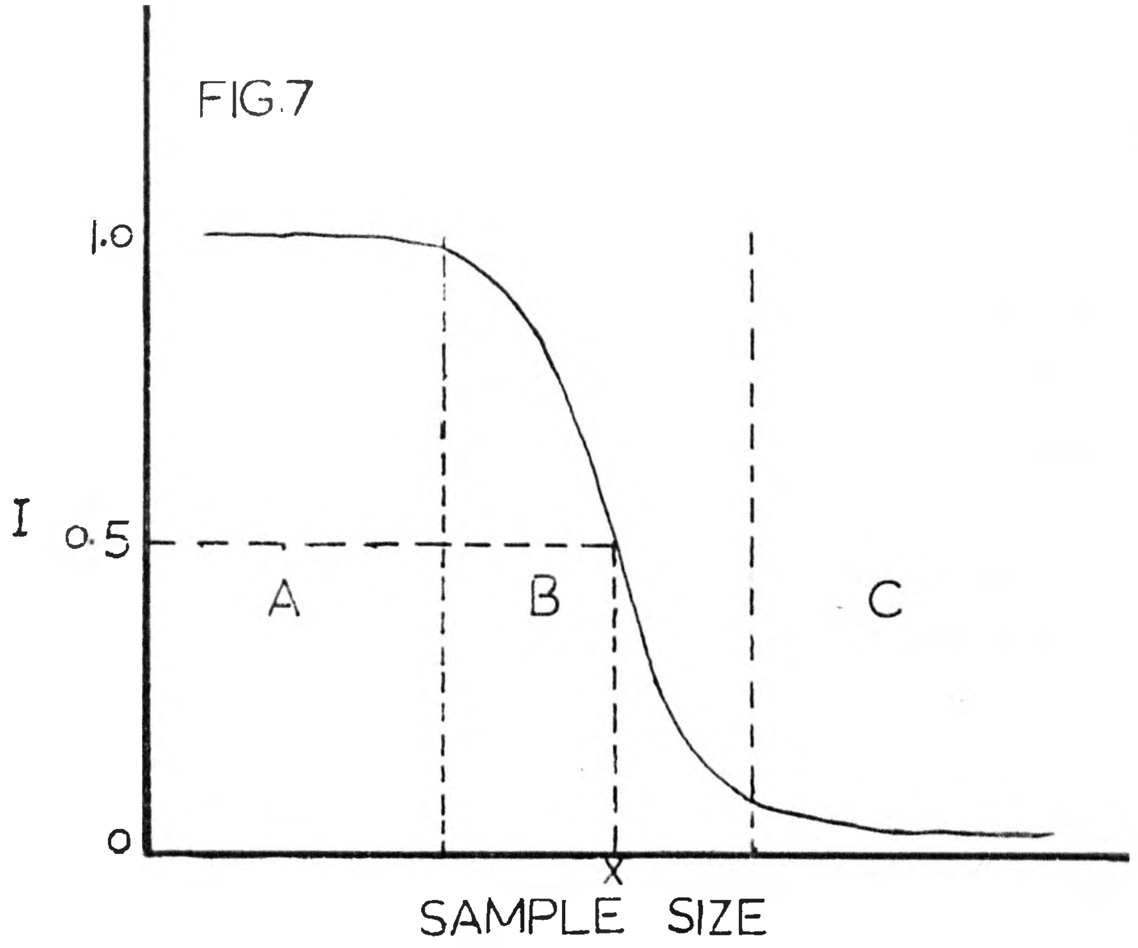
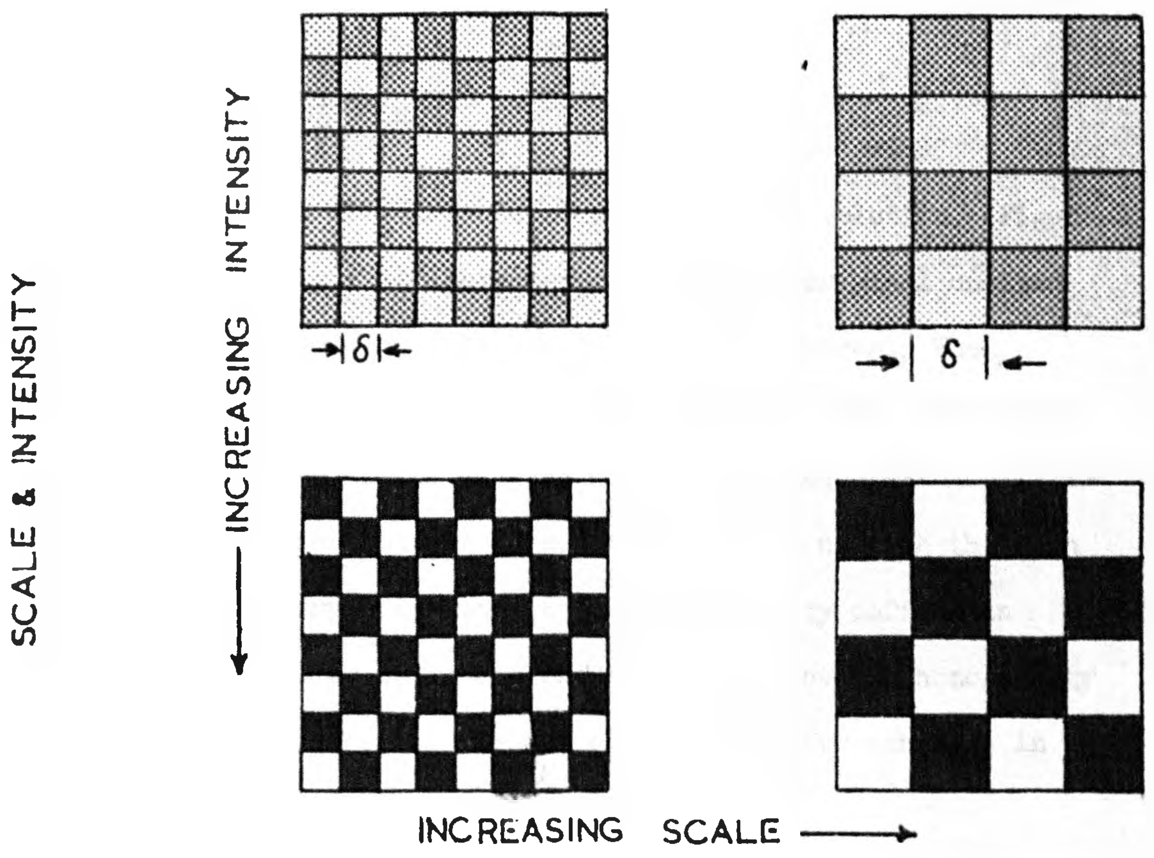


FIG.7

I
1.0
0.5
0
A
B
C
X
SAMPLE SIZE

FIG. 8



SCALE & INTENSITY
INCREASING INTENSITY
INCREASING SCALE
δ
δ

(ii) Intensity of segregation

This is a convenient measure of the width of the distribution of the property measured. It is a statistical parameter describing the data such as variance or standard deviation; it is common to use the variance. Its value is a maximum with maximum segregation and goes to zero when mixing is perfect. It is convenient to define the intensity so that its value is 1 when mixing is as bad as possible. Danckwerts[15] has discussed this and defines I as

$$I = \frac{\sigma_a^2}{\bar{a}(1 - \bar{a})}$$

where a is the concentration of one component, $\bar{a}$ is the mean concentration of the same component in the mixture and σ^2 is the variance of the concentration of the component obtained experimentally. When even for perfectly homogeneous body σ^2 is not zero because of errors in method of measurement, it is better to define intensity of segregation as

$$I = \frac{\sigma_a^2 - (\sigma_a^2)_{F.M.}}{a(1 - a)}$$

where $(\sigma_a^2)_{F.M.}$ is the variance of a fully mixed solution. Figure 8 shows qualitatively what these terms mean. The original unmixed components are represented by black and white squares. When perfectly mixed the body would be uniformly grey. The striation thickness δ is used as the measure of scale of segregation. It is the minimum distance between adjacent intersections with the mean concentration. Very often the (average) intensity defined as suggested and average scale are enough to describe the homogeneity in practice. However, this is not always true, for example, in strength measurements maximum tensile stress is likely to be more important than the average value because it is the tensile stresses that weakens the article.

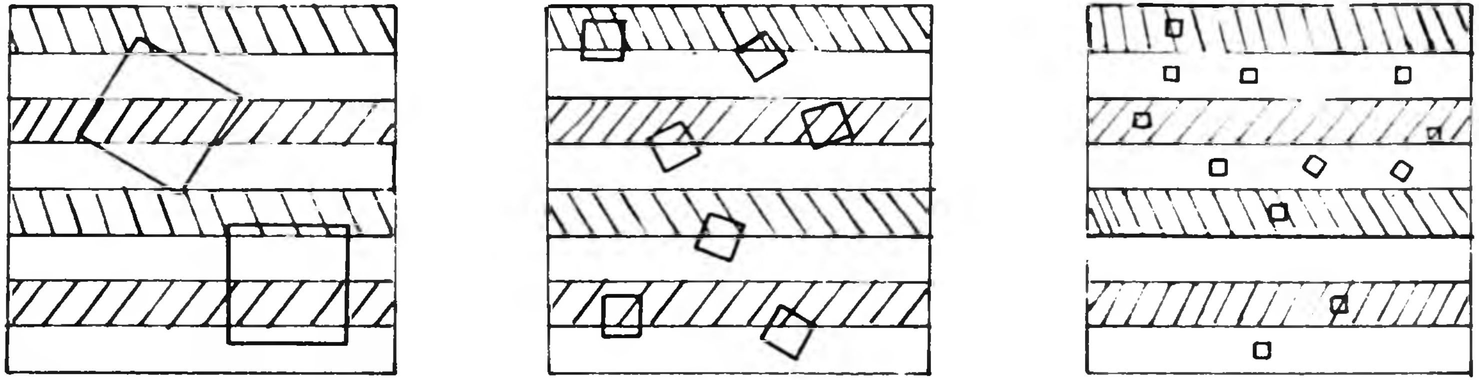
Before homogeneity can be properly described it is necessary to be able to measure some property on a sample, small in relation to scale of inhomogeneity, to know the size of the sample and its position and to repeat the measurements for samples taken from many position. The most important factors in measuring the homogeneity are accuracy of the measurement, the size of the individual samples and the method of sampling the body to obtain them.

The size of the sample depends upon the size of the inhomogeneities present. If the sample is very much larger than the average size of inhomogeneity, it will probably differ very little from the average in properties and yield little information. There will be no advantage using samples much smaller than the size of inhomogeneity, because the samples already give very close to the maximum possible intensity of segregation. If the sample is very small, the less accurate will be the value of property measured. By decreasing the size of the samples taken one also reduces the probability of obtaining a representative result unless the number of samples is considerably increased.

This is illustrated by examination of a glass system with different layers (Figure 9). The thickness of each layer is "x" units. If the thickness of the sample is a lot larger than "x" units, the measured intensities will not differ much from the average and will not detect the actual intensities of the layers.

FIG. 9

EFFECT OF SAMPLE SIZE ON INTENSITY



VALUE OF INTENSITY :-

CONSIDERABLY BELOW MAXIMUM

SLIGHTLY BELOW MAXIMUM

MAXIMUM

Samples of the size equal to "x" will mostly comprise parts of two adjacent layers and the maximum deviation observed in intensity will be rather less than the true spread. A sample size of about x/2 will give very close to the true range of intensities and further decreasing samples size will not appreciably increase the range.

For obtaining a representative sample it is very difficult to lay down specific rules. It depends very much on the distribution of inhomogeneities through the body. In general a method of obtaining samples at random through the whole body is required. For practical reasons the smallest sample giving useful results is to be preferred. The only way to be sure sampling is sufficiently representative is to check the reproducibility.

After deciding the method of measurement, size of the individual samples, the number and position of the individual samples, the problem remains of the sampling technique. The ideal sampling technique is that there should be no disturbance in the body while removing the sample but this is often difficult to achieve. This requirement can easily be met for glass, as the whole glass melt can be cooled in the crucible and removed without any disturbance. Then thin sections may be cut from this melt to investigate the homogeneity.

CHAPTER II

REVIEW OF THE EARLIER WORK

1 METHODS OF ASSESSING HOMOGENEITY OF GLASS

(i) Containers

The degree of homogeneity required varies according to the purpose for which the glass is to be used. The requirement of an optical glass is that it should be of uniform refractive index throughout the whole body. The containers glasses do not require uniform refractive index but they need to withstand some rough handling i.e. they must have reasonable strength. Bottles intended for carbonated beverages, beer and products packed under gas pressure must meet requirements of pressure resistance. Some highly carbonated beverages may develop pressures of 125 p.s.i. during very warm weather. So the most important criterion for the containers is often strength because of resistance to internal pressure and long life of multi-trip bottles.

The most common method of investigating day to day homogeneity of containers is the Swicker[16] rating examination. In this method a ring section type of examination is used to determine and evaluate the degree of cordiness of the glass containers. It is a feature of all blown glass ware that the cord is nearly always found running parallel to the blown surfaces, forming concentric cylinders and the examination of ring sections is thus a useful test. Evaluation of the degree of cordiness is based on the amount and positioning of the cords with respect to the normal glass, together with the measurements or estimation of the amount of stress present. These stresses are usually the result of an inhomogeneous condition in the glass. This is a quite good method for daily routine but it is essentially qualitative, depending on comparison with arbitrary standards.

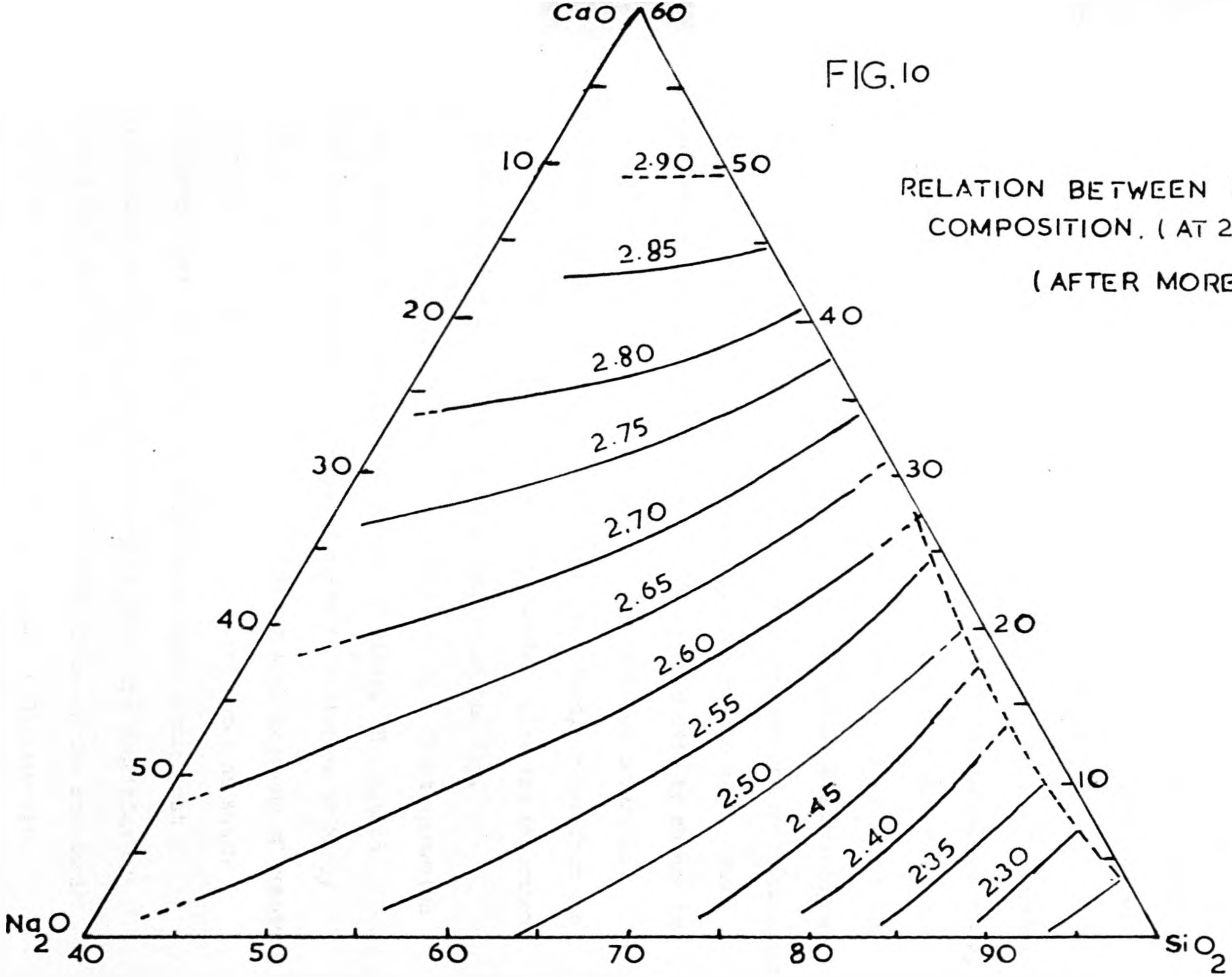
An enormous amount of work has been done in past years, in studying the physical properties of the glass, to study closely the causes of inhomogeneity in glass. In the continuous tank furnaces, the chemical composition of the glass may be controlled by routine chemical analysis or by the routine measurement of some physical property of the glass which is known to change with variation in the chemical composition. Density, refractive index and softening point are three of the more common physical properties that are influenced by the chemical composition and their measurements can be used as a means of routine control. The density of the glass is a function of its composition and since it can be measured with very high accuracy, in a relatively short time, on large numbers of samples, it is often used as a means of operating control in furnace operation. Table I shows the relative quantitative effects of CaO, SiO_2, Na_2O and Al_2O_3. A change of about 0·5% in CaO has a greater effect on density than a corresponding change in SiO_2, Na_2O, or Al_2O_3. An increase in lime content gradually raises the density, an increase in silica diminishes it. The relation between density and composition in the system Na_2O-CaO-SiO_2 at room temperature is shown in the Figure 10.

J. C. Turnbull[17] was the first to separate inhomogeneities in bottle glass by density difference. A quantitative method of measuring the homogeneity of glass is the density spread and centrifuge of Turnbull and Ghering[18]. This consists essentially of separating the powdered glass into density ranges by centrifuging

FIG. 10

RELATION BETWEEN DENSITY & COMPOSITION. (AT 20 C°)

(AFTER MOREY & MERWIN)



in a suitable dense liquid with accurately controlled temperature. The particles are first separated into light and heavy fractions which may be removed and subdivided by further separation. This method has several advantages over other methods. The chemical analysis of the separated fractions may be used to determine the materials with which glass is diluted or it may be used to distinguish further among the various types of cords. The particle size of the sample is near to the true size of the inhomogeneities, and the method of sampling the body is much better than the other methods. Also different grain sizes from one sample may be used to determine the striation thickness of the cord. Disadvantages are the fact that the method is a destructive one and no information can be obtained about the original position of the cord. The separation of the fine particles is interfered with by change in density and flocculation produced by any absorbed material. Another difficulty which also limits the method, arises from the compressibility of the heavy organic liquid. Also the experiment is too lengthy to be done on many samples in one day.

Preston[19] has described a simplified sink float apparatus and method for measuring the density of glass. The method involves the settling of lumps of glass in a mixture of heavy liquids. This is accomplished in a water bath by means of constant heating of the liquid. The temperatures are noted at which unknown lumps and pieces of standard glasses settle past a reference level in a tube of heavy liquid. The densities of the test lumps are then calculated from those of the standards by means of the coefficient for the change of density with temperature for the liquid and for the glass. This method is precise, simple, and easily operated. It is much more rapid than the other methods. The temperature difference corresponding to the test piece of maximum density and minimum density, taken from the same bottle, can readily be expressed as the equivalent density spread.

In principle it is a good method but there are certain disadvantages. The common practice is to take only five samples from one container once a day which can hardly be a representative sample. Scatter of densities indicates inhomogeneity but the method is not a sensitive indicator of inhomogeneity because the sample size is much bigger (3/8 to 5/8 inch square) than the true inhomogeneities.

A. T. Coe[20] tried to relate the density spread determined by the Preston method to possible glass making troubles. He reported the control limits of ± 0·0030 gms/cc on density as being satisfactory in container glass production. In connection with trends in the density data, he considered a trend of 0·0015 g/cc in 24 hours to cause only slight inhomogeneity. If the trend continues, however, for another day then severe troubles would be likely to appear. Coe[20] used density spreads as indications both of current homogeneity and of impending trends.

Shelyubskii[21] used the principle of the christiansen filter and developed a method for determining the homogeneity of glass. It is based on the variation of scattering of parallel beams of monochromatic light by a layer of glass powder in an immersion liquid with small variations in temperature. On heating, the refractive index of the liquid is decreased and as the refractive indices of two phases become closer to each other, the scattering is decreased and so by raising the temperature of the suspension the transmission of light through it will be increased until the two values of refractive index are equal. On further heating the refractive indices diverge and this again increases the scattering. In other words the transmission reaches a maximum at the temperature at which the two refractive indices are equal. Thus the relation between the intensity of the light travelling through the vessel and temperature will take the form of bell shaped curves. Shelyubskii[21] plotted transmission against the ρ where $\rho = (n_1 - n_2)$ (Figure 11). For a perfectly homogeneous glass, the peak formed is very narrow and showed a maximum transmittance of 100%. The less the homogeneity of the glass, the more comparatively wide and slanting will be the peak, as some grains will be matched at different temperatures. The amount by which the height of the peak is altered is dependent on the intensity and amount of cord and can therefore be used as a measure of homogeneity.

Raman[22] showed that the intensity of a parallel beam passing through the cell should be

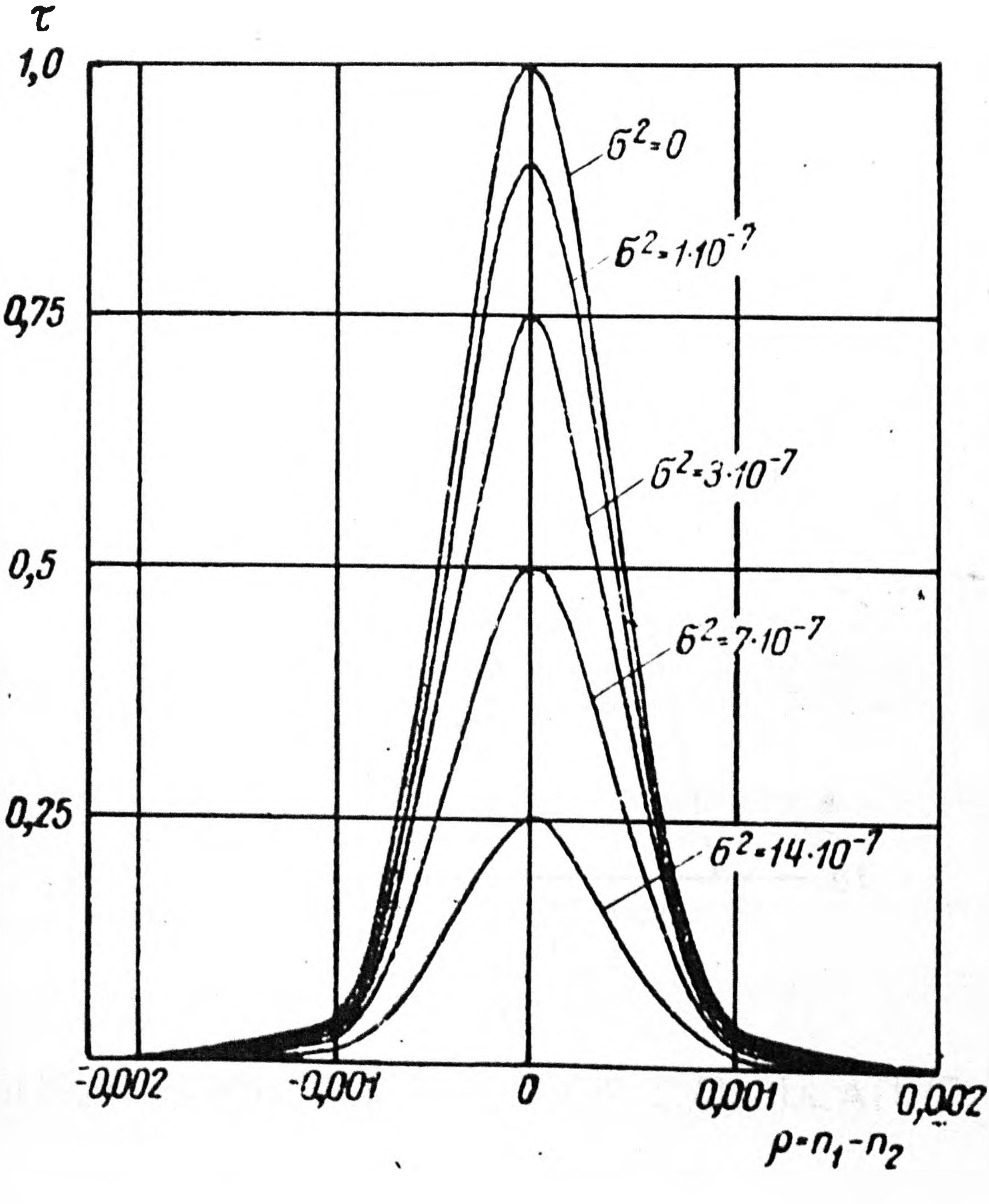
$$I = I_0 \exp\left[-\frac{K^2\pi^2 z\Delta}{\lambda^2}(n_1 - n_2)^2\right]$$

where I_0 is the incident intensity, I the emergent intensity, K factor depending on proportion and shape of glass particles, $(n_1 - n_2)$ the difference between refractive indices of homogeneous glass and liquid, Δ is the size of glass particles, z the length of the cell and λ the wavelength of light.

Shelyubskii[21] assumed that there was a Gaussian distribution

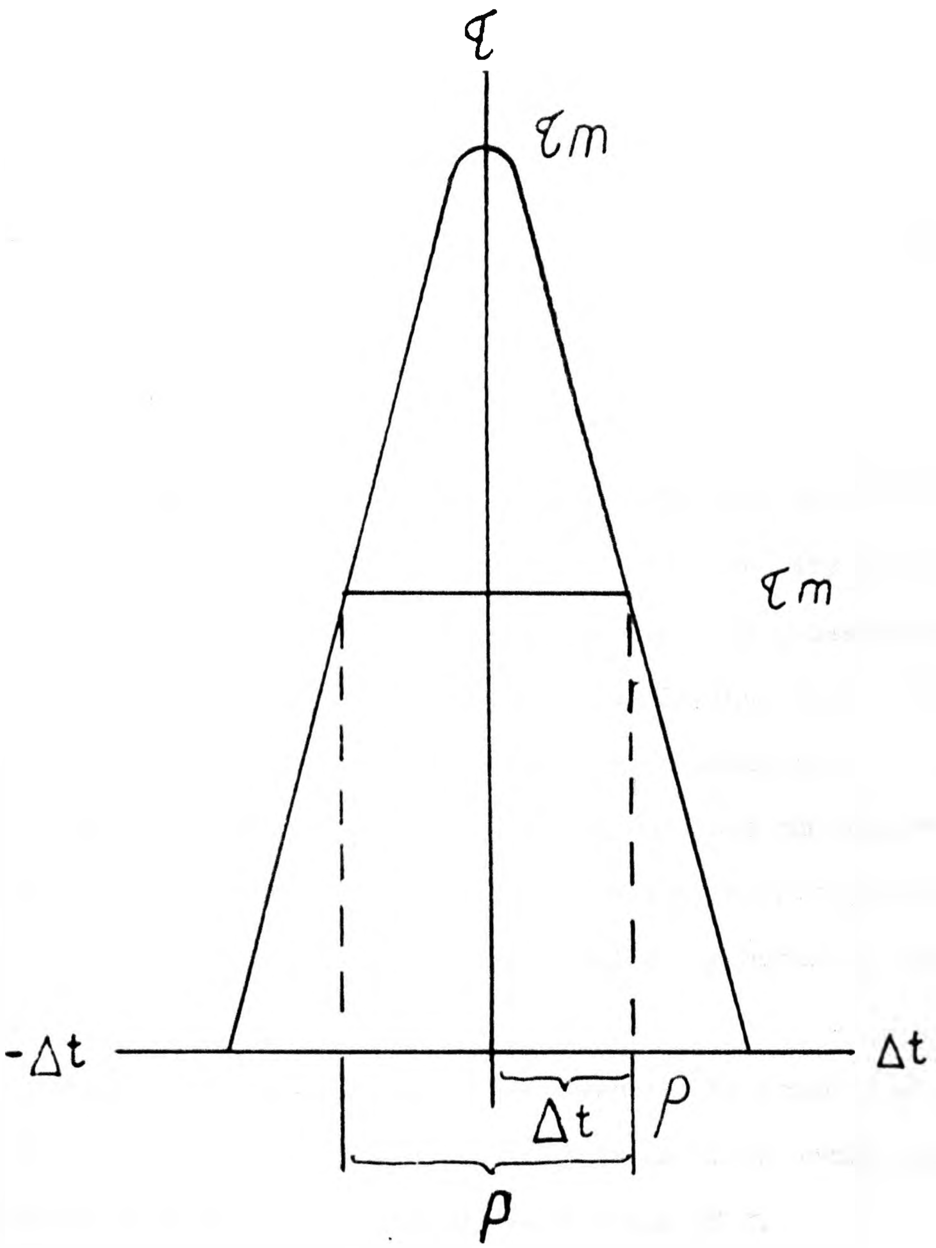
FIG. 11

PLOT OF TRANSMISSION, τ VS ρ



(AFTER SHELYUBSKII)

FIG. 12



SHELYUBSKII'S METHOD OF CALCULATING "a"

of refractive index of the glass so that

$$N_x = No/(\sigma\sqrt{2\pi}) \; .. \; \exp\left(\frac{-x^2}{2\sigma^2}\right)$$

The standard deviation σ^2, which indicates the deviation of refractive index of small particles of the glass from its average, is used to measure inhomogeneity. Following Raman's[22] treatment and introducing the parameter $\underline{a} = \frac{K^2\pi^2\Delta z}{\lambda^2}$ & $\rho = (n_1 - n_2)$ leads to

$$I = I_0 \exp - \underline{a} \, (\rho^2 - \sigma^2)$$

The coefficient $\underline{a}$ can be calculated from the value of ρ at the half width of the peak (Figure 12).

$$\ln\,(Tm/T^{\frac{1}{2}}) = \ln 2 = a\rho^2$$

$$\underline{a} = \frac{\ln 2}{\rho^2}$$

No doubt the method is rapid and can be used for daily check but it is incapable of defining the size and intensity of inhomogeneity as two separate parameters. The author assumed a gaussian distribution of refractive index but it is highly unlikely that this is generally the case. The refractive index at maximum transmission is due to the major component but it does not tell us about the amount of major component present there. The experiment cannot give precise information about the shape of the actual distribution of refractive index.

Budd and Blanchard[23] have shown one way in which this method may be used for coloured glasses and this involves making measurements at two wavelengths and taking the mean value of σ.

Schilling and Weiss[24] also investigated the homogeneity of different glasses by Shelyubskii's[21] method. The reproducibility of the homogeneity coefficient is about ±1%. According to them the method is useful in optical industry but not for blown glassware, where quality is more related to a uniform viscosity.

A method by which cord in glass can be identified without destruction of the sample is described by Carr and Shoneberger[15]. This method is based on a comparison of sample containing cord with a sample of glass, from the same object, free from cord. A glass sample is placed on the turntable of an x-ray fluorescence apparatus and a beam of x-rays is directed into a small area of the surface. The elements in the sample will absorb x-radiation, when the voltage of the primary radiation is increased above the excitation voltage for each element. As the radiation is absorbed, the energy is released in the form of x-rays, the wavelengths of which are characteristic for the atom from which they originate. The sample must be cut in such a way that the cord is exposed on the surface, as the omission of secondary radiation occur only within about 0·1 mm of the surface. By comparing the counts from the base glass and one containing cord, the composition of the cord can be determined. The method is only useful when the scale of inhomogeneity is not much smaller than the diameter of the x-ray beam. Also the method does not give any quantitative value of homogeneity.

Löffler[26] analysed the inhomogeneities in glass by a combination of etching and optical interference methods. The rate of solution in glasses is dependent on the composition of the glass and of the solvent. As cords are due to variation in composition, etching a plane section through cordy glass produces contours which may be evaluated by interference measurements. Löffler[26] examined the individual inhomogeneities by this method.

He has demonstrated that two etching experiments with different attacking solutions enable the composition to be estimated more precisely. Since this method gives all the information necessary it can also be used to obtain a quantitative description of the homogeneity.

(ii) Flat glass

The flat glass is usually viewed against a back ground of zebra stripes i.e. alternate black and white stripes. Inhomogeneities or surface irregularities cause the stripes to appear distorted. Viewing either by transmission or reflection may be used, and it is often helpful when examining flat glass to tilt so as to observe at a glancing angle.

Holland and Turner[27] used a photo optical method to determine the homogeneity of glass. The method is also known as the "Schlieren" method and apparently is due to A. Topler[28]. It consists in determining the proportion of light lost by scattering from any cordiness present in a polished, parallel sided specimen. The apparatus is very simple, a reduced image of a small source of light is formed at a diaphragm, an image of this diaphragm is then formed by a large, well corrected lens at a second "stop", behind this stop a photocell or camera is located. The test specimen is introduced between the large lens and the second stop. The light falling on the photocell is determined as a percentage of the incident light on the disc and the intensity of this scattered light, expressed as a percentage of the incident light, can be used as a quantitative measure of homogeneity. However, it should be noted that no information about the scale of the inhomogeneities is given.

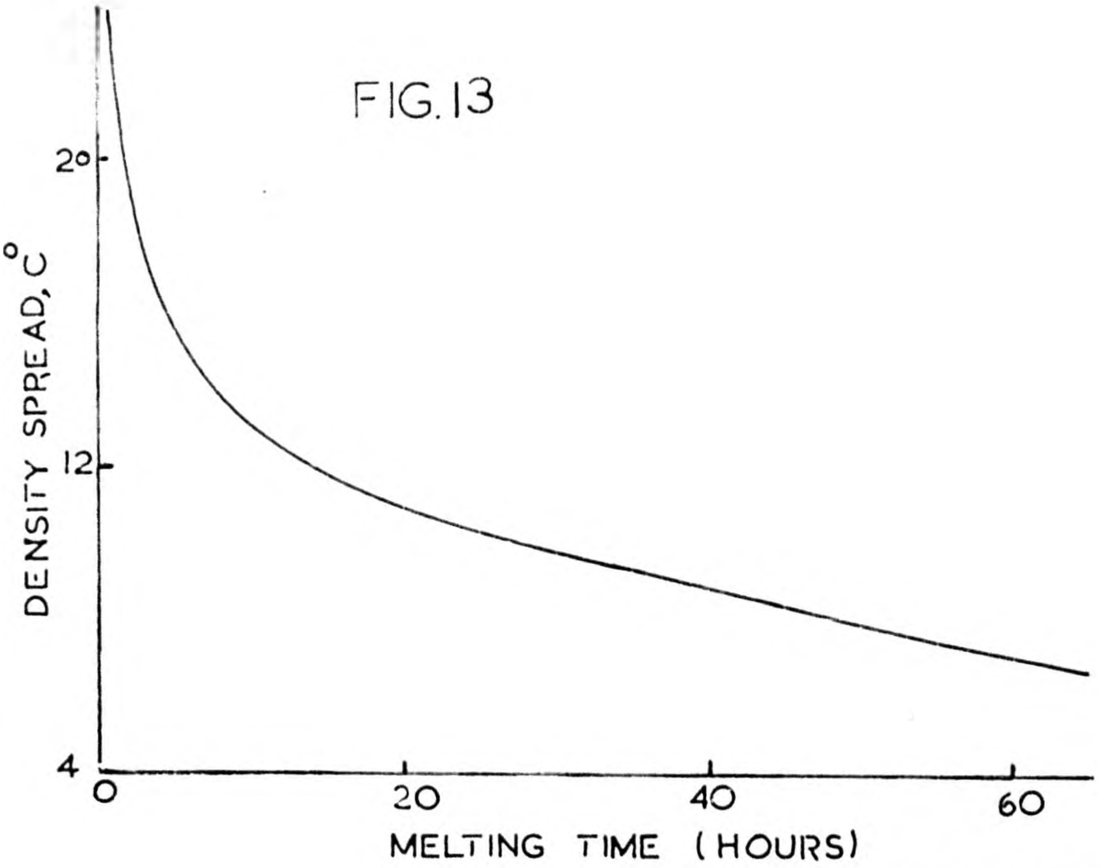
The sensitivity of the method depends upon the size of the image of the source, accurate alignment of the optics and the sensitivity of the cell used. The disadvantages are that the method is not truely quantitative. If the cords present are all in parallel layers, no distortion may be seen and if the surfaces are not flat and parallel or internal layers not parallel, distortiom will appear.

2 INVESTIGATION OF HOMOGENISATION OF GLASS

A fairly comprehensive study of the factors, such as temperature, time, batch formulation, degree of mixing, segregation tendency in conveying and melting, was carried out by Tooley and Tiede[29]. They used the density spread technique to measure the homogeneity of the glass. The first series of glasses were melted in a platinum crucible at 1400°C under conditions of minimum convective mixing. The melting time varied from 1 to 64 hours. The experimental results are shown graphically. Figure 13 indicates a rapid decrease in density spread during the first 16 hours of melting and a slower decrease up to 64 hours. The authors suggested that the portion from the top of the melt gave greater density spread than the bottom (Figure 14). This innomogeneity was due to the volatilisation from the surface and a tendency of less dense particles to seek the surface.

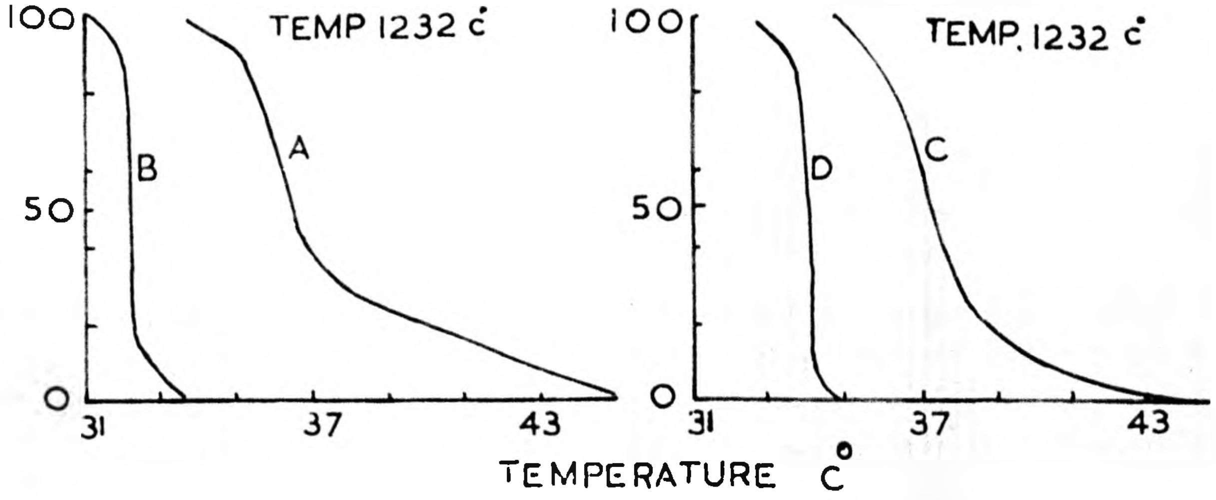
Later work showed the effect of temperature on the homogeneity rate of glass. Glasses were melted at temperatures ranging from 1232°C to 1454°C for four hours under minimum conditions of convective mixing. The results showed a sharp drop in density in the range 1232°C to 1288°C and a minimum at about 1325°C. Above this temperature a slowly increasing density spread was observed (Figure 15). Again the greater density spread was observed from the glass concentrated in the top half of the melt. Also the homogeneity was improved in the bottom layer as the temperature was increased. A possible explanation for the increase density spread at higher temperature is that initial segregation at high temperature is more intense due to the increased fluidity of the melt. It was observed that by repeating cracking and remelting

FIG. 13



(AFTER TOOLEY & TIEDE)

FIG. 14

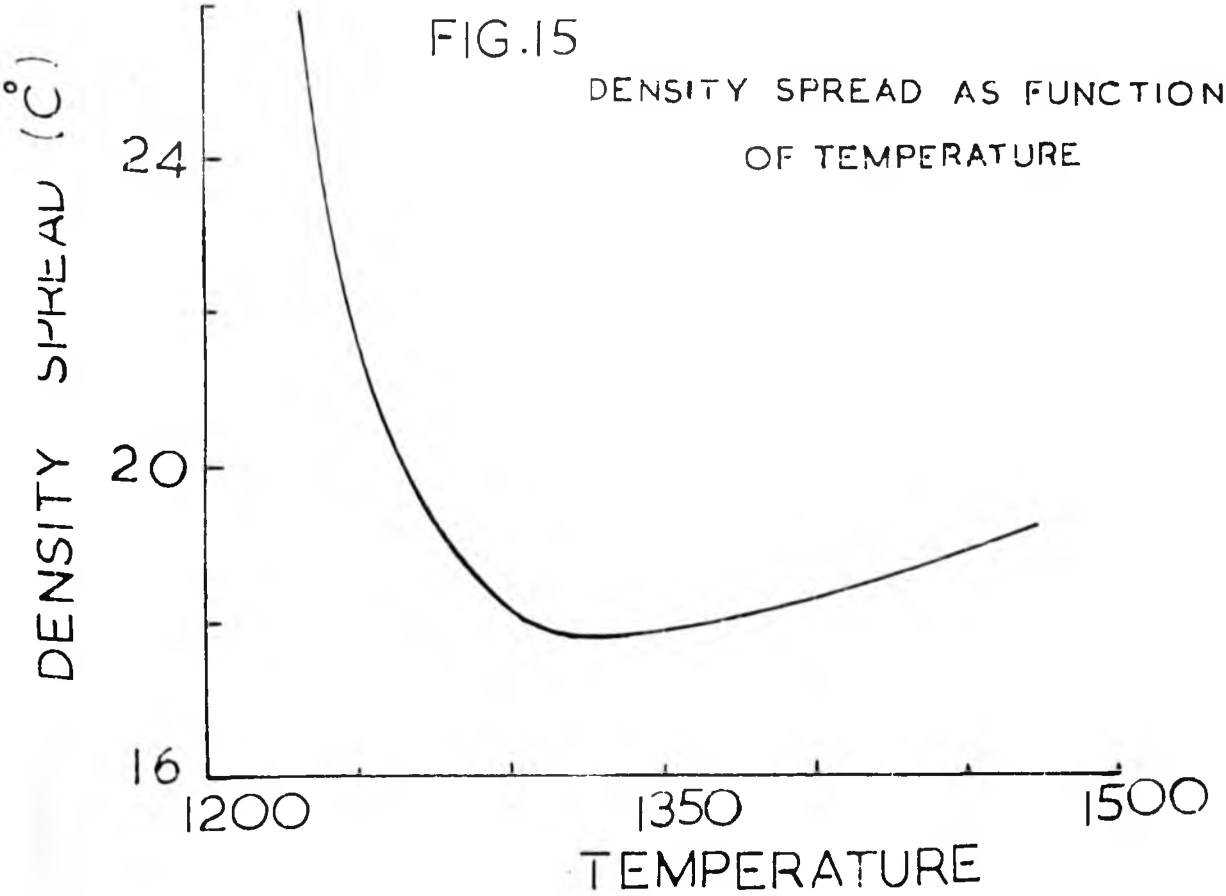


DENSITY DISTRIBUTION OF BOTTOM & TOP GLASS FROM SAME CRUCIBLE

A:- TOP, DENSITY SPREAD 12.3 C°] MELTING TIME $4\frac{1}{2}$ HRS.
B:- BOTTOM, DENSITY SPREAD 2.3 C°

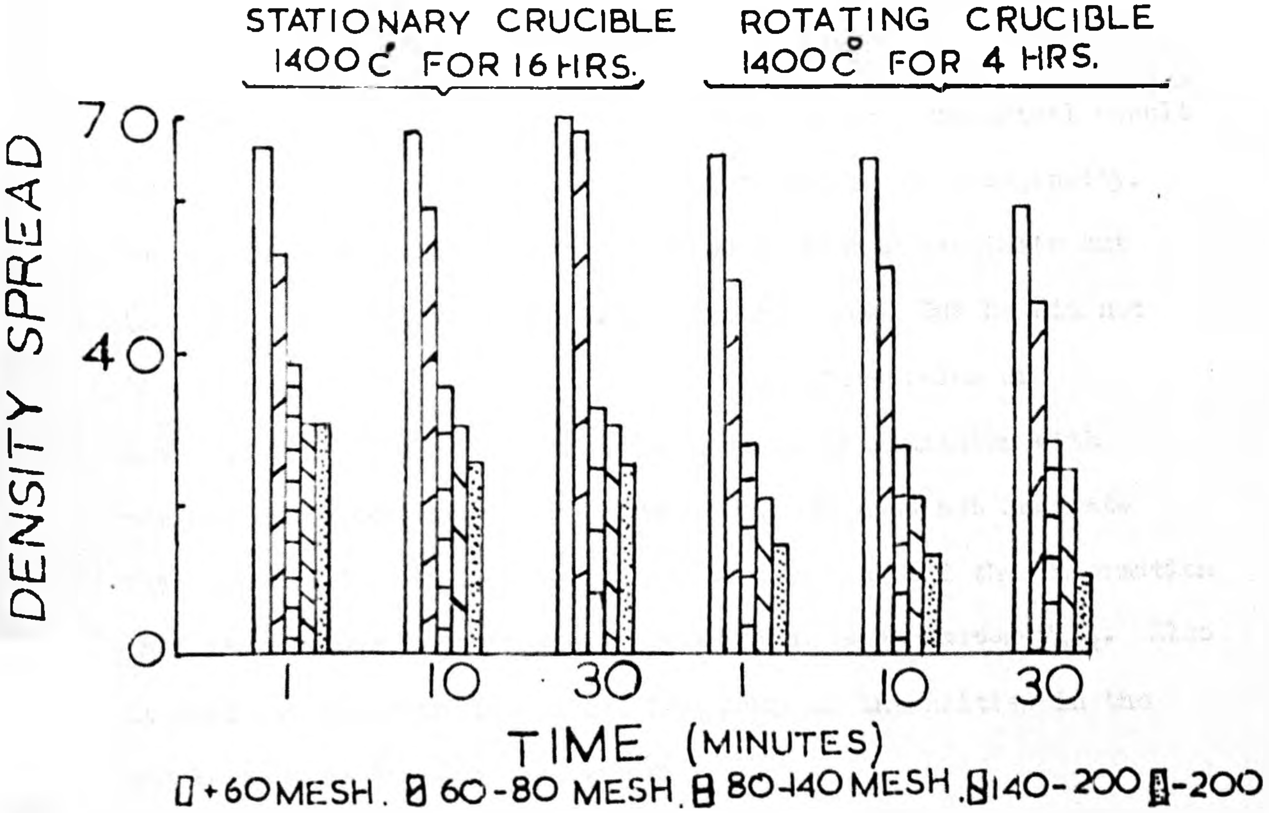
C:- TOP, DENSITY SPREAD 9.6 C°] M. TIME $7\frac{1}{2}$ HRS.
D:- BOTTOM, DENSITY SPREAD 2.0 C°

FIG.15



DENSITY SPREAD AS FUNCTION OF TEMPERATURE

FIG.16

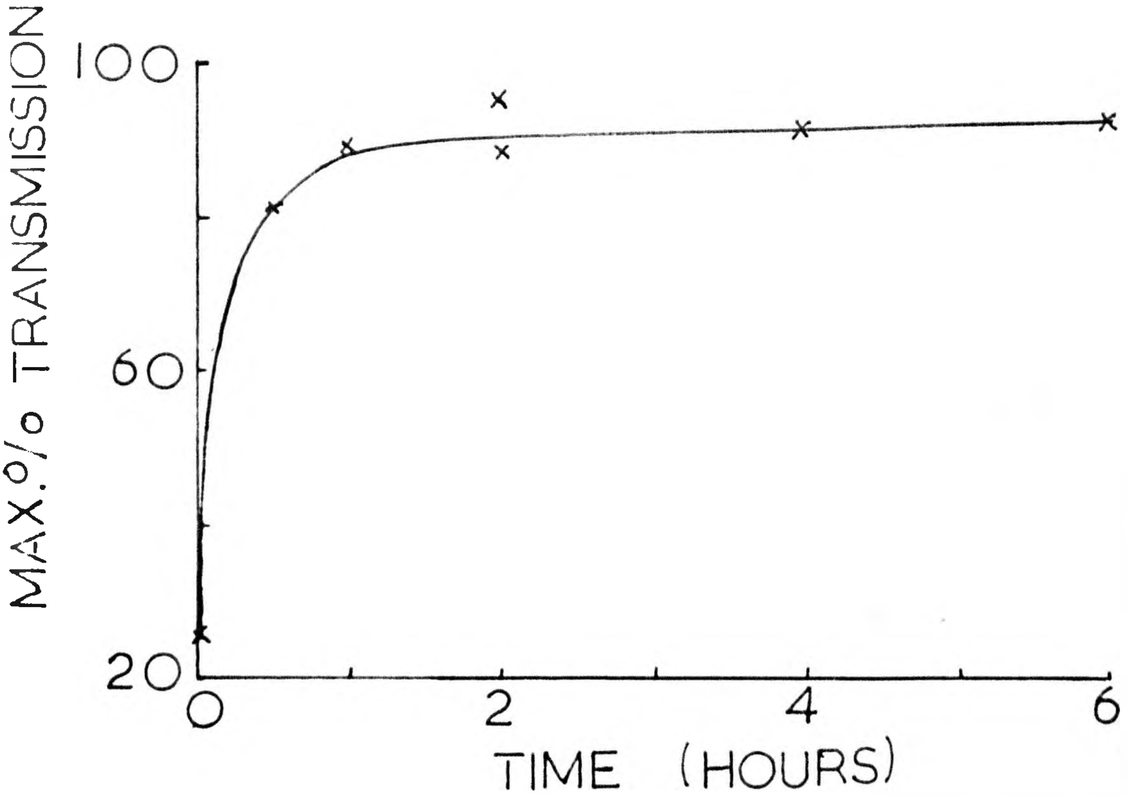


EFFECT OF BATCH MIXING TIME & GRAIN SIZE ON DEGREE OF HOMOGENISATION these glasses or by melting in a rotating tilted crucible, a marked effect in lowering the density spread can be obtained. The homogeneity was found to increase with decrease in batch grain size, more so in the rotating crucible than in the stationary one and batch mixing time had relatively little influence as indicated in Figure 16.

Bower[30] used two different methods to measure the homogeneity of glass melts; Shelyubskii's[21] light scattering method and Loffler's[26] etching and interferometery technique. He melted 50 gms of glass in a platinum - 40% Rh crucible. The stirrer used was a platinum thimble on the end of a refractory tube. Two series of melts were made both of the same composition and melted at 1400°C. One set was melted for two hours with a variable speed and the other stirred at a constant speed for different times. The transmission results are shown in the Figure 17. Bower[30] reports that no doubt the light scattering method gives a nmmerical result but it does not give a quantitative measurement of homogeneity. The etching and interferometery method is rather lengthier but is capable of giving all necessary information. But he did not develop this method fully to get a quantitative value of homogeneity. He also compared the maximum transmission with maximum scale and intensity (Figure 18). It does not indicate that the shape of transmission peak varies, and all the information that it provides is represented by the single parameter T_{max}. Also it does not indicate the actual frequency of intensities in the sample as does the density spread.

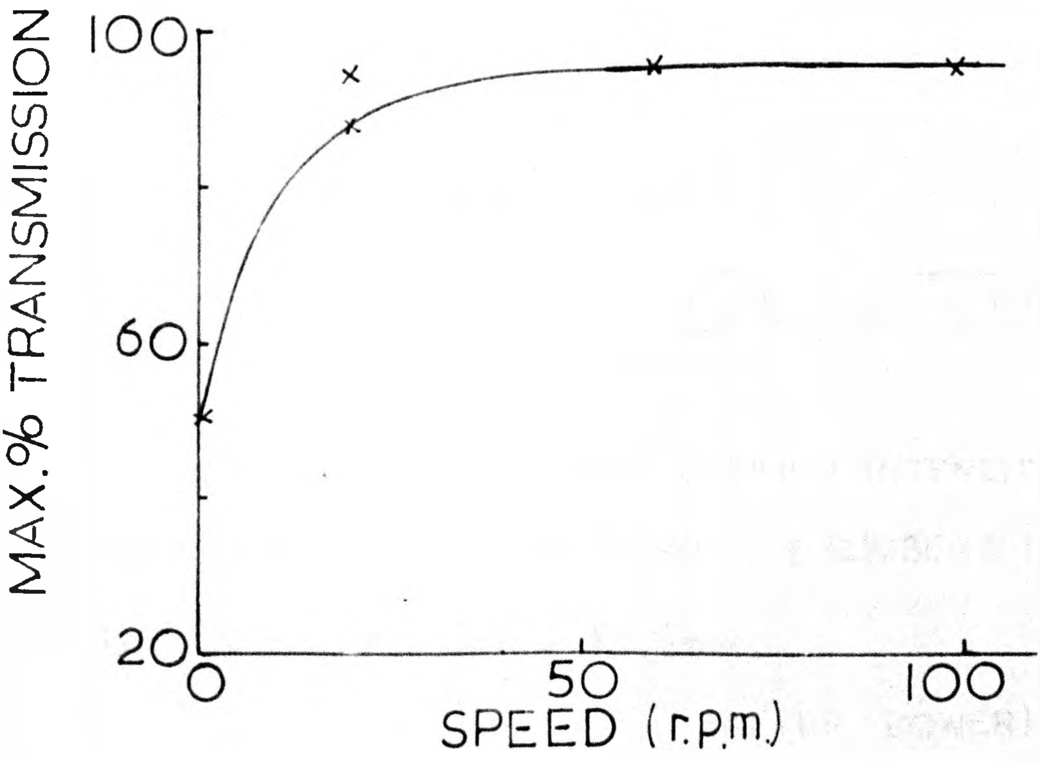
Plumat et al[31] have studied the degree of homogeneity of molten glass by using a strioscopic apparatus. The apparatus

FIG.17



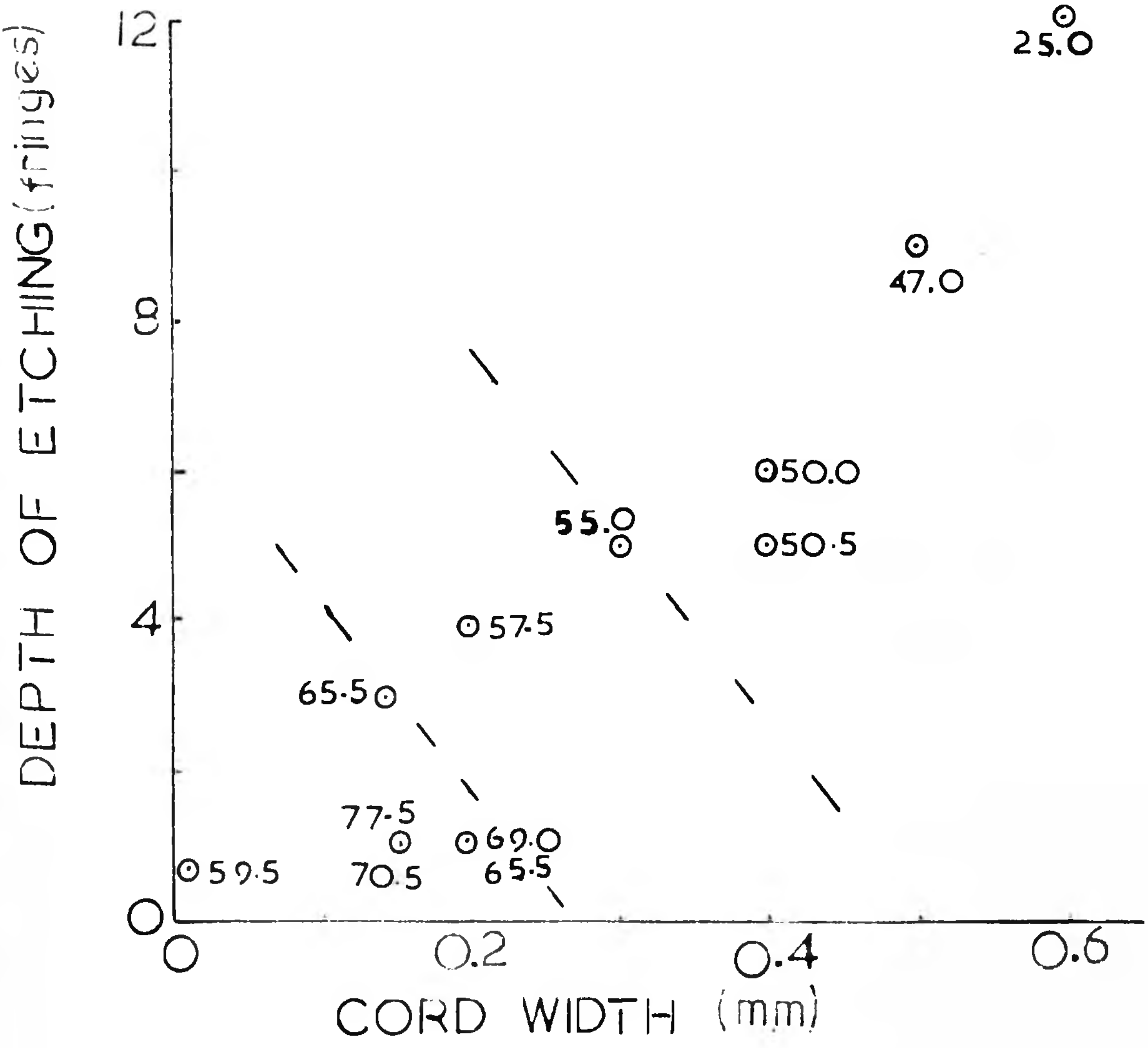
EFFECT OF STIRRING TIME (20 r.p.m)

(AFTER BOWER)



EFFECT OF SPEED (CONSTANT TIME)

FIG.18



CORRELATION OF T_{max} WITH MAXIMUM INTENSITY AND MAXIMUM SCALE OF CORD. THE NUMBERS IN THE FIGURE ARE VALUES OF T_{max}.

(AFTER BOWER)

consists of an optical system mounted above the melting furnace with arrangements to illuminate and photograph the melt from above. The glass is melted in an electrically fused alumina crucible. The bottom of the crucible is covered with molten lead to produce a clean, bright mirror-like surface. The path of any light reflected from this surface depends upon the refractive index of the glass above it. If the glass is inhomogeneous, light and dark patches are seen where cords alter the refractive index in the light path. Thus the progress of homogenisation can be followed by studying size, shape and distribution of these patches indicating inhomogeneity. The method has the advantage that the observations are taken at the melting temperatures. The disadvantages are that the patches may be due to the cord or temperature difference and it is difficult to differentiate between them. Also the method gives the average over the whole depth of melt.

CHAPTER III

ROOM TEMPERATURE MODEL EXPERIMENTS

Bradford[32], Howse[33], and Tunaley[34] studied mixing of glycerine in a room temperature model of a crucible. The present work was designed to see if their results had any relation to the behaviour of glasses.

Complete modelling of mixing requires that both the diffusion and flow processes be matched. The impeller power should be a function of the geometery of the impeller and tank, the properties of the fluid, and the rotational force of the impeller. The most important similarities are geometric, kinematic and dynamic.

Geometric similarity requires that all corresponding dimensions in systems of different size bear the same ratio. If inertial and viscous forces alone are important then the ratio of inertial to viscous force should be matched.

$$\frac{\text{Inertial}}{\text{viscous}} = \frac{VL\rho}{\eta}$$

which is called the Reynolds number (Re). Since this ratio determines whether the flow is laminar or turbulent it is a critical group in correlation of power requirement. If surface waves are important, then the ratio of inertial to gravitational force should be the same in both systems, which is the Froude number.

$$Fr = \frac{\text{Inertial force}}{\text{Gravitational force}} = \frac{\rho V^2/L}{\rho g} = \frac{V^2}{gL}$$

The shape of the surface and flow pattern in the vessel may be sufficiently affected by the gravitational field if the surface is appreciably deformed from the horizontal. When the temperature differences bring about differences in density, it is necessary to include buoyancy force. Thus we should match the Grashof number

(Gr) as well as the Re number.

$$\frac{\text{Buoyancy force}}{\text{Inertial force}} = \frac{\rho g\beta\Delta T}{\rho V^2/L} = \frac{g\beta\Delta TL}{V^2} = \frac{\rho^2 g\beta\Delta TL^3}{\eta^2} \cdot \frac{1}{Re^2} = Gr \cdot \frac{1}{Re^2}$$

so $$Gr = \frac{\rho^2 g\beta\Delta TL^3}{\eta^2}$$

where ρ is the density, g is acceleration due to gravity, β the coefficient of thermal expansion, ΔT the temperature difference, L the diameter of the stirrer, and V is the speed of stirrer.

A model meets similarity criteria for flow patterns when Re, Fr, Gr, have the same numerical values in both systems. If it is desired to match diffusion as well as flow it is necessary to match Schmidt number (Sc).

$$Sc = \frac{\text{diffusivity of momentum}}{\text{diffusivity of mass}} = \frac{\nu}{D} = \frac{\eta}{\rho D}$$

The general relationship for similarity may be written as

$$(Re, Fr, Gr, Sc...) = 0$$

In practice one has to examine the process to try to determine what forces control the behaviour and hence what dimensionless numbers it is most important to match.

In a complex system it may not be possible to match all the parameters that might be important. In such cases one has to match as well as possible those thought most important. Only experiments in both systems can confirm whether matching was good enough to use the model to predict behaviour of the real system.

A great deal of experimental work, on mixing of viscous liquids, has been done. Spencer and Wiley[11] reported that as the turbulance can not play a part in mixing of viscous liquids, the mixer must continuously move the liquid in a complex fashion to disperse the components to the greatest degree possible. The mixing is most efficient when the stirrer induces flow in the liquid in direction at right angles to the striation containing the inhomogeneity. If rapid mixing of viscous liquids is required, the method of deforming the material becomes important. A flow pattern is desirable that moves fluid readily into all parts of the vessel. If there is fluid in any part of the vessel which is not easily moved to the other parts of the vessel, then the fluid in that is not easily deformed and mixed with the rest of the solution. Such zones of slow movements are often found in a viscous liquid because viscous drag quickly consumes the kinetic energy of a moving viscous liquid. Among the methods used at room temperature to determine the homogeneity of solutions are colour, density, electric conductivity and chemical analysis.

In their model work, Bradford[32], Howse[33] and Tunaley[34] assumed that the only parameters that it was essential to match would be Re and Sc numbers. But not knowing the diffusivity in glass, they could not match Sc number and therefore matched only Re number.

Bradford[32] started with a known distribution of glycerine solutions and mixed these with a rod or disc stirrer. The mixing was studied by measuring the electrical conductivity of the solution. He concluded that the disc stirrer was superior to the rod. This was because the disc induced much greater radial and vertical components of flow in the solution than the rod.

Howse[33] tried three different stirrers, a disc, a combination stirrer and a crank stirrer. He concluded that combination of the crank and disc stirrers proved to be a more efficient mixer than the disc as investigated by Bradford. He suggested that the ideal stirrer should induce tangential, vertical and radial shear in equal amounts into the solution. The disc stirrer certainly induces tangential and radial shear and some vertical shear. The effect of the combination stirrer is to disrupt the dead spot produced in the centre of the toroid resulting from the disc part of the stirrer but it does not increase the vertical flow in the solution. To increase the vertical flow Tunaley[34] used a helical screw stirrer. He reported that the screw satisfied the requirement of well developed vertical flow although use of a draught tube would increase this even further.

In all these experiments, done in this department the homogeneity of the solution was expressed quantitatively in terms of two parameters, I, the intensity of segregation and $\bar{\sigma}$, the mean normalised electrical conductivity for any number of revolutions of the stirring device used. The derivation of these values involved the use of a random sampling technique. The values for the intensity of segregation were shown to be a measure of heterogeneities within the main matrix, whilst values for the mean normalised conductivity gave information about the progress of diffusion in reducing the true intensities of the striations.

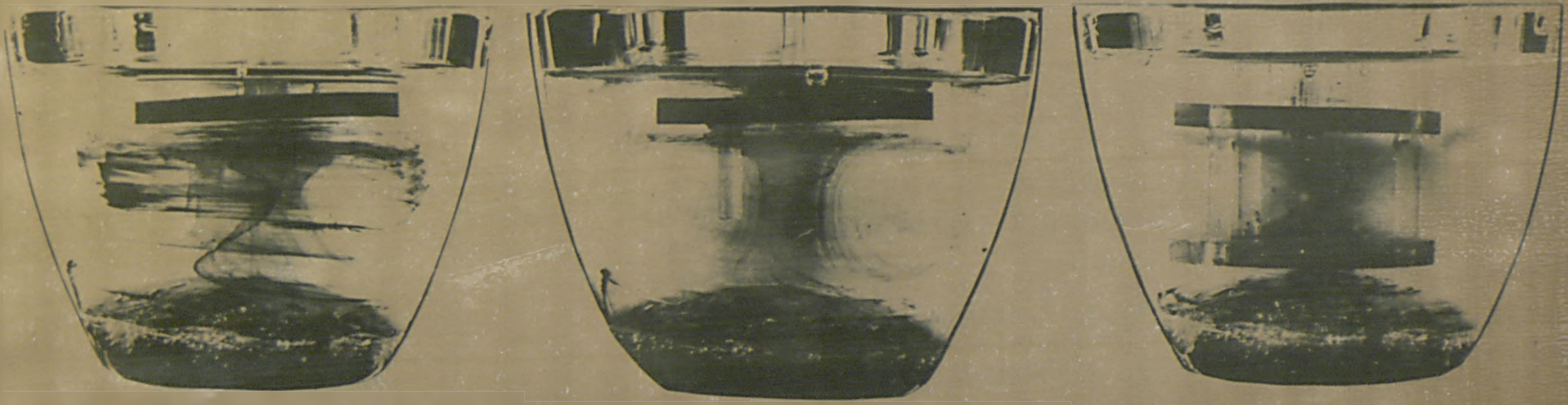
CHAPTER IV

THE PRESENT WORK

The project was designed to study the homogenisation of glasses using different types of stirrers. To compare the efficiency of different mechanical stirrers, some estimation of degree of homogeneity is necessary. A qualitative assessment can be obtained by observing the flow patterns induced by stirrers. Difference in flow patterns set up by various stirrers aid in explaining the observed differences in mixing time. In model experiments, flow patterns can be studied by taking photographs. Figure 19 shows some photographs of flow patterns induced by different stirrers in model experiments. These photographs were taken after equal number of revolutions, using two glycerine solutions of the same viscosity and density, one of which is coloured blue. Photograph No. 1 shows the simple flow patterns generated by a rotating disc in the surface of the liquid. The layer below the disc rotates as the disc transfers power to it by friction and is also moved away from under the disc by centrifugal force. The motion is compensated by liquid moving up under the central part of the disc and taking the place of the liquid thrown out to the side. This means that there exist three velocity components, in the radial direction, r, the circumferential direction, ϕ, and the axial direction, Z, which can be denoted respectively by u, v, w. An axonometric representation of this flow is shown in the Figure 20. However, it should be mentioned that the flow pattern shown here is for a disc rotating in an infinite body of liquid. When stirring

FIG.19

FLOW PATTERNS IN ROOM TEMPERATURE MODEL



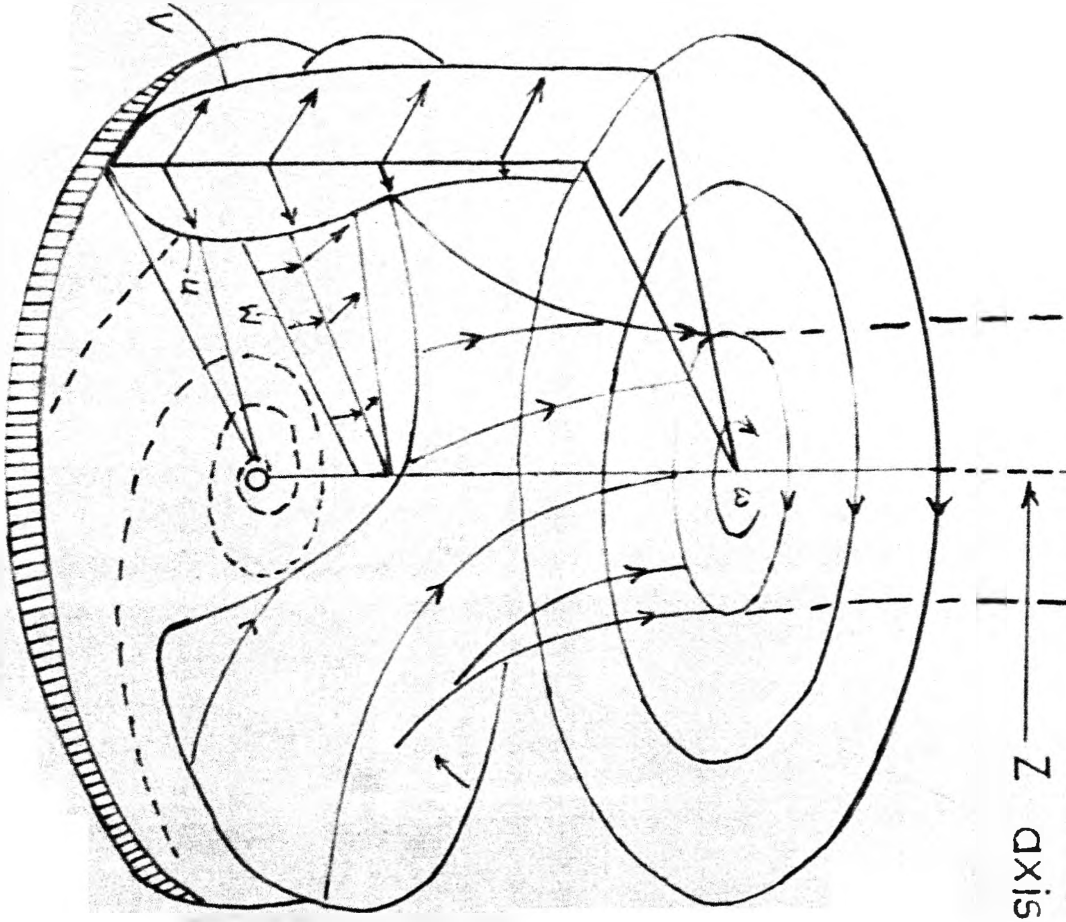
PLAIN DISC DISC WITH BLADE COMPLEX DISC

VISCOSITY OF MODEL 7·9 Poise

REVOLUTIONS 200

FLOW DUE TO ROTATING LIQUID OVER STATIONARY WALL

FIG.21



FLOW DUE TO ROTATING DISC IN STATIONARY LIQUID

FIG.20

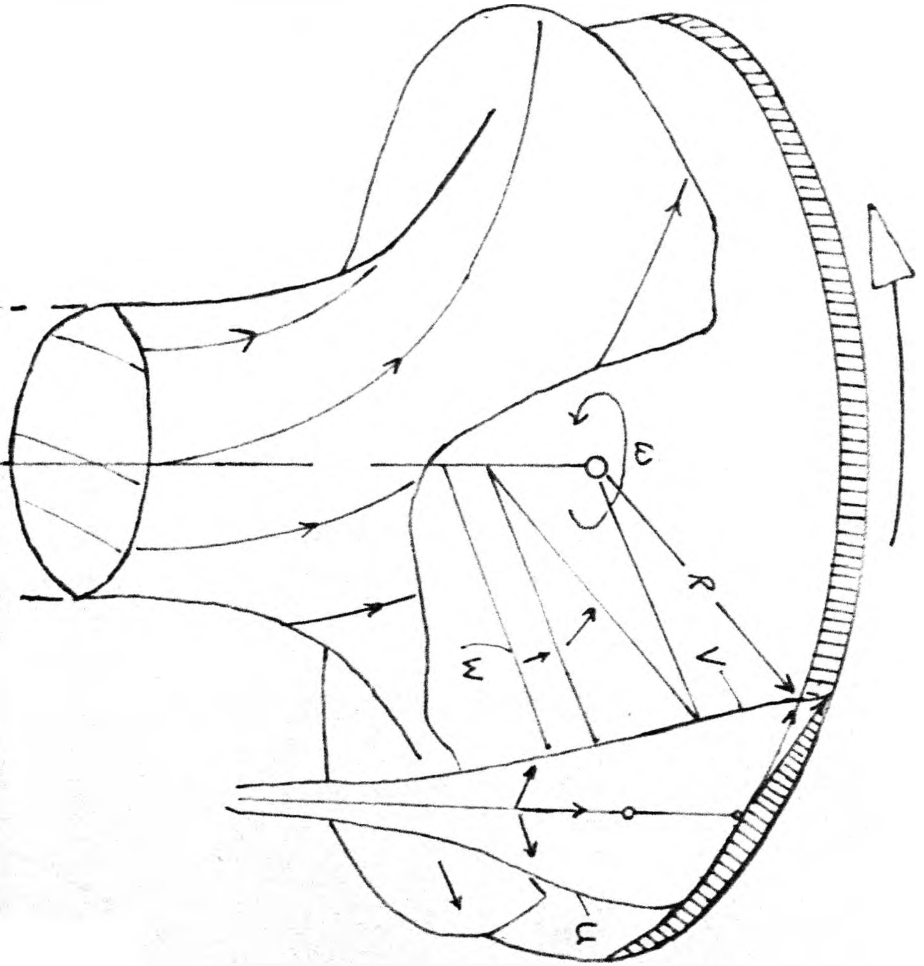
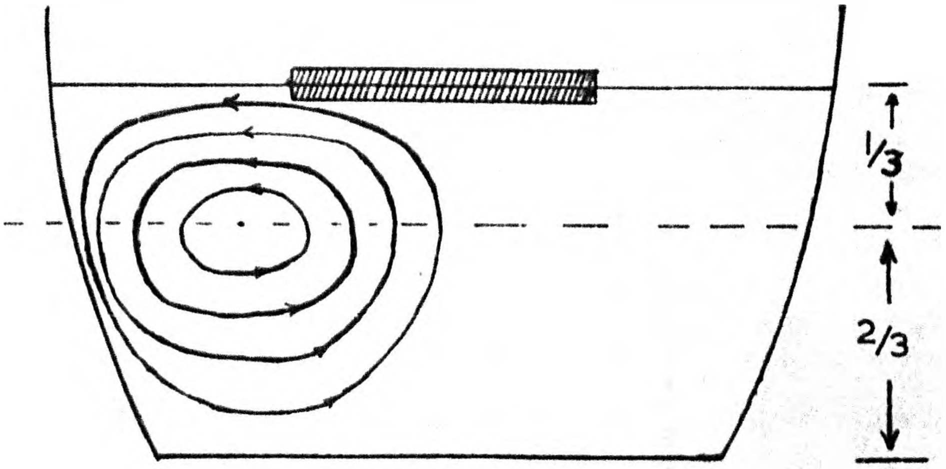
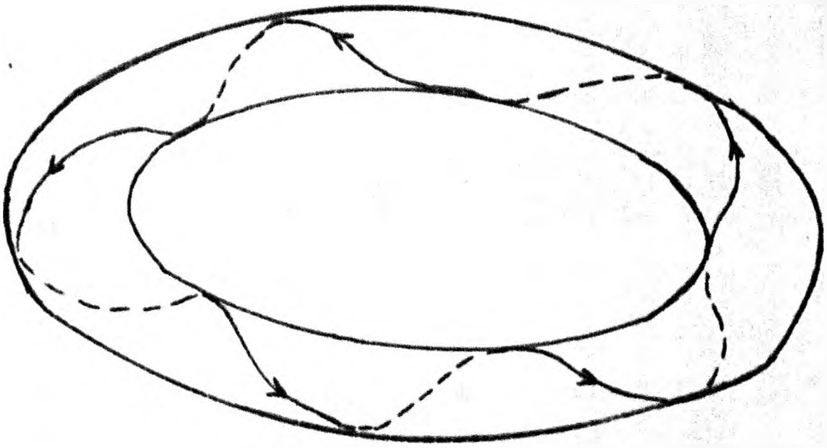


FIG. 22

FLOW GENERATED BY PLAIN DISC



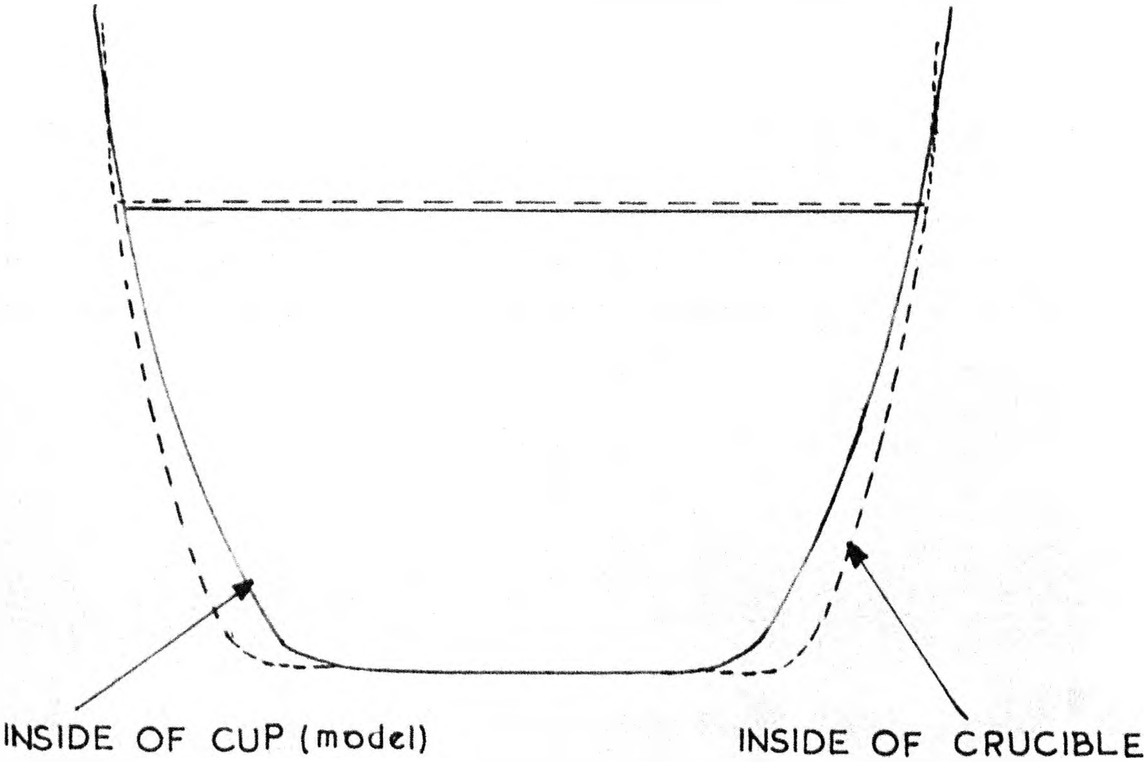
STREAMLINES



PATH OF INDIVIDUAL PARTICLE

FIG. 23

GEOMETRIC SIMILARITY



SCALED UP X 1·31

liquid in a vessel where the diameter and depth of the body of fluid are not very large compared with the diameter of the disc, the flow near the disc will differ from that shown here. When a body of fluid rotates over a flat plane a rather similar kind of flow pattern develops (see Figure 21). By considering these two flows, the condition of continuity and the boundary conditions one can build up a qualitatively accurate picture of the flow to be observed in a finite vessel stirred with a rotating disc immersed in the top surface of the liquid. (see Figure 22).

To study the mixing process in glass, two different composition glasses, coloured and colourless were mixed in a Rh/Pt crucible. The size and shape of the crucible and of the model are given diagramatically in Figure 23.

(i) Matching of Reynolds number

If the glasses have the same viscosity and density, Re can be matched as follows.

$$Re = \frac{D^2 N \rho}{\eta}$$

where D is the diameter of stirrer, N the speed, ρ the density of the liquid and η the viscosity.

For glass, $Re_1 = \frac{(2\cdot6)^2 \times N_1 \times 2\cdot3}{100} = 0\cdot155\ N_1$

For the model using glycerine at room temperature,

$$Re_2 = \frac{4^2 \times N_2 \times 1\cdot25}{15} = 1\cdot33\ N_2$$

If $Re_1 = Re_2$ one must have

$$N_1/N_2 = \frac{1\cdot33}{0\cdot155} = 8\cdot56$$

In this case, if the speed is 20 r.p.m. in the glass the speed of stirrer in the model should be 2·35 r.p.m.

If the two glasses have viscosities η_1 and η_2 and densities ρ_1 and ρ_2, the position is more complicated. For ρ, we can probably assume a linear relation between ρ and composition and therefore simply use the average density. It is rather unlikely that the relation between η and composition is linear and in this case simply using the average value may not be satisfactory.

Sc number could not be matched, because the diffusivity in glass was not known.

(ii) Choice of experimental conditions

The initial orientation was selected to be horizontal as in the room temperature model, because usually the inhomogeneities lie in parallel horizontal layers in a crucible of glass unstirred by convection or mechanical stirrer. One layer of glass was put on the top of the other, so as to start with the worst possible distribution of the two phases. If batch is melted, the distribution of the inhomogeneities cannot be reproduced accurately from one experiment to another and it is very difficult to define the situation for which I = 1; for this reason a known distribution of previously melted glasses was preferred because this allows I = 1 to be defined.

The flow patterns generated were studied by taking shadow photographs and ordinary photographs of the thin sections of glass. From the ordinary photographs one can assess the mixing by observing the colour distribution. The shadow patterns give details of the flow of the glass induced by the stirrers because of the tendency for inhomogeneities to become aligned parallel to the direction of flow.

(iii) Determination of intensity of segregation

To measure it quantitatively, the degree of homogeneity was defined in terms of a dimensionless parameter, I, the intensity of segregation. To assess, I, for any particular sample one needs information about any convenient property at a number of random points. So in this investigation, it was decided to use chemical corrosion as the criterion.

Following Danckwerts[15] the intensity of segregation, which varies from one in a fully segregated solution to zero in a fully mixed solution, is defined as follows.

$$I = \frac{S^2 - S^2_R}{S^2 max} = \frac{\Sigma(a - \bar{a})^2 - \Sigma(a - \bar{a})^2_R}{N\, a'(1 - a')}$$

where

a = volume fraction of A in each sample

$\bar{a}$ = mean value of A in each set

a' = fraction of A in whole system

S^2 = measured variance of a

S^2_R = variance of homogeneous solution

N = number of observations

In this investigation depth of etching, x, is measured instead of a. If we assume a linear relation between a and x, (which is permissible for these experiments)

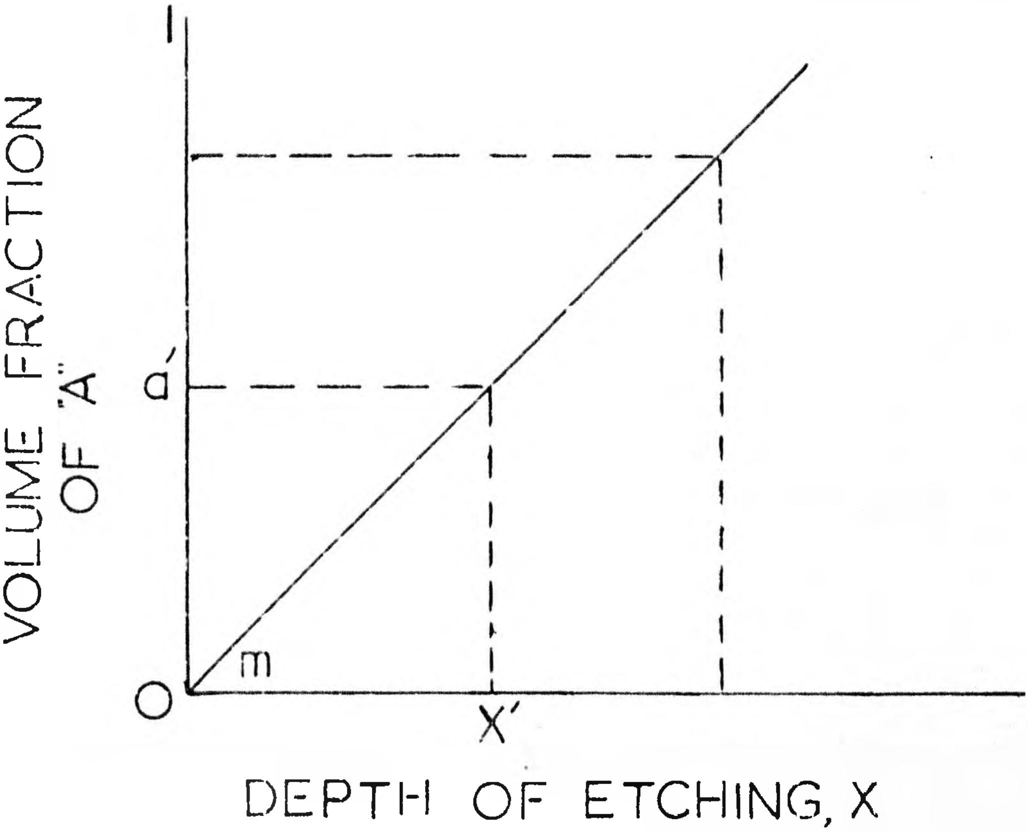
$a = a' + m(x - x')$ (see Figure 24)

$$m = \frac{da}{dx} = \frac{1}{x_A - x_B}$$

where x_A = depth of etching of glass A

FIG. 24

ASSUMED RELATION BETWEEN COMPOSITION & DEPTH OF ETCHING



x_B = depth of etching of glass B

Unless mixing is very poor, causing sampling to be unrepresentative,

$$(\bar{a} - a') \longrightarrow 0$$

so that we may write.

$$(a - \bar{a}) \overset{-}{=} (a - a') = m(x - x')$$

hence $$I = m^2 \left[\frac{\Sigma(x - x')^2 - \Sigma(x - x')^2_R}{Na'(1 - a')} \right]$$

or $$I = \frac{\Sigma(x - x')^2 - \Sigma(x - x')^2_R}{N\,(x_A - x_B)^2 \cdot a'(1 - a')} .$$

If the two glasses mixed together are equal in proportion by volume, then $a' = \frac{1}{2}$

$$\therefore I = \frac{S^2 - S^2_R}{\frac{1}{4}(x_A - x_B)}$$

(iv) Size of sample (scale of examination)

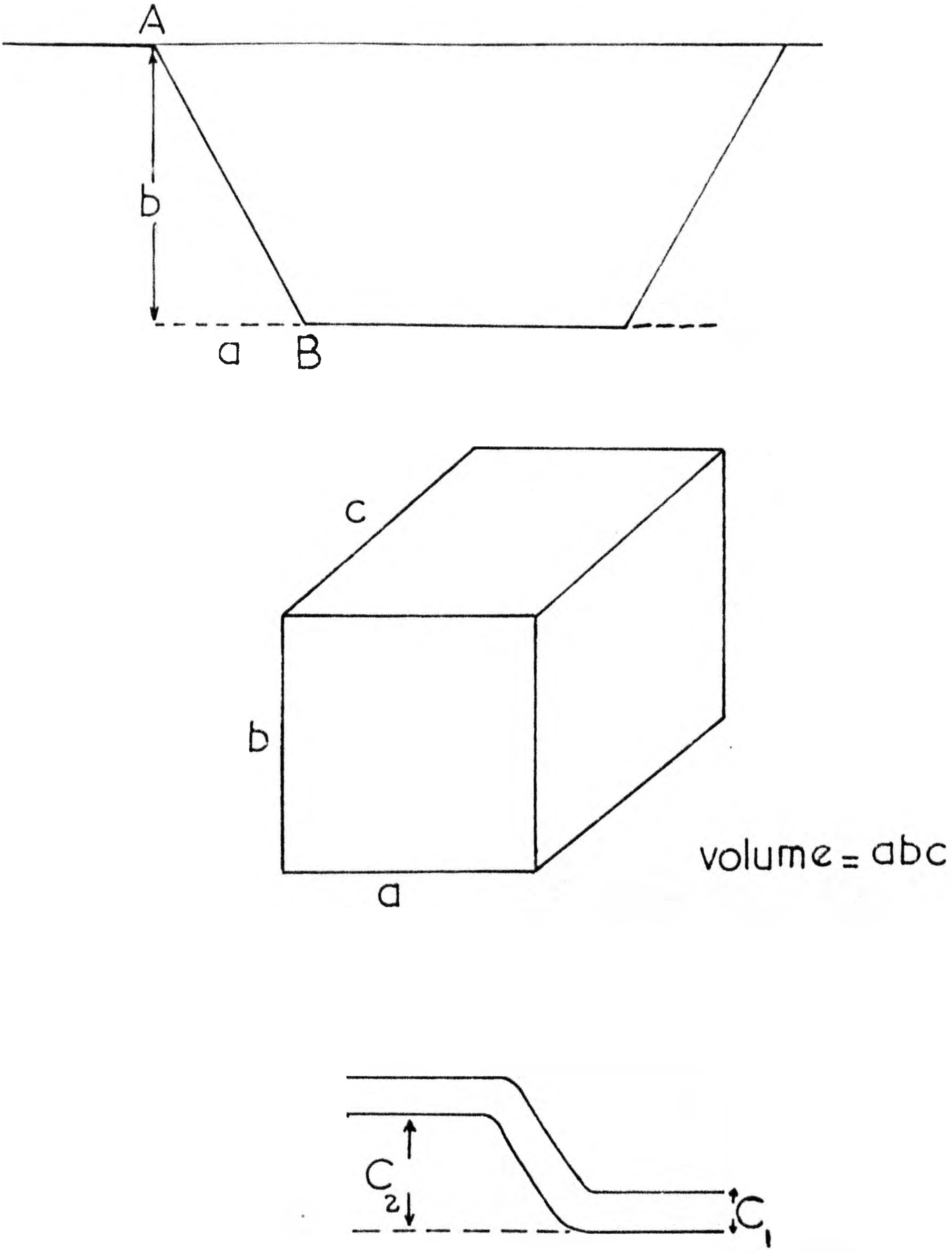
In the previous chapter it has been already mentioned that the best size of sample to take depends upon the sizes of the inhomogeneities present. It should not be much larger or much samaller than the inhomogeneities. For the present investigation the sample size may be estimated as follows.

The depth, b, of the etch pit is measured in terms of the wavelength of sodium light by counting the number of fringes between A (at the top edge) and B (at the bottom) of the etch pit. (see Figure 25). This distance, b, obviously represents the vertical dimension of the sample size and is obtained by measurement between two points a horizontal distance a apart which represents another dimension.

Since intensity is defined in terms of volume fractions the sample size should also be defined as a volume and this

FIG. 25

SCALE OF EXAMINATION



requires definition of another distance $\underline{c}$. Since the minimum distance apart at which it would generally be useful to make two different measurements would be one fringe, this gives a minimum sample size, c_1. (see Figure 25). In fact, with a good interferometer measurements to about 1/10 fringe can be made, so this represents a quite realistic sample size. It would be possible to measure depth of etching by tracing the deviation of one particular fringe as it passes across the edge of the etch pit and in this case $c = c_2 = n \times c_1$, where n is the number of fringes. This gives a much larger sample size but this is not relavent here because this method of measuring depth of etching was not used.

For a typical case

$a = 130$ microns

$b = 16$ wavelengths $= n\lambda = 9{\cdot}4\ \mu$

$c_1 =$ Fringe separation $= 190\ \mu$

$c_2 =$ Total horizontal deviation of 1 fringe $= 3040\ \mu$

Thus the minimum sample size is $abc_1 = 130 \times 9{\cdot}4 \times 190 = 230000\ \mu^3$ and the larger sample size is $abc_2 = 130 \times 9{\cdot}4 \times 3040 = 3714880\ \mu^3$ We propose to assume that sample size is about 200,000 μ^3, which is the volume of a cube of side about 60 μ.

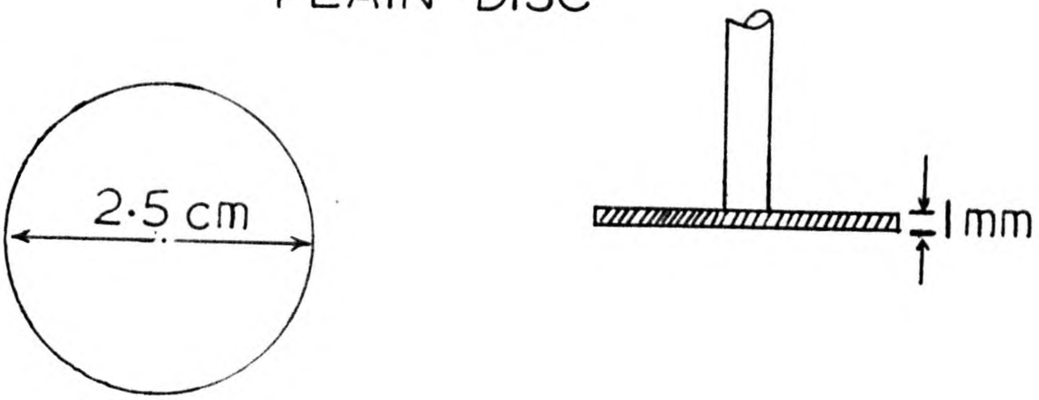
(v) Choice of stirrers

The disc (Figure 26 a) was chosen as the basic stirrer since the flow patterns generated by it in a liquid are simple and symmetrical and the flow can easily be interpreted, at least qualitatively, from data already available. In addition, by covering a large fraction of the surface of the melt, it can be

FIG.26

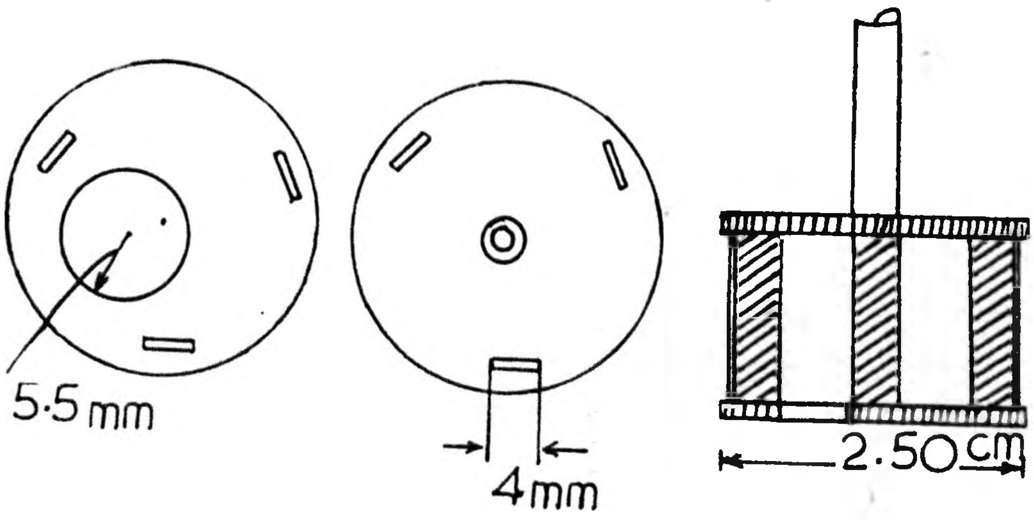
STIRRERS

(a) PLAIN DISC



(b) DISC WITH BLADE

(c) COMPLEX DISC



expected to decrease volatilisation from the melt. Thus, all other stirrers were compared with the disc and in this work they were all based on the disc. The two chosen, after studying the results obtained by Howse[33] and Tunaley[34], were disc with blade and complex disc.

The disc with blade (Figure 26, b) would appear to be useful in a stratified system such as the horizontal distribution studied. This stirrer was originally designed to disturb the relatively stagnant ring existing in the flow developed by the simple disc. Also, if the end of the blade is below the liquid-liquid interface, it would be expected that mixing would be faster than for the disc because of the disturbance of the interface by the blade.

The complex disc (Figure 26. c) would only be suitable if the lower disc lies above the liquid-liquid interface. If the two discs are in two different liquids much of the mixing will be due to the disturbance of the liquid-liquid interface by the supports. Because both discs are fixed relative to each other the liquid between them will not be subject to the steep velocity gradients necessary to attenuate the cords very much. In general, the complex disc may only be suitable for mixing a thin layer of one liquid into the bulk of another.

The stirrers were made of pt-Rh alloy and were drivem by a small motor fixed above the furnace.

CHAPTER V

THE MAIN EXPERIMENTAL WORK

1 APPARATUS AND METHOD

(i) Design of the furnace

The furnace used was of the silit rod type normally used in the department and shown diagramatically in the Figure 27. The inner tube was fitted with a refractory stopper, with a large hole in it, so that stirrer shaft could pass through it. The stirrers were driven by an electric motor fitted on an adjustable platform, to change the depth of stirrer in the glass melt.

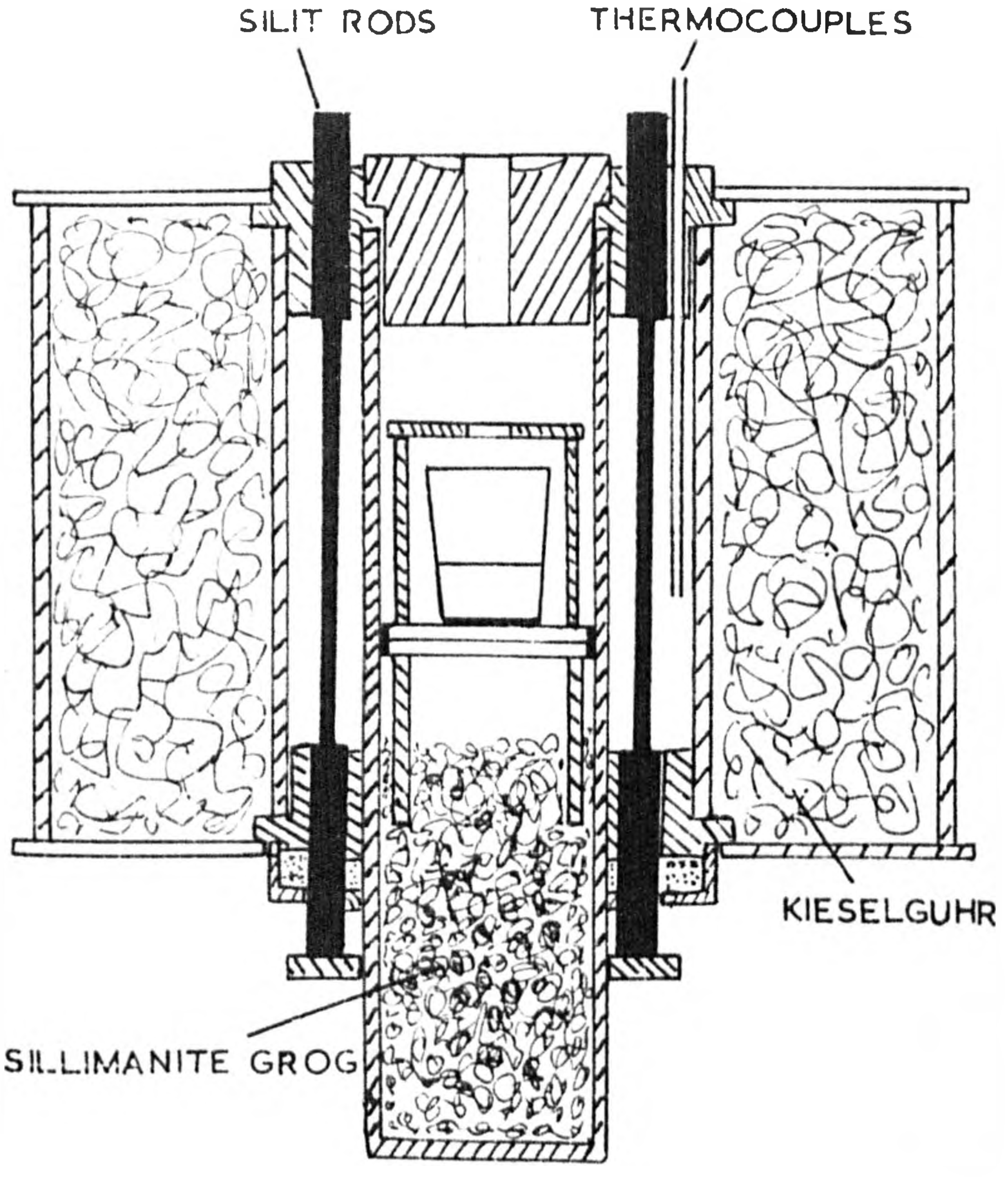
The whole apparatus is shown in the photograph (Figure 27a) The platinum rhodium crucible was enclosed in a refractory shield fitted with a refractory lid with a large hole for the stirrers.

(ii) Temperature measurement and control

The furnace temperature was recorded by one Pt/Pt-Rh thermocouple and controlled by another, both were projected through the refractory ring so as to reach near the level of the refractory shield. In the beginning the temperature was controlled by a cambridge regulator, cutting resistance in and out of the circuit after a fixed voltage had been tapped from a transformer, but later on this was replaced by an Ether temperature controlling unit (Type 1292, Ether Thyristor Unit Type 2620/50/250). The furnace temperature was set up by inserting a standard thermocouple through the stopper and lid into the centre of the refractory shield. The e.m.f. of this thermocouple was measured by a potentiometer and the controller setting adjusted until the standard thermocouple indicated the required temperature (usually 1400°C).

FIG. 27

CROSS SECTION OF FURNACE



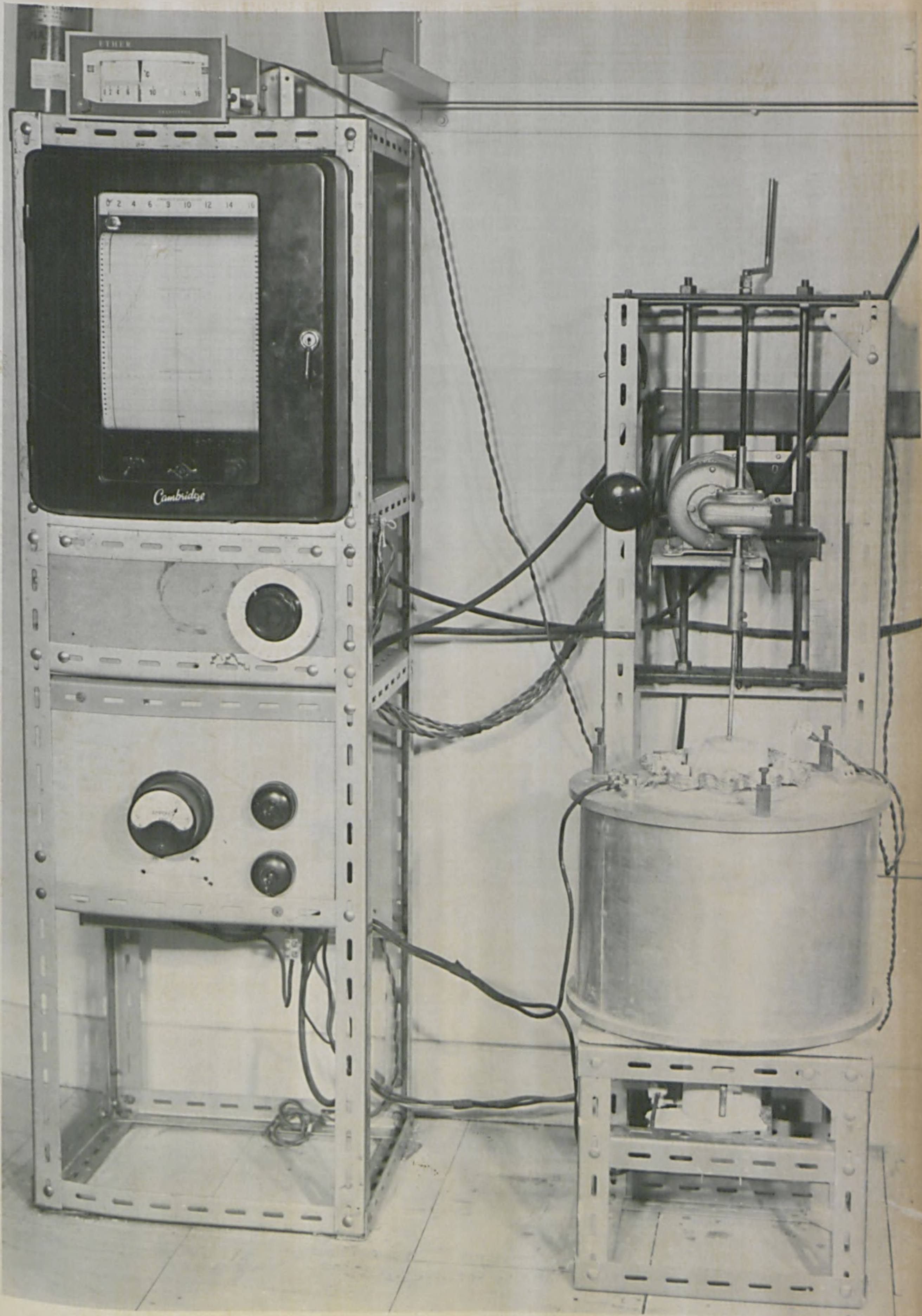


FIG. 27a

Temperature distribution vertically down the furnace is shown in the Figure 28. A slight variation of 2°C in temperature was found over the depth of the crucible.

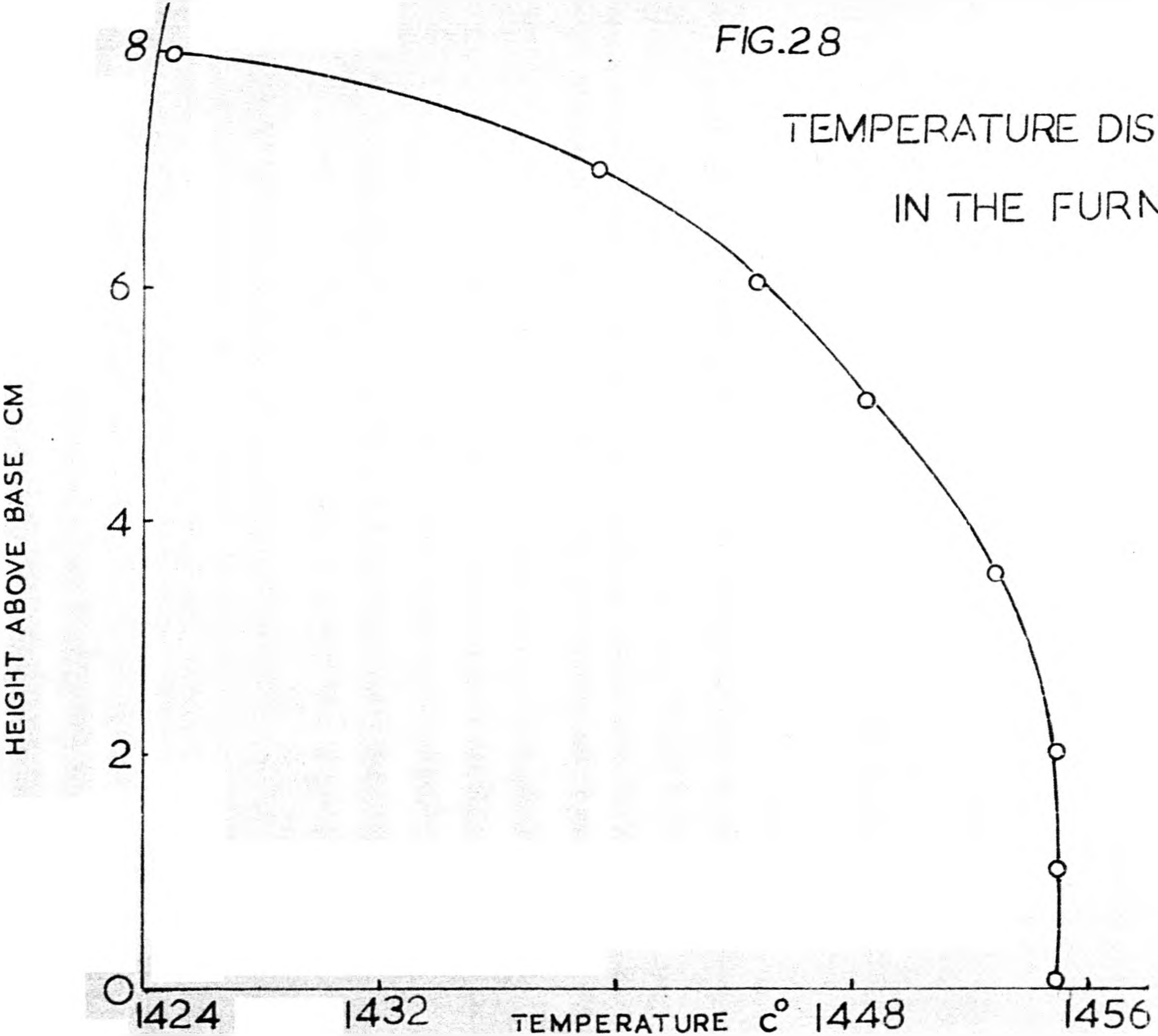
(iii) Glass composition

Since the determination of homogeneity by etching with HF depends on the composition of the glass, two glasses were selected which gave a difference in the depth of etching of about 16 fringes. The relation between composition and the depth of etching according to Bower is shown in the Figure 29. These glasses also had different densities and viscosities. In one of the glasses, Cobalt oxide was also added to identify it and also to observe the flow patterns generated by the stirrers. During the early stages, it was thought that difference in densities of these glasses had a very important effect, so from the data alreddy available two other glasses expected to have the same densities were also tried. But later experiments showed that the densities were not equal and the data in the literature are therefore not reliable. The compositions of these glasses are given in the Table II.

(iv) Batch materials

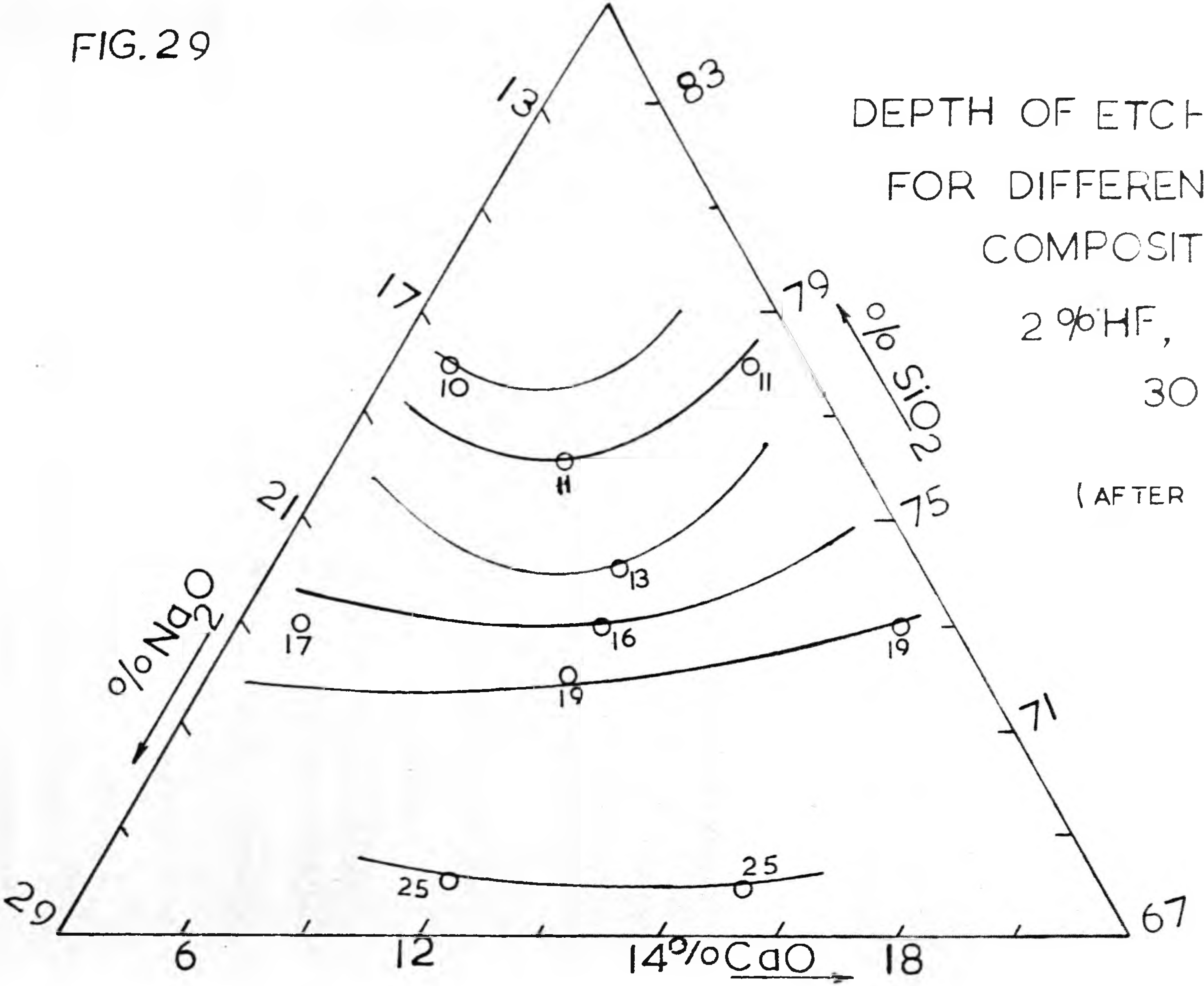
The main batch materials used were sodium carbonate, calcium carbonate and sand. All the sand used was taken from a single batch and was ball milled, sieved, washed in acid and water, dried at 110°C and stored in screw capped bottles. Two kilogram portions of sand were milled for about two hours and sieved through a set of cylindrical rotary sieves. The sieves available

FIG.28



TEMPERATURE DISTRIBUTION IN THE FURNACE

FIG. 29



DEPTH OF ETCHING
FOR DIFFERENT
COMPOSITIONS
2 % HF, 20 C°
30 MINS.

(AFTER BOWER)

and the sizes of sand grains that was possible to obtain are given in the Table III. The sand grain size of 0·15 mm was used in these investigations.

The other materials, Na_2Co_3 and $CaCo_3$ were analytical reagents and were dried at 110°C before use. As they were considerably finer than the sand used, they were not sieved before use.

(v) Melting procedure

Each batch, to make 90 gms. of glass, was weighed out separately. The batch was mixed thoroughly with a spatula. All the batch was not put into the crucible at the same time but two fillings had to be used because of the risk of the melts boiling over. The batches were melted at 1450°C for four hours. One hour after putting the batch in the furnace, the melts were stirred for ten minutes at 100 r.p.m. and then the stirrers were stopped. After another one hour again the melts were stirred but only for five minutes at the same speed. After four hours melting, the crucible was withdrawn and the glass was taken out after cooling the crucible to room temperature, it was then annealed in a muffle furnace.

2 MIXING OF TWO GLASSES

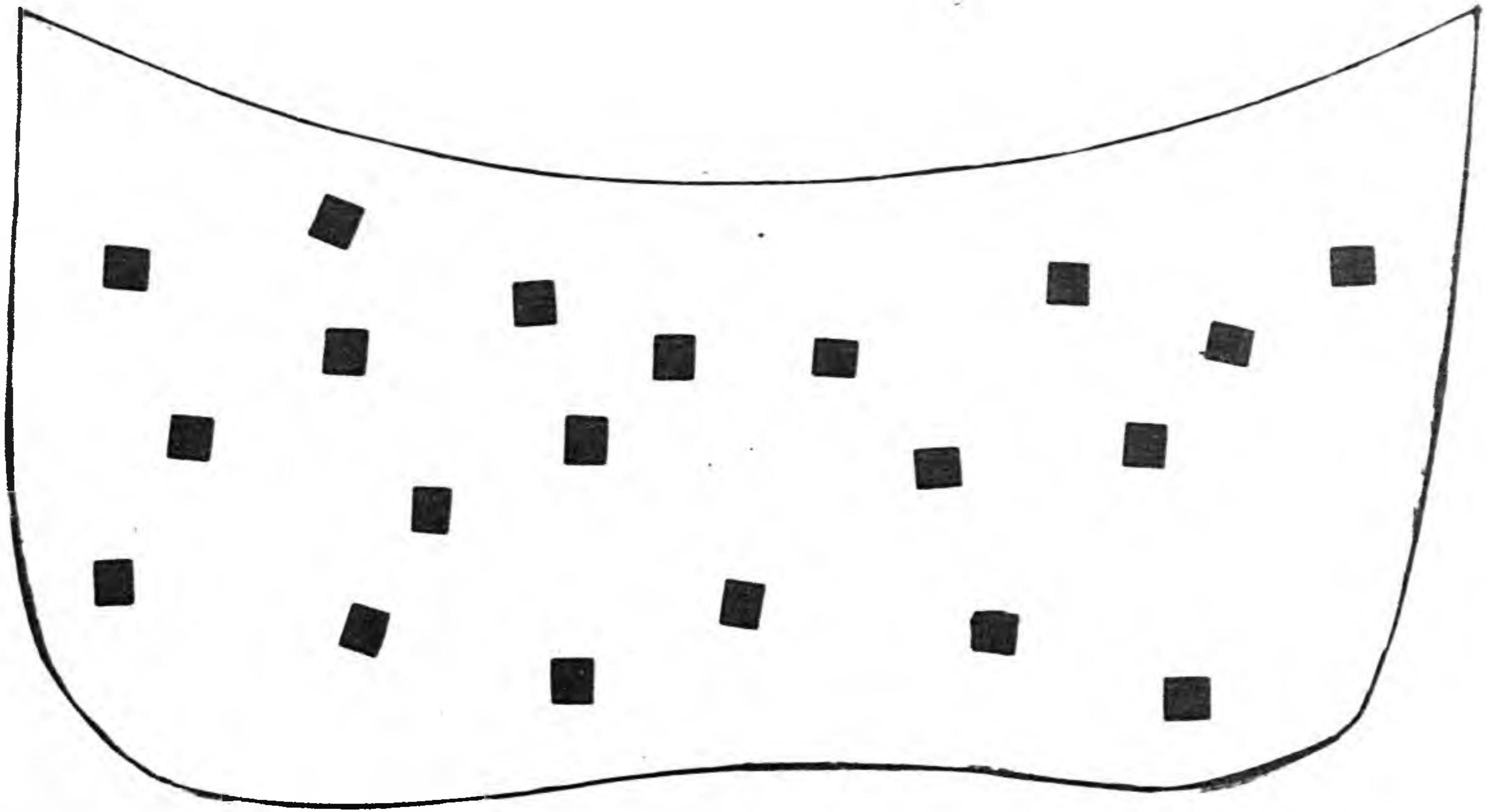
After annealing, the glasses were cut horizontally into two equal portions. Then the two equal halves of the glasses A and B were put into the crucible. The initial orientation of the interface was horizontal in all experiments but in some sets the coloured glass was on the top and in others it was at the bottom. The crucible was then put in a pot furnace at about 650°C and the temperature was raised up to 1000°C. The viscosity of the glasses was so high at this temperature that very little flow could occur during preheating. The crucible was then transferred to the main furnace and the glasses were stirred for the required time and speed. After stirring the crucible was withdrawn as soon as possible (after about two minutes) and after cooling to room temperature, the glass was taken out in one piece without disturbing the flow patterns and annealed.

3 PREPARATION OF SAMPLE

After annealing the glass was cut vertically to obtain a thin section (2-3 mm thick) across one diameter. The faces were then ground flat on a grinding wheel, using coarse carborundum powder, followed by finer grades. The surfaces were finely ground by rubbing the sample on a flat glass plate using sira as abrasive. Polishing was done on a polishing wheel using jewellers rouge. In this way a flat well polished surface of the sample was obtained. To etch the specimen at twenty randomly distributed points, a mask was prepared, as shown in the Figure 30, using Kodak mechanical orthofilm. A Kodak photosensitive resist, KPCR, was coated on the surface of the specimen then allowed to stand at room temperature for a few minutes to allow most of the solvent to evaporate. It was then dried in an oven for five minutes at about 60°C. The photographic negative mask, was placed in contact with the resist coated on the sample and exposed to a high pressure mercury-vapour lamp (Mazda 250 watts) for five minutes at a distance of two feet. The purpose of exposure was to

FIG.30

SAMPLING PATTERN



polymerise or harden the selected areas of the resist layer not covered by opaque parts of the mask. These areas were insoluble in the developer and therefore remained on the surface of the glass, to form the chemicallyresistant stencil. The unexposed areas of the resist were dissolved using PC developer for about two minutes at 20°C and washed in water. After development the resist image was dried in an oven at 80°C for five minutes. Now the specimen was ready for etching.

4 ETCHING AND INTERFEROMETERY

The surface was etched in a 2% HF solution at 20°C for ten minutes in a polythene tub containing HF and placed in a water bath. The temperature was adjusted automatically using a toulene thermoregulator. The HF solution was stirred by a polythene stirrer. The apparatus is shown in the figure 31. The etched surface, after washing and drying was silvered in a vapour plating appartus. The apparatus used to produce interference fringes is also shown in the Figure 32. A diagramatic description of this apparatus is given in the Figure 33. The monochromatic light source was a sodium lamp mounted on an optical bench. A glass strip one certimeter wide mounted on an adjustable stand at an angle of 45° was used to deflect light on to the microscope stage. This strip was mounted between the sample and the microscope objective, so that part of the light beam, coming from sodium lamp, was reflected on to the sample. Part of the light reflected back from the sample passed through the glass strip into the microscope objective. The glass sample was mounted on an adjustable microscope stage with etched surface facing the objective.

FIG.31

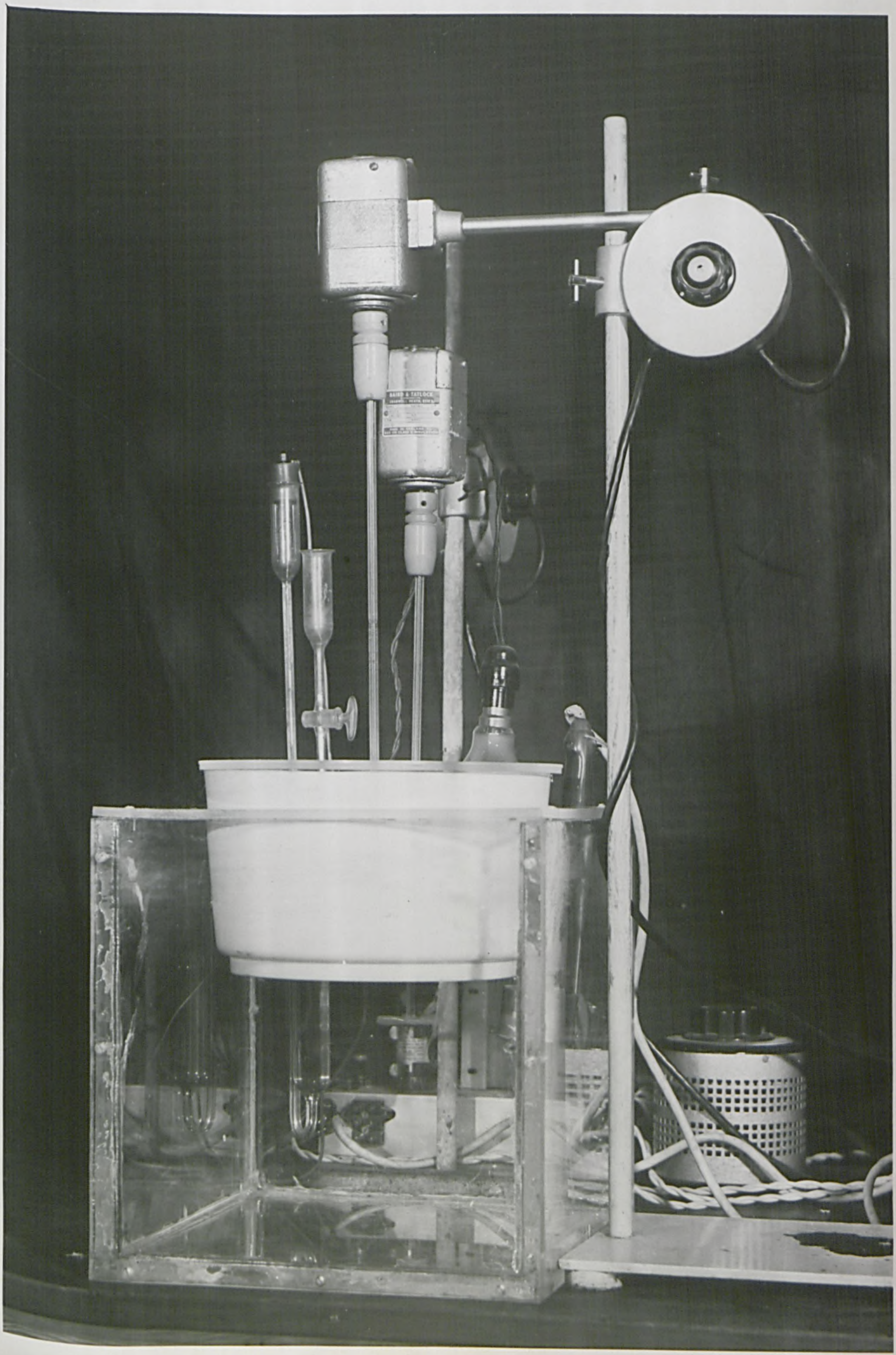


FIG. 32

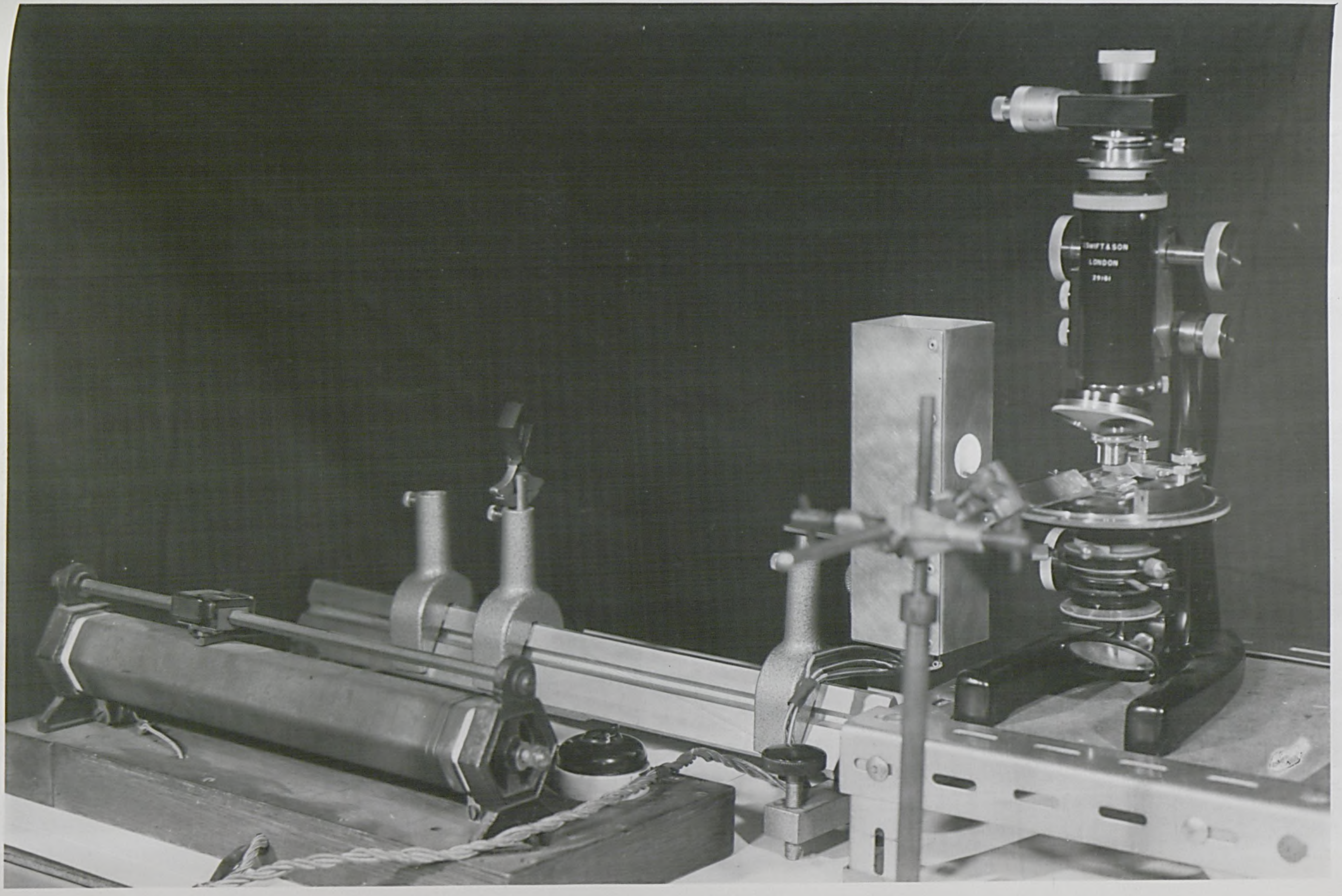
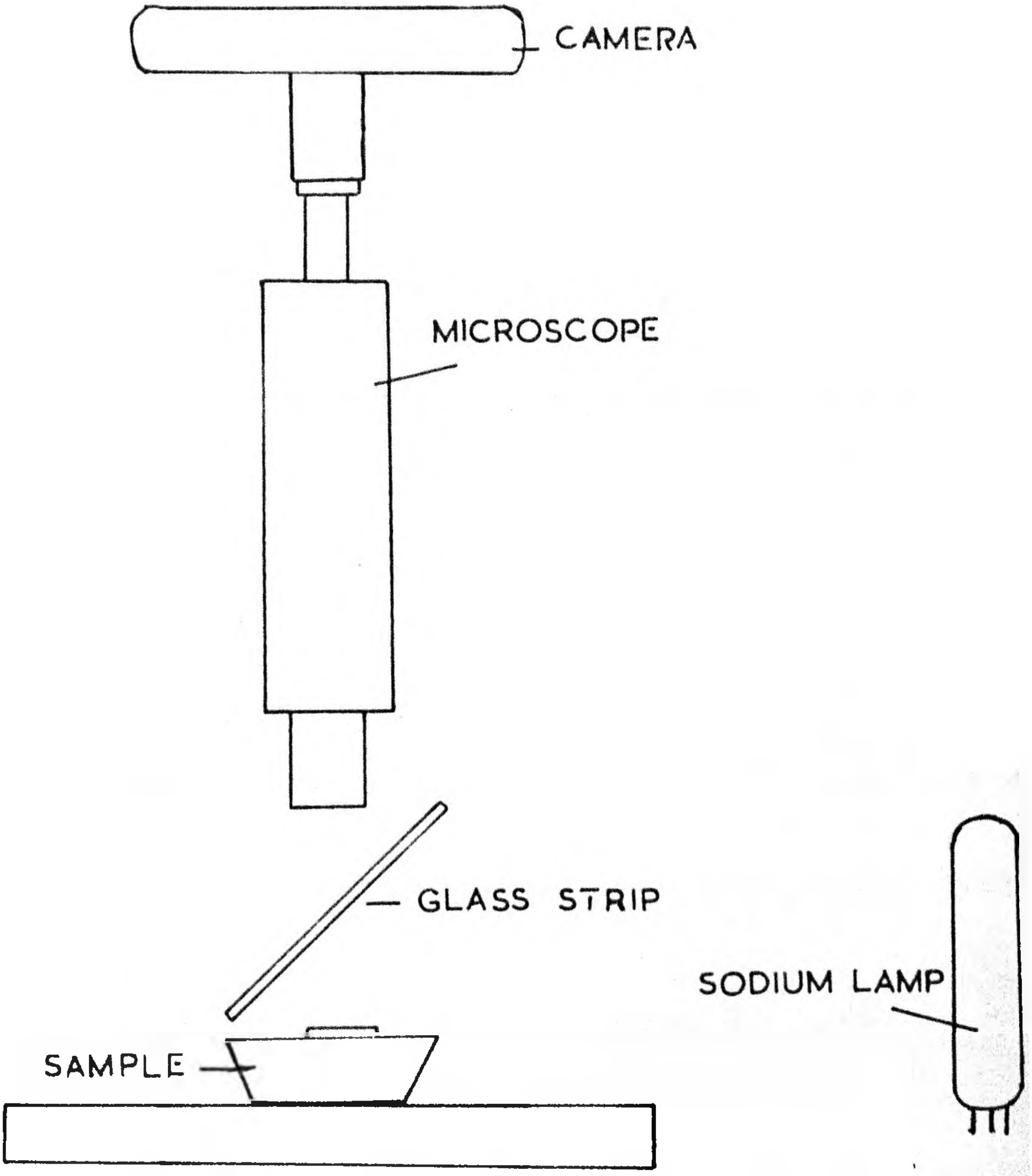


FIG. 33



SCHEMATIC DIAGRAM OF INTERFEROMETER

A microscope slide cover previously silvered to still transmit a reasonable proportion of light was then placed over the area to be examined. A special eye piece with crosswires and fitted with micrometer was used to count the number of fringes. Photographs of the interference fringes were also taken using a Pentax reflex camera mounted above the microscope eye-piece. The total magnification was 100, 10 times each from the objective and the eye-piece. The depth of etching was measured in one place on three sides of every pit giving a total of about sixty readings.

5 CALCULATIONS OF RESULTS

Taking as a specimen calculation the results obtained for 400 revolutions (glasses 1 and 2) of the disc stirrer, the following readings were obtained on the interferometer.

Number of fringes = 15.15.16, 15.15.15, 19.17.17, 19.19.18, 19.17.17, 15.15.15.15, 14.15.16, 15.15.15.15, 14.14.14, 19.18.20.19, 18.18.16, 20.20.24, 16.16.16, 13.13, 10.10, 12.13.12, 15.15, 14.16.17, 20.19.19.

f	x	Δx	$f\Delta x$	$(\Delta x)^2$	$\Sigma f(\Delta x)^2$
2	10	-5	-10	25	50
2	12	-3	-6	9	18
3	13	-2	-6	4	12
5	14	-1	-5	1	5
16	15	-	-	-	-
9	16	1	9	1	9
6	17	2	12	4	24
4	18	3	12	9	36
10	19	4	40	16	160
4	20	5	20	25	100
61			66		414

True mean depth of etching = $15 + \frac{66}{61} = 16{\cdot}08$

S^2, variance = $\frac{414}{61} - \left(\frac{66}{61}\right)^2 = 5{\cdot}52$

The mean depths of etching for the individual glasses were $x_A = 26$, $x_B = 10$, giving an expected mean of 18 fringes if the relation between composition and depth were exactly linear.

The intensity of seregation, I was therefore calculated as

$$I = \frac{1}{(x_A - x_B)^2 . \frac{1}{4}}(S^2 - S^2_R)$$

where S^2_R is the variance for fully mixed glasses. These glasses were stirred at 100 r.p.m. for one hour. After one hour these glasses were again stirred for half an hour at 100 r.p.m. and the crucible was then taken out of the furnace and cooled to room temperature. The variance S^2_R was then calculated as usual, which was equal to 0·07.

$$\text{So intensity } I = \frac{1}{(26 - 10)^2 \times \frac{1}{4}}(5{\cdot}52 - 0{\cdot}07)$$

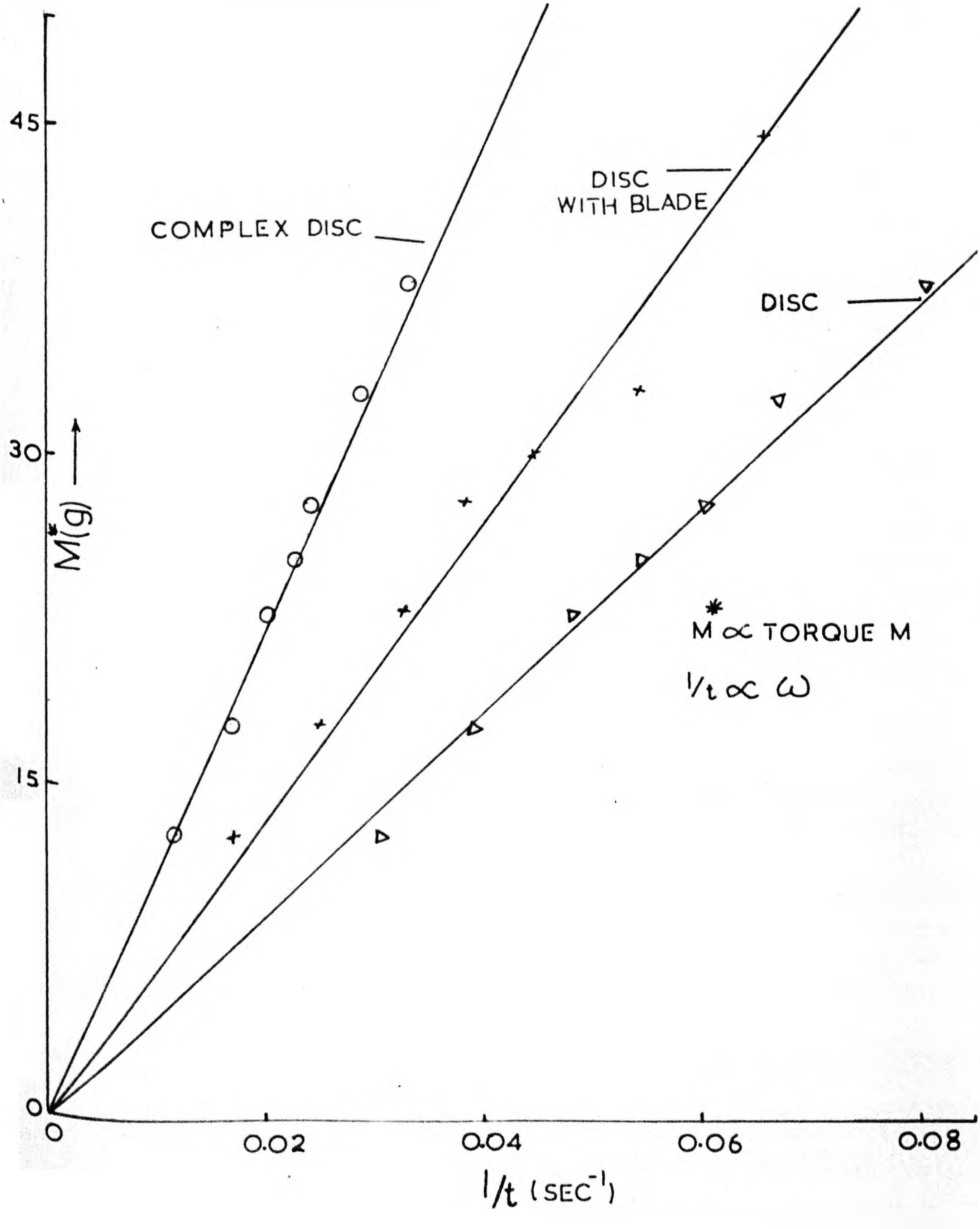
$$\text{or } I = 0{\cdot}085$$

Although the information was not usually used, it may be noted that this experiment allows one to see how the inhomogeneities are distributed. For example, whether the major inhomogeneity lay on the top or bottom of the sample.

TORQUE MEASUREMENTS AT ROOM TEMPERATURE

Torque measurements were made in a simple apparatus used for viscosity measurement by the Margules method. The stirrer was immersed in golden syrup, a known weight applied to the scale pans and the time to complete six revolutions noted (Figure 34). The form of the relation between torque and angular velocity helped to interpret the observed flow patterns. This is discussed later.

FIG.34 PLOT OF THE APPLIED WEIGHT VS THE RECIPROCAL OF TIME NEEDED TO COMPLETE 6 REVOLUTIONS



CHAPTER VI

RESULTS AND DISCUSSION

ROTATING DISC

The disc is one of the simplest possible mechanical stirrer for which the flow can easily be interpreted at least, qualitatively. The velocity components can be calculated for a disc rotating in the surface of an infinite fluid and for an infinite fluid rotating over a plane wall. In suitable conditions these results would be expected to agree well with actual flows in the central region of the crucible.

Consider a disc rotating in a large volume of a fluid. The layers near the disc are carried around through friction and are thrown outwards owing to the action of centrifugal forces. In the case of a fluid rotating over a plane, there is a similar effect but its sign is reversed, the particles which rotate at a large distance from the plane are in equilibrium under the influence of the centrifugal force and the radial pressure gradient. The peripheral velocity of the particles near the plane is reduced and so the centrifugal force is decreased but the radial pressure gradient remains the same and flow spiralling inwards towards the axis of rotation is produced. These cases of flow, a flow near a rotating disc and rotation near a plane, in large bodies of fluid were mentioned earlier and diagrams of both shown.(see Figures 20, 21).

According to L. Prandtl[35] the boundary layer thickness, defined as the distance from the plane or disc at which peripheral velocity is 2% different from the velocity of the body of fluid or the disc, respectively, for these cases is

(i) rotating disc = $\delta_1 = 4\sqrt{\frac{\nu}{\omega}}$

(ii) rotating fluid = $\delta_2 = 8\sqrt{\frac{\nu}{\omega}}$

The boundary layer thickness in the latter case is twice the thickness of the former case. Thus one would expect the flow near the axis in a finite vessel to agree with this simple flow only if the depth of melt exceeded $\delta_1 + \delta_2$ and the diameter of the vessel was much greater than diameter of the disc. It should also be pointed out that this analysis applies, in principle only to a very large disc ($R \longrightarrow \infty$) and in practice is likely to agree accurately with measurements only if $R > \delta_1$. If $R < \delta_1$ it seems that the flow pattern will be similar but not fully developed.

On putting in appropriate values for η & ρ for glass and a suitable value for w one gets the total boundary layer thickness ($\delta_1 + \delta_2$) equal to 47·85 cms. The values used were $w = \frac{2\pi}{3}$, $\eta = 80$ poise,

So the depth of melt and the radius of the disc should exceed 47·85 cms, if very close agreement between experiment and theory is to be obtained near the axis of the vessel when depth and radius are much less, then radial and axial flows will be greatly suppressed compared with rotational flow about the axis.

Evidence supporting this was obtained by measuring the dependence of angular velocity of torque applied in room temperature model of golden syrup having viscosity of 418 poise at 26°C.

For the disc rotating over an infinite fluid

$$M = 0{\cdot}616\,\pi\rho R^4(\nu\omega^3)^{\frac{1}{2}}$$

For creeping rotational flow (no radial or axial components)

$$M = \tfrac{1}{2}\pi\eta\frac{\omega}{z}.$$

where z is the depth of the layer of liquid.

Figure 34 shows that the results agree with the second equation. However, observation of the flow did show the definite presence of radial and axial flows but these were, as suggested, very much slower than the predictions from the disc rotating in an infinite fluid. One important implication of this is that the exact flow pattern might be sensitive to Re number. Another important effect will be that the disk will not mix as efficiently as expected from the theoretical model. One feature of the simple theory that the experiments do agree with is the position of the stagnation points on the vertical section about which the fluid rotates under axial and radial flows. The theoretical model predicts $\delta_1 = \frac{1}{2}\,\delta_2$ and observation of room temperature models shows that the stagnation points do lie about 1/3 the depth below the disk.

The results obtained for the model do not agree with the results obtained for the glass. One obvious reason for this is that Re number is not matched in both systems. The proper matching of Re requires

$$\frac{D_1{}^2 N_1 \rho_1}{\eta_1} = \frac{D_2{}^2 N_2 \rho_2}{\eta_2}$$

or $$\frac{(2\cdot6)^2 \times 20 \times 2\cdot3}{100} = \frac{(4)^2 \times N_2 \times 1\cdot25}{15}$$

or $N_2 = 2\cdot35$ r.p.m.

This means that room temperature model to match glass should have been stirred at 2·35 r.p.m. The original model experiments used 60 r.p.m. and the radial and axial flow was more developed. Nevertheless the difference observed between glass and room temperature model cannot be explained only by difference in Re number.

This is because the model considered the mixing of equal volumes of liquid of the same viscosity and density. Whereas in the experiments with glass the density and viscosity of both components are different. In the earlier model experiments, no significance was attached to interface stability. Later work has shown that the interface stability is important and is a function of viscosity and height ratio.

Comments on the flows seen in the different experiments with glasses follow. (All the results were obtained for the stirrers with glasses 1 and 2 at 20 r.p.m., unless otherwise stated.)

1 DISC STIRRER

(i) Denser glass on top

The flow patterns and ordinary photographs are shown in the Figure 35.

50 revs:- From the shadow pattern it is clear that the denser glass is falling to the bottom under the influence of gravity although the axial symmetry suggests that stirrer is having some influence.

100 revs:- There is a fairly large region of denser (colourless) glass at bottom, which is not mixed at all. There is a very thin film of coloured glass, which was originally on the bottom, left underneath it.

200 revs:- After 200 revolutions the flow pattern is developing fairly symmetrically, under the influence of the disc but still with a large volume of unmixed denser glass at the bottom. The dark central "tail" of lighter (coloured) glass is rising right

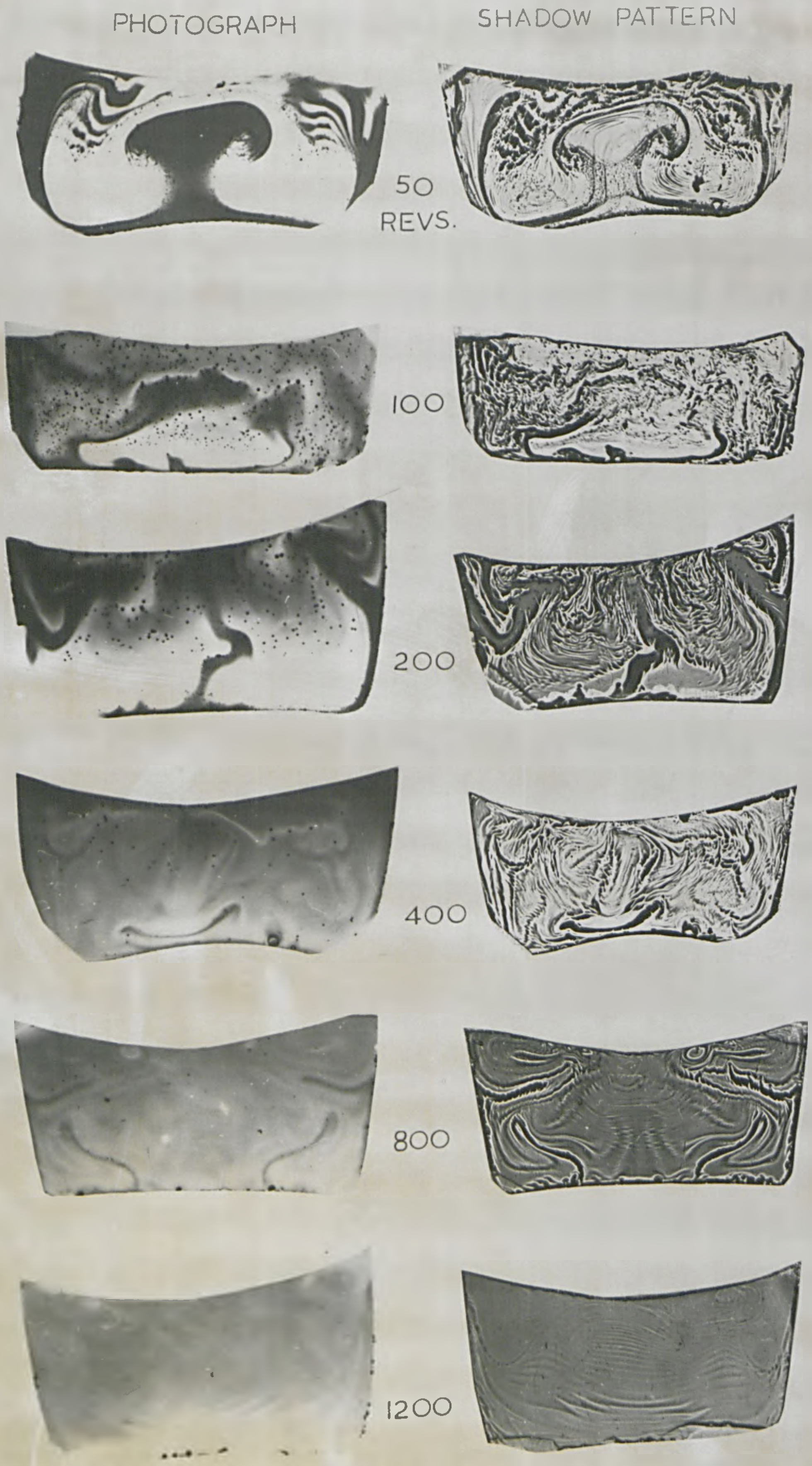


FIG. 35 DISC STIRRER *DENSER ON TOP*

from the bottom in the centre as the thin layer of coloured glass is slowly being drawn up into the main circulation.

400 revs:- The ordinary photograph shows little of original colourless or very dark glass. There is an indication of a ring of blue glass around the rim which was very marked at 200 revolutions. This is presumably the less dense glass adhering to the crucible walls rising towards the surface but why it takes up this particular form is not clear. General flow pattern is similar to those of 200 revolutions but the central tail is less distinct.

800 revs:- After 800 revolutions very symmetrical flow pattern can be seen, showing two unexpected features; a distinct ring of blue glass around the edge just above the centre and a dish shaped ring of blue glass in the bottom half of the melt. The first of these looks as if it might represent an interface between the two separate circulations, one above and one below. It also seems that this interface could be the natural evolution of the rather similar feature seen at 200 revs and 400 revs (left hand side).

Variation of depth of etching with position no longer shows distinct segregation of denser glass at bottom.

1200 revs:- The shadow pattern shows very well developed rotation about the axis but vertical circulation is not well developed. There is a distinct sign of a ring around the edge already mentioned, though much less obvious than that seen at 200 and 800 revolutions. No sharply defined fine detail is left (as compared with 50-400 revolutions) and this shows that diffusion has greatly reduced the true intensity of the small scale inhomogeneities.

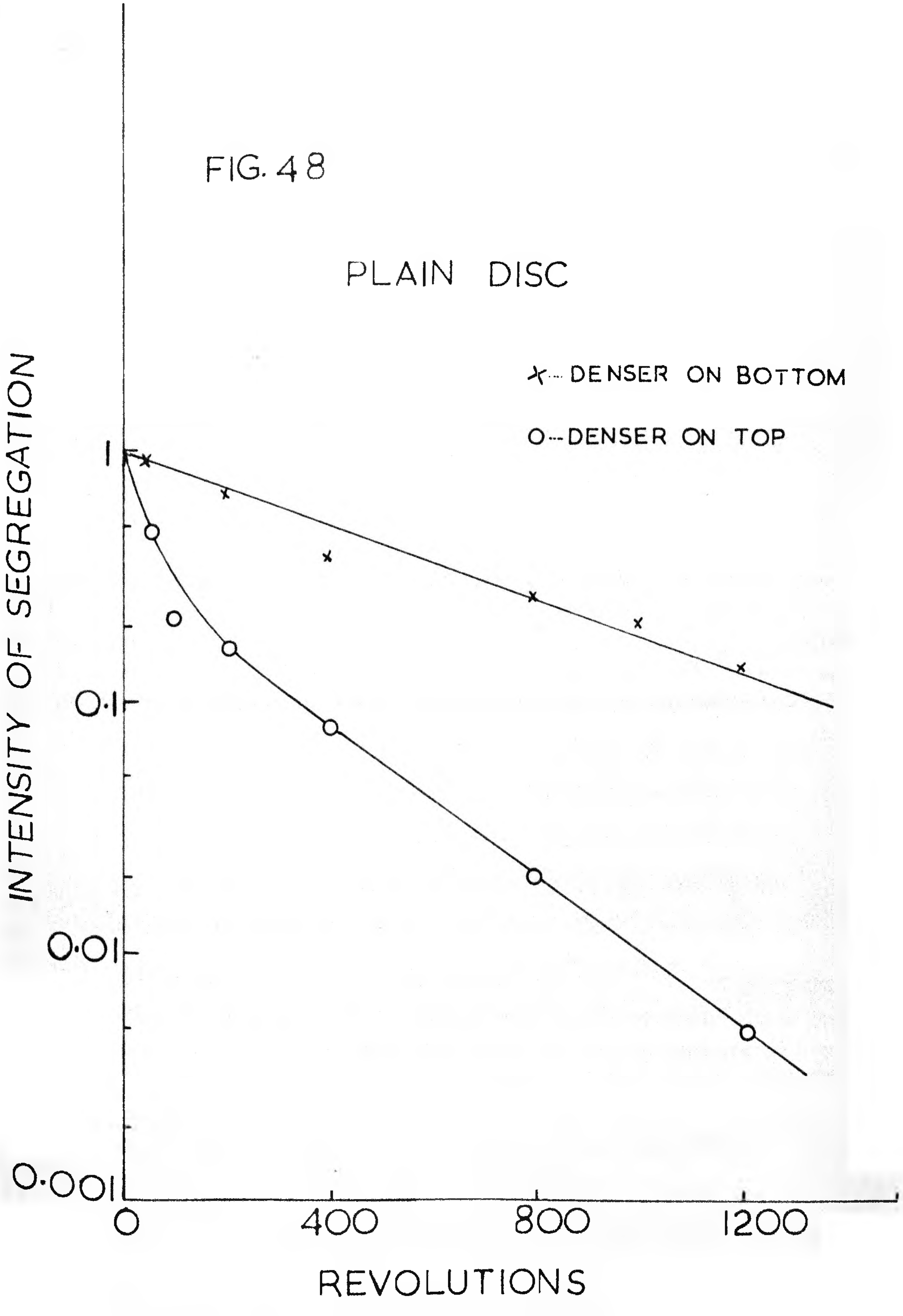


FIG. 48

PLAIN DISC

A plot of intensity (I) against time (Figure 48) shows steady progress of homogenising and photographs also suggest the same trend. However the distinct decrease in intensity between 100 and 400 revolutions is not immediately obvious by eye, showing the visual observation is not always reliable.

Flow patterns are not at all like the room temperature model. It is because the Re matching is not exact and also due to the difference of density and viscosity. Possibly flow under difference of densities, before stirring began, may have had some influence (e.g. difference between 400 and 800 revolutions).

(ii) Denser glass on bottom

To see if density difference was important the above series of experiments was repeated with the same glasses but the other way up. The shadow patterns and photographs are shown in Figure 36.

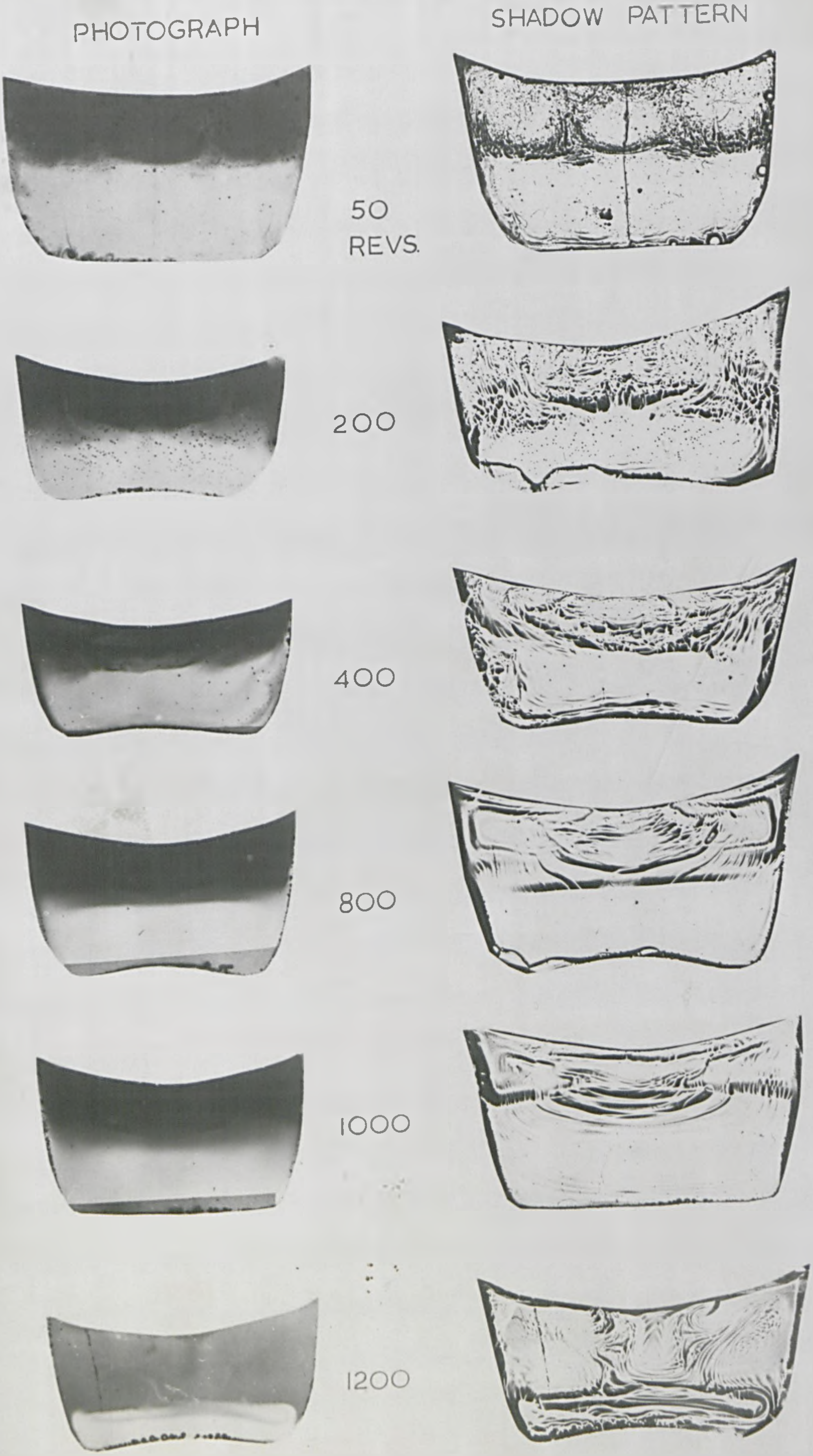
50 revs:- There is hardly any mixing. The main effect of stirring is that a ring of denser glass is drawn up into the lighter near the edge of the disc.

200 revs:- Again there is very little mixing although the ring seen at 50 revolutions seems more dispersed and rising gas bubbles are also producing some mixing.

400 revs:- The general appearance is not very different from 200 revolutions but it begins to show some development of rotation about the axis. A large volume of original colourless glass is still unmixed.

800 revs:- A distinct development of radial and vertical

FIG. 36 DISC STIRRER



circulation can be seen near the top but not in the bottom where there is still a large volume of colourless glass not mixed at all.

1000 revs:- It seems that flow is following the evolution of flow pattern seen at 800 revolutions. The vertical circulation is fairly well developed just below the disc but still there is a large region at the bottom, where radial and vertical circulation is small.

1200 revs:- An unmixed layer at the bottom shows very little mixing but it is much thinner than seen at 800 and 1000 revolutions. There is a very curious flow pattern in the relatively well mixed region which does not seem to be an obvious development of the flow pattern at 800 and 1000 revolutions.

Both photographs and the plot of intensity, I, against time (see Figure 48) clearly show that the density difference is very important. The mixing is much better when the denser glass was originally on top, producing more complex flow than with denser on the bottom. The flow patterns are very different from the room temperature model of equal density and viscosity in both cases.

Results at 1200 revolutions suggest further progress in mixing than indicated by results at 800 and 1000 revolutions, this might be due to rather smaller depth of the melt or different depth of immersion of the disc. The interface originally present between the two glasses seems to be stable but convection probably accelerates mass transfer across it.

2 DISC STIRRER (GLASSES 3 AND 4)

As it is evident from the previous results that density has an important effect, another pair of glasses was selected from the scanty evidence available which were expected to differ much less in density whilst still differing in viscosity. The flow patterns and photographs are given in Figure 37.

(i) Denser on bottom

50 revs:- There is little mixing, a dome shaped region is drawn up under the disc and there is a horizontal region between the layers in which some mixing has occurred but most of the denser glass remains undisturbed.

200 revs:- The interface between the layers is still stable and distinct. The mixing above the interface has proceeded beyond that at 50 revolutions. There is a slight indication of radial and vertical circulation above the interface.

1200 revs:- The interface between the layers is still stable across most of the section but it is disturbed beneath the stirrer and this region presumably represents the evolution of the central dome seen at 50 revolutions. Examination of the depth of etching results shows that, despite the stability of the interface, the bottom layer has changed appreciably in composition and this is confirmed by the considerably reduction in I (in this melt I = 0·039).

The flow pattern at 200 revolutions looks rather similar to that at 200 revolutions in the previous experiment (glasses 1 and 2) but less disturbed by gas bubbles.

The interface between the layers still seems to be stable but flow patterns are not identical with previous experiments. Mixing

FIG. 37 <u>DISC STIRRER</u>

DENSER ON BOTTOM

GLASSES 3&4

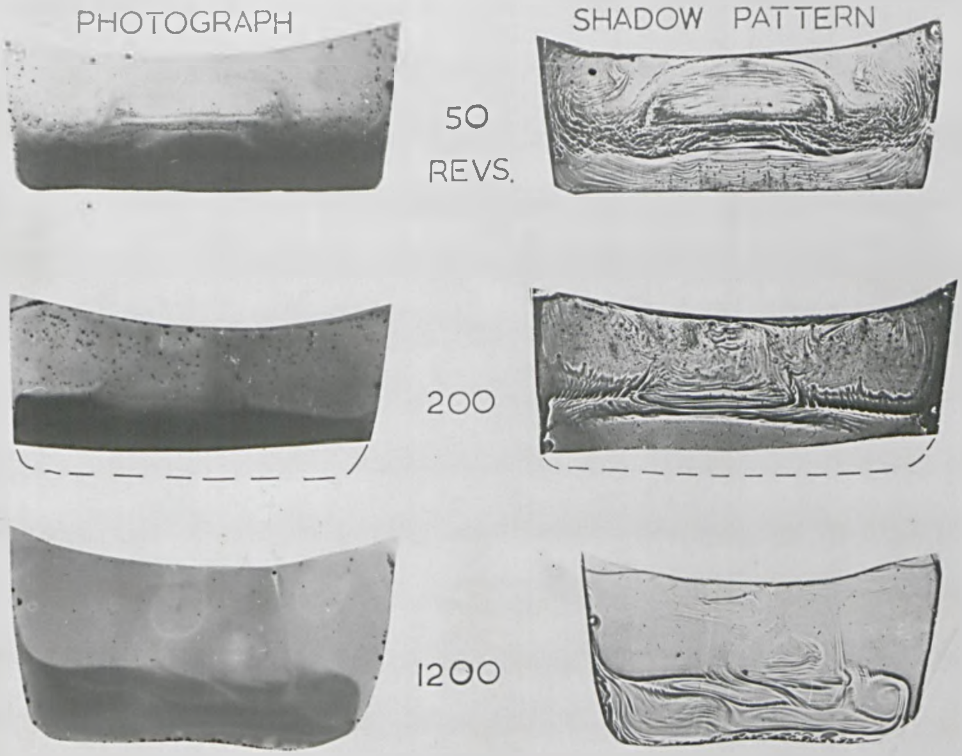
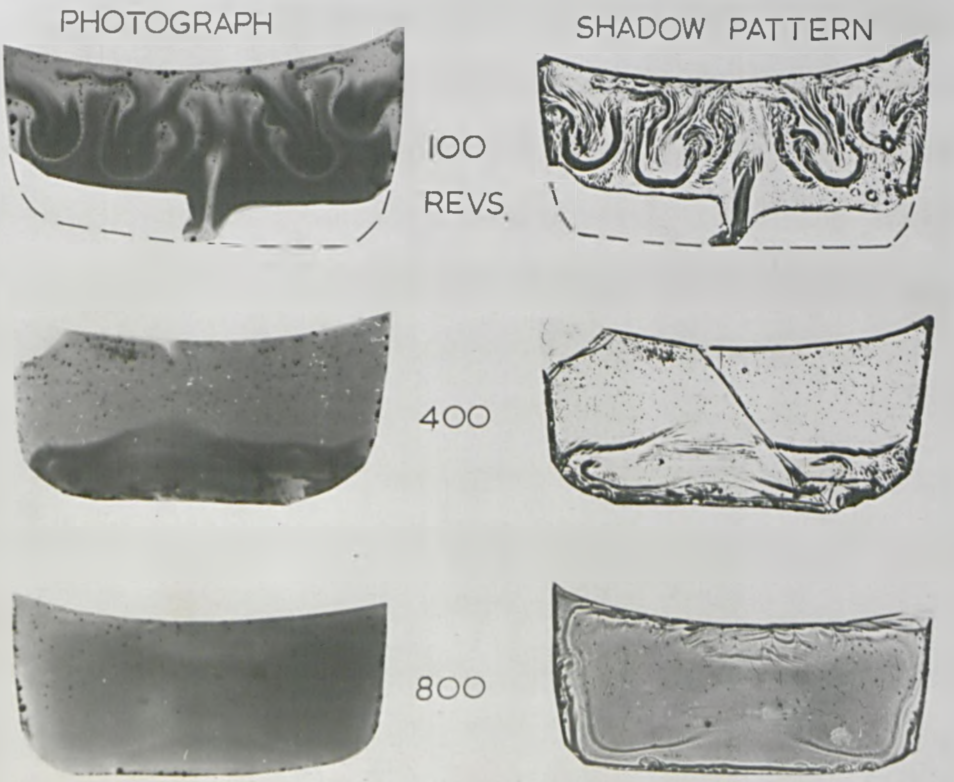


FIG. 38 <u>DISC STIRRER</u>

DENSER ON TOP

GLASSES 3&4



is faster in this pair of glasses than the other in the same arrangement (see Figure 48).

(ii) Denser on top (see figure 38)

100 revs:- This clearly shows irregular flow (good for mixing) due to density differences. The denser glass is falling down under the influence of gravity and corresponding streams of lighter glass rising.

400 revs:- Flow system shows a layer of coloured (denser) glass on the bottom but the bulk of the melt already contains a significant proportion of denser glass (because it is distinctly blue). The interface seems to be stable and mixing above it is fairly good (no fine detail in shadow pattern).

800 revs:- A thin layer on the bottom and around the sides and the indication of a central column suggest some vertical and radial circulation.

Mixing again is faster than when the denser glass is placed on bottom (Figure 49) and is also faster than for the other pair of glasses (glasses 1 and 2) with the same arrangement (denser on top). The smaller density difference may aid mixing of glasses 3 and 4 but differences in viscosity and effective diffusivity may have played some part.

3 DISC WITH BLADE (GLASSES 1 AND 2)

(i) Denser on top

The shadow patterns and photographs are shown in Figure 39.

200 revs:- The denser (colourless) glass has flowed towards bottom in rather irregular way but there is an indication of upturned ring

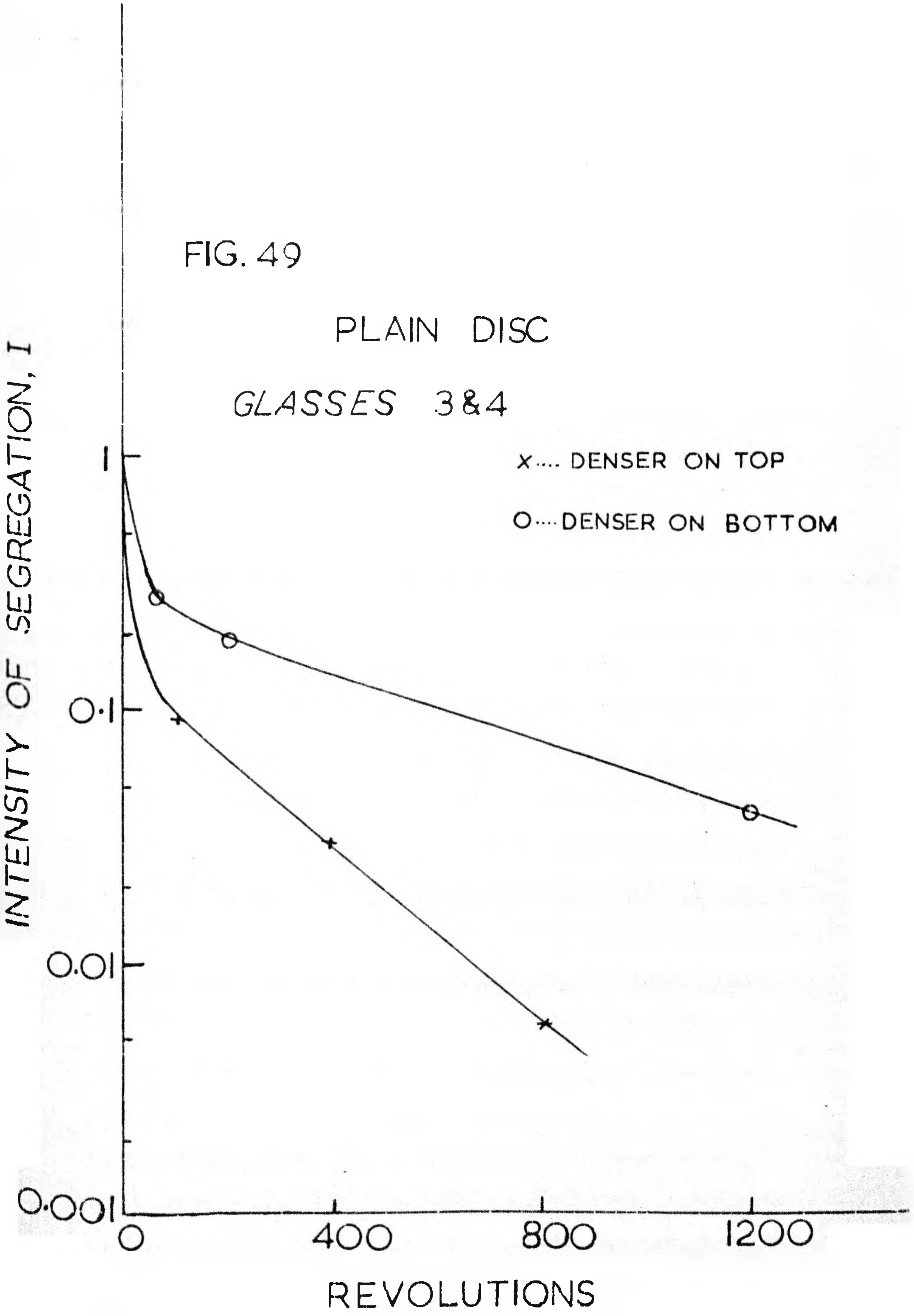


FIG. 49

PLAIN DISC

GLASSES 3&4

around outside above half way down which might owe its existance to the action of the stirrer.

400 revs:- The shadow pattern looks like an obvious development of that at 200 revolutions. The photograph indicates more mixing than at 200 revolutions and an unmixed layer is still on the bottom but considerably thinner. Both melts at 200 and 400 revolutions show that gas bubbles have attenuated some inhomogeneities.

600 revs:- A very thin layer of coloured glass still adheres to the bottom. The gas bubbles are many fewer than at 400 revolutions. From the colour pattern it is evident that mixing is not good (very fine detail is still seen in the shadow pattern) but mixing is nevertheless obviously better than at 400 revolutions.

800 revs:- Nearly all gas bubbles are gone there is an indication of stable interface on the shadow pattern except where it is disturbed by the tip of the blade. The vertical circulation is not well developed. The shadow pattern does not show as much fine detail as is seen for 600 revolutions. Some almost colourless glass still lies near the bottom.

1200 revs:- The colourless glass is still not completely mixed but a thin layer can still be seen on the bottom and around the sides. There is some suggestion of development of vertical circulation.

1500 revs:- Mixing has obviously progressed further, the colour pattern now shows very little difference in colour. The shadow pattern was made more contrasty than the others and did in fact show less detail than at 1200 revolutions. The rather curious

FIG. 39

DISC WITH BLADE *DENSER ON TOP*

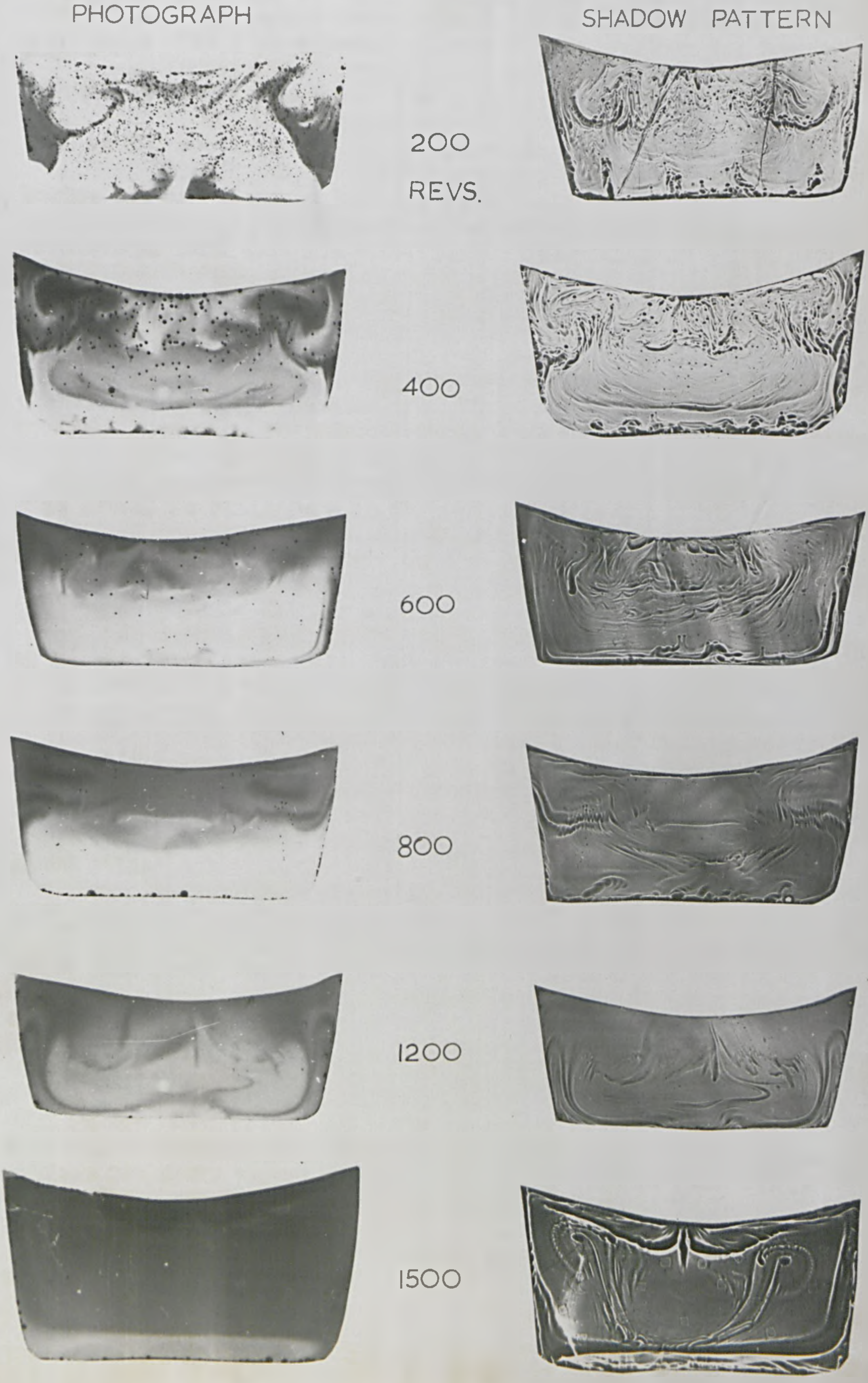


FIG. 40

DISC WITH BLADE

DENSER ON BOTTOM

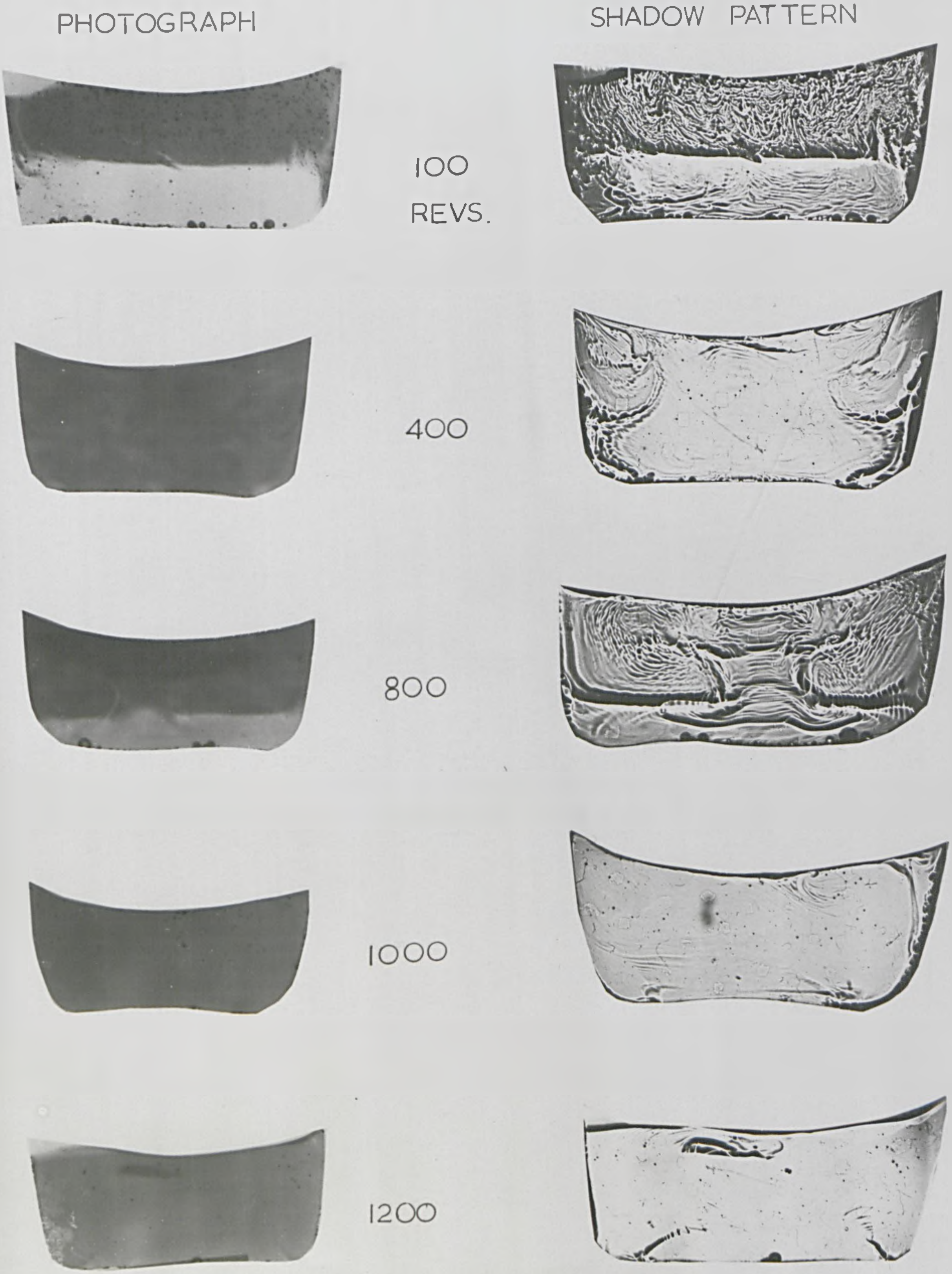
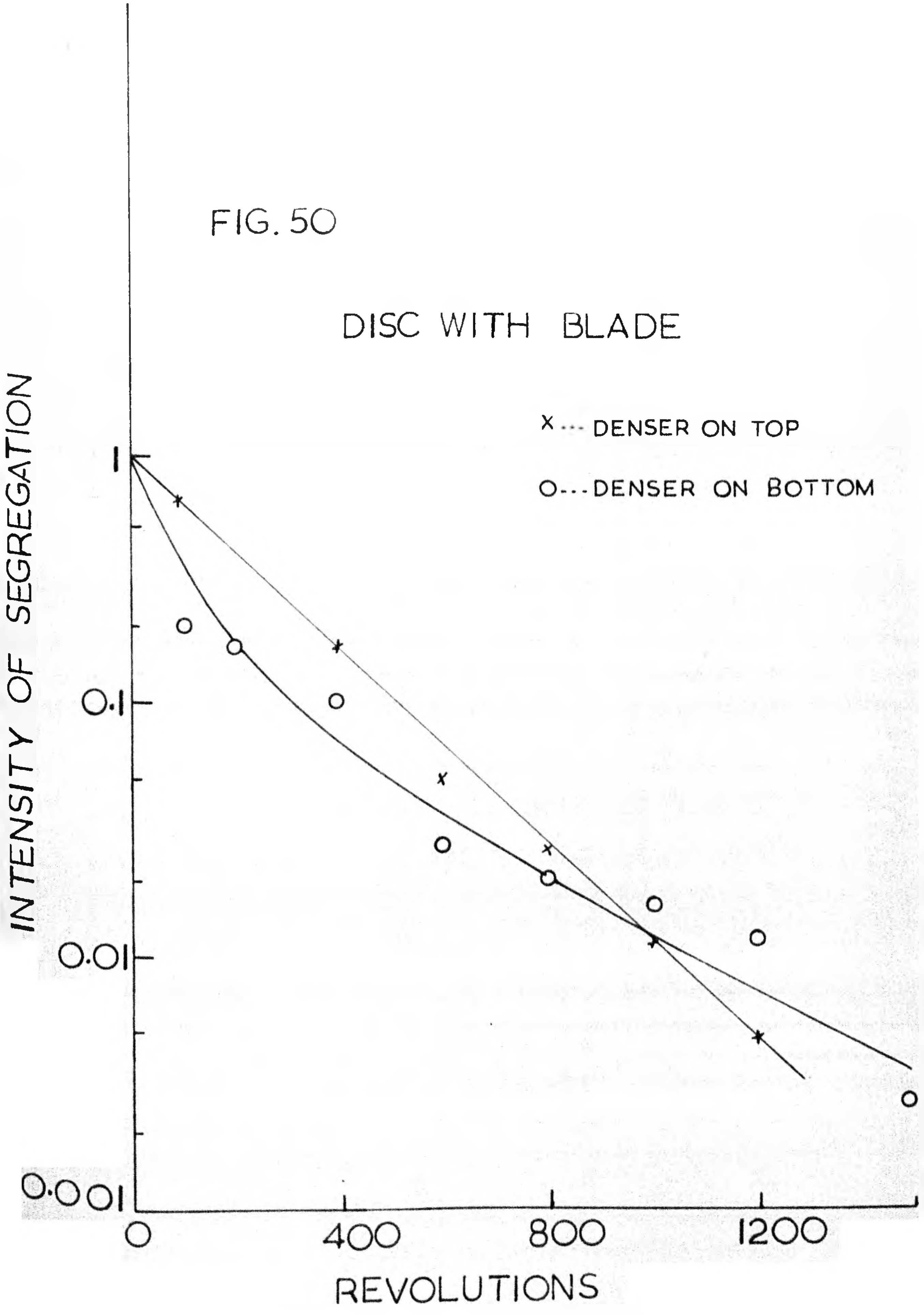


FIG. 50



DISC WITH BLADE

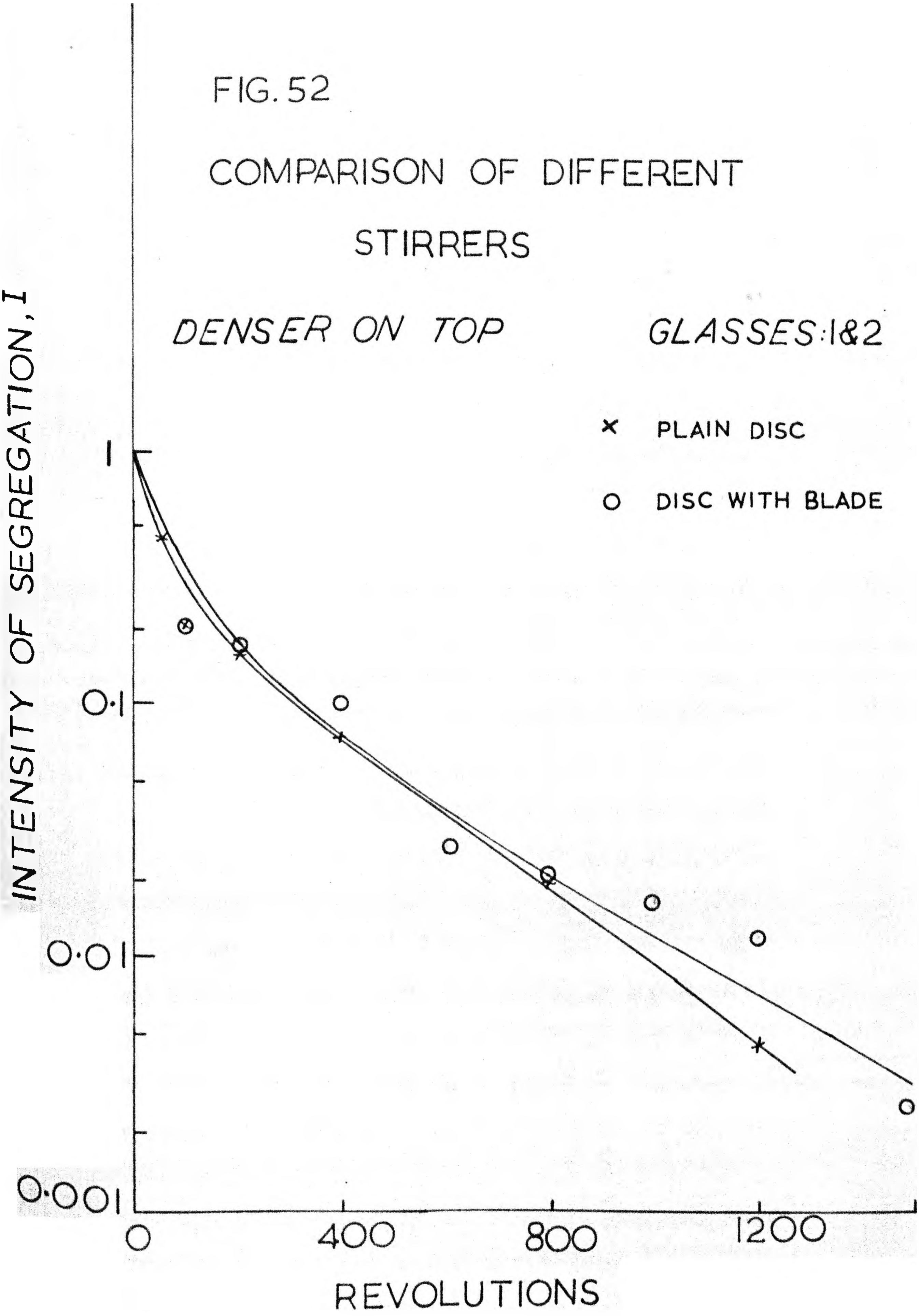


FIG. 52

COMPARISON OF DIFFERENT STIRRERS

pattern seen suggests further development of vertical and radial flow.

The comparison of flow patterns, especially at 400, 800 and 1200 revolutions suggests rather different flow from that produced by plain disc, mixing being better in the regions travelled by the blade.

Graphs of I against time (Figure 52) however shows not much difference between stirrers in this case. This may be because the blade suppresses further development of vertical and radial flow.

(ii) Denser on bottom (see Figure 40)

100 revs:- The interface seems very little disturbed. There is very little indication of development of flow of stirrer.

400 revs:- The colourless glass is not completely segregated, the whole section being blue. An upturned ring can be seen in the shadow pattern, which is apparently a part of the original interface. There is an indication of vertical and radial flow just below and outside the stirrer.

800 revs:- The colour patterns suggest that mixing is not better than for 400 revolutions. The shadow patterns are of rather similar type but the layer below the interface is much thinner and the interface flatter. The central column drawn up is also smaller but intensity is nevertheless lower at 800 than at 400 revolutions (see Figure 50).

1000 revs:- The shadow pattern does not show any very fine detail. The flow seems to be mainly rotation about the axis. A ring can be seen drawn up from the base near the corners.

1200 revs:- Very little detail is visible in shadow pattern except near the centre at top. (disturbance on withdrawing the stirrer). A ring is again rising from the base near the corners. The flow still seems to be almost entirely rotation about the vertical axis.

The relation between log I and time is very smooth with little scatter (Figure 50). Comparison with same initial distribution stirred by disc shows very marked differences. Mixing in this case is much better with blade, probably because its tip disturbs the interface. One result, that for 800 revolutions, does not exactly fit the general trend. This might be due to slightly different distance of tip of blade from the interface.

4 COMPLEX DISC

(i) Denser on bottom (see Figure 41)

100 revs:- A thin layer of denser glass remains on the bottom. The flow is not fully developed. A central region of lighter (dark) glass on the bottom is very distinct. Considerable attenuation by gas bubbles is seen.

400 revs:- A layer of denser glass is still on the bottom. A "tail" of denser glass is probably drawn up through the hole in lower disc and bent outward forming the shape like a handle.

800 revs:- Now the mixing of the bottom layer is beginning but flow is not well developed.

1000 revs:- The original interface has not completely disappeared but not much of it remains. The rotational flow about the axis is beginning to look well developed.

FIG. 41

COMPLEX DISC STIRRER

DENSER ON BOTTOM

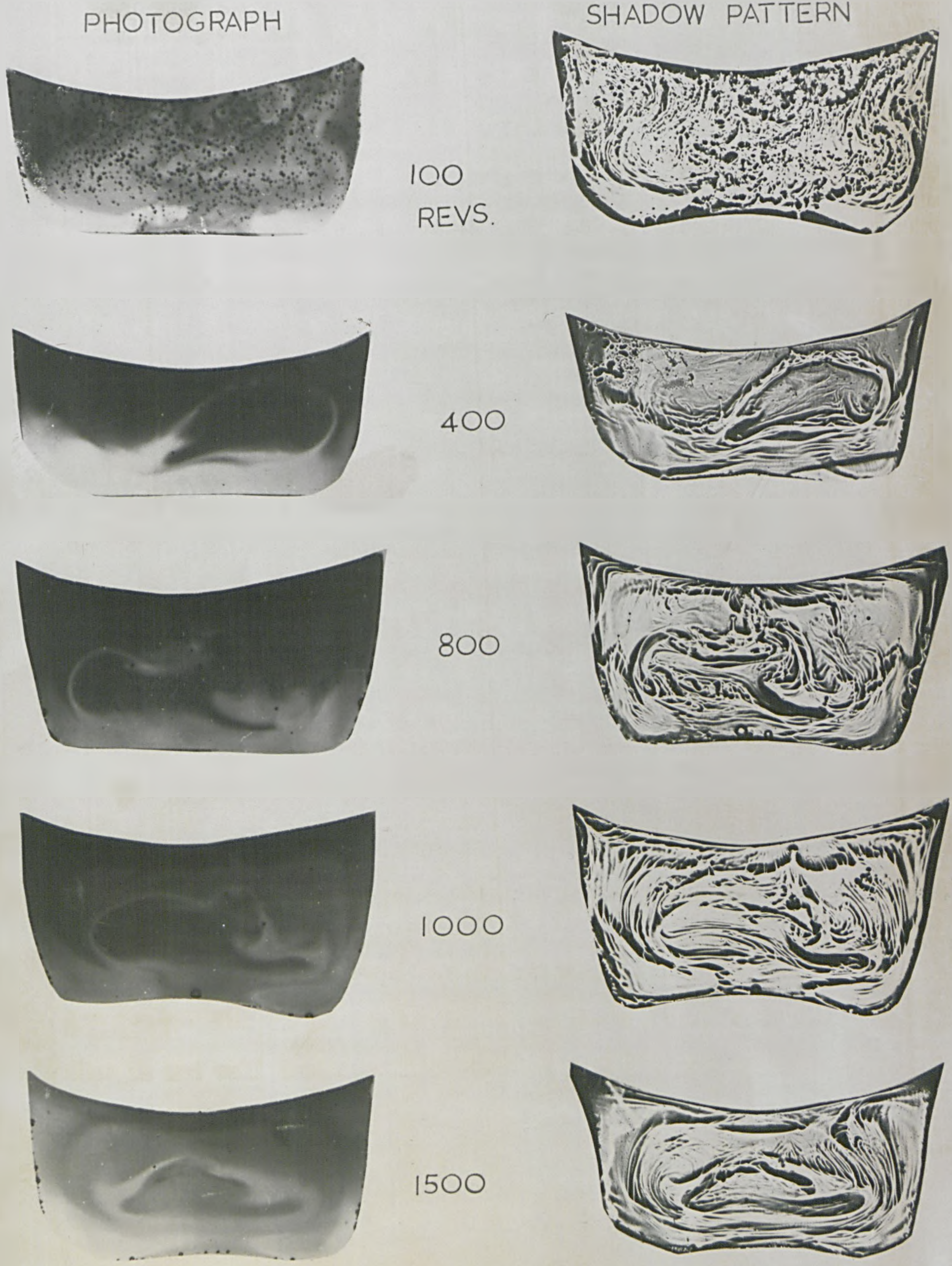
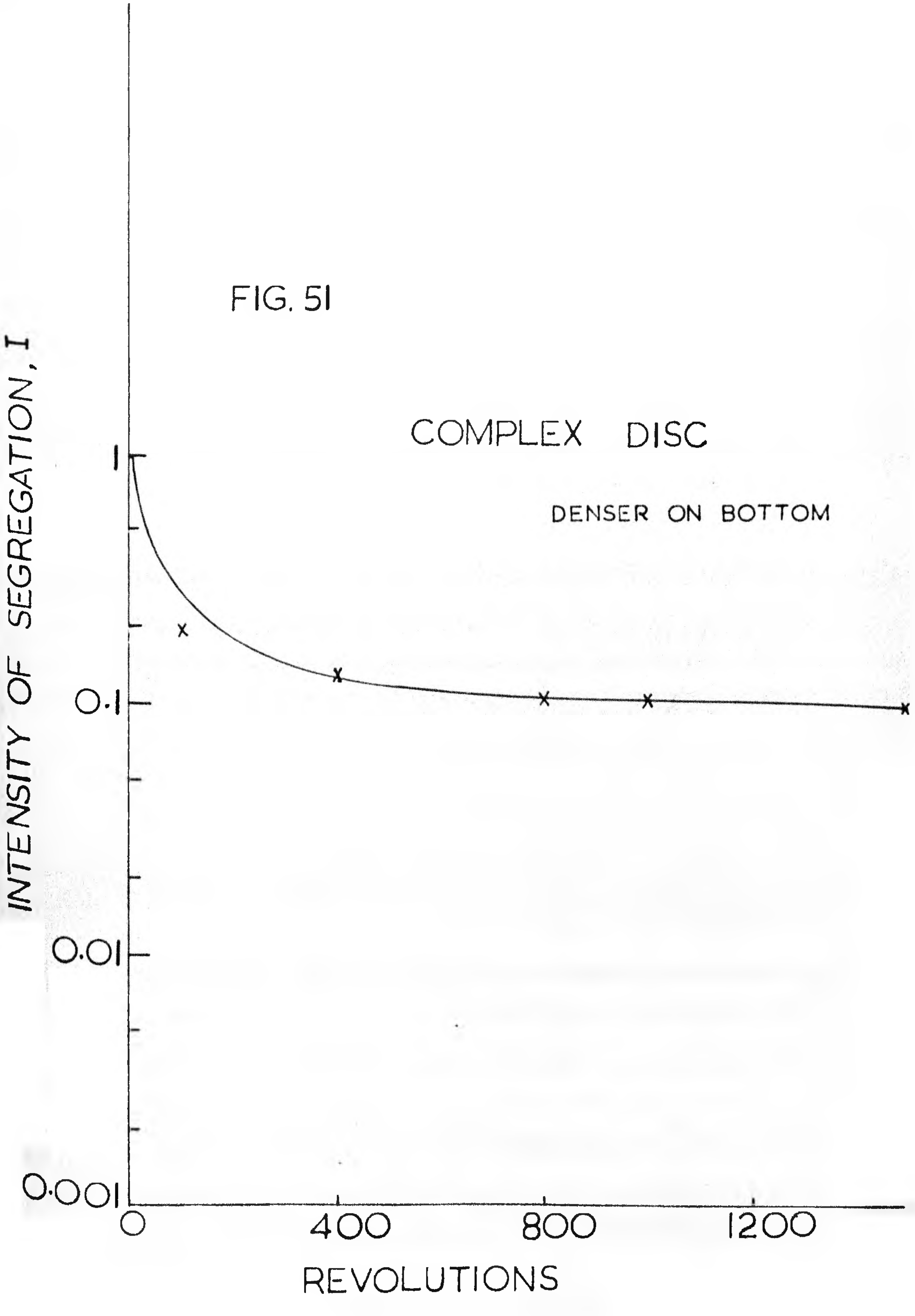


FIG. 51


COMPLEX DISC
DENSER ON BOTTOM
INTENSITY OF SEGREGATION, I
1
0·1
0.01
0.001
0
400
800
1200
REVOLUTIONS

1500 revs:- There is no distinct remnant of either layer on bottom or original interface. Vertical and radial flow is beginning to develop but there is still a roughly lens shaped region not well mixed, just above the position of lower disc.

Comparison with simple disc

The simple disc shows a stable interface at all times even up to 1200 revolutions for this initial arrangement. The complex disc stirrer disturbs and destroys the interface giving much better mixing early in the process. But the rate of mixing with the complex disc soon decreases and extrapolation of results suggests that plain disc would give rather better mixing beyond about 1700 revolutions. (see Figure 53).

This is probably due to decreased shear of the relatively large volume of liquid held in the space between the two discs which tends to rotate between them with little axial or radial flow.

Comparison with disc with blade

The disc with blade disturbs the interface somewhat, but less than complex disc stirrer. Up to about 500 revolutions greater disturbance of the interface with the complex disc gives better mixing. Beyond 500 revolutions the disc with blade is better even though the interface is less disturbed. This presumably happens because of larger velocity gradients and more attenuation with disc plus blade.

The comparison of flow patterns is shown in Figure 42.

FIG. 42 COMPARISON OF FLOW PATTERN

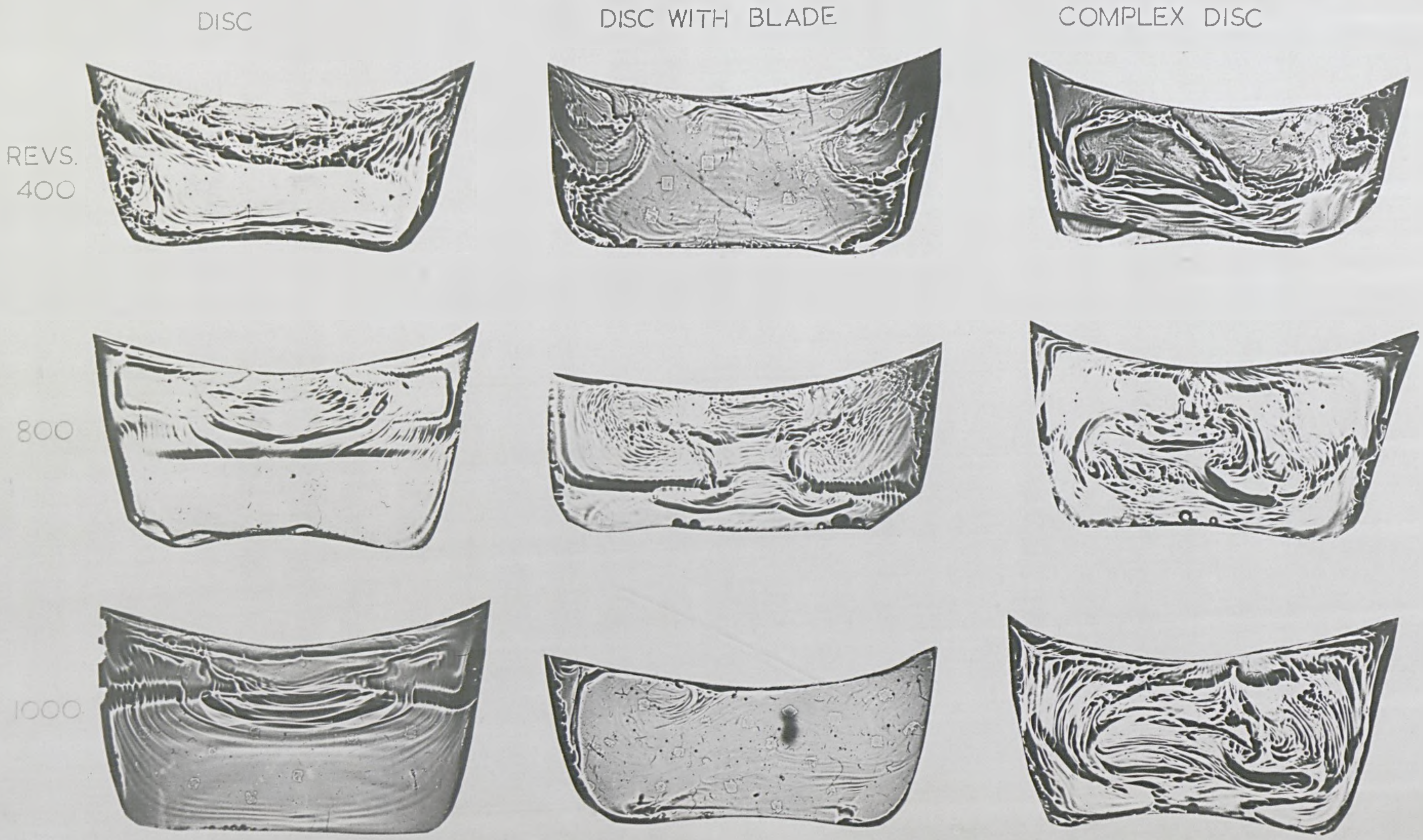
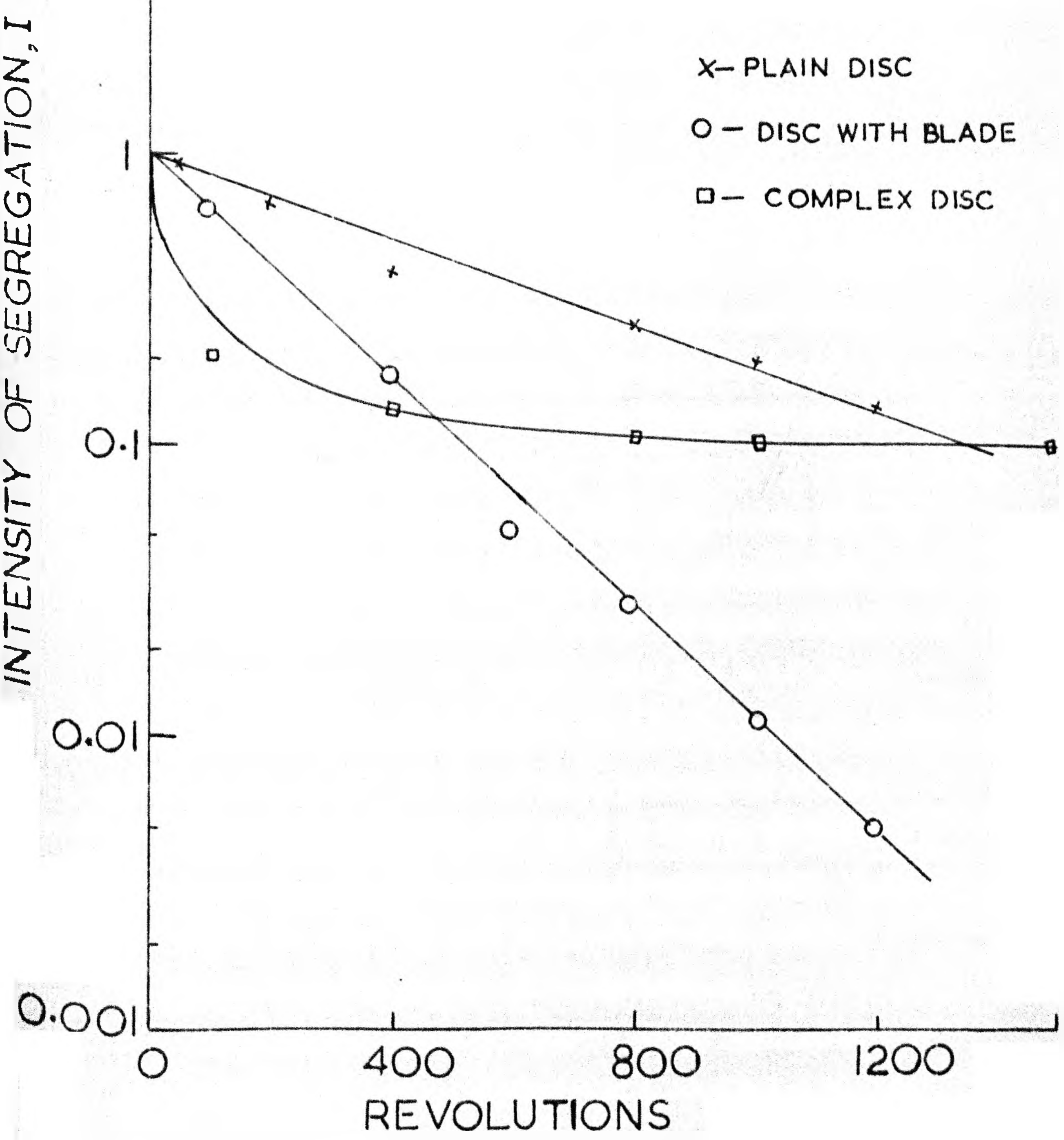


FIG. 53

COMPARISON OF DIFFERENT STIRRERS

GLASSES: 1&2 DENSER ON BOTTOM



5 EFFECT OF SPEED

(i) Disc stirrer (denser on bottom)

A comparison was made between several melts stirred for the same number of revolutions (1200) at several speeds. The shadow patterns and photographs are shown in the Figure 43.

20 r.p.m.(60 min):- A thin layer at the bottom shows very little mixing but it is much thinner than the original layer. There is a very curious flow pattern in the relatively well mixed region.

40 r.p.m.(30 min):- The interface is stable but mixing is appreciable.

60 r.p.m.(20 min):- The interface is much more disturbed though it is not entirely destroyed. There is hardly any denser glass which is not mixed at all. The flow seems to be affected by gas bubbles.

100 r.p.m.(12 min):- The interface still looks stable but only a very thin layer or hardly mixed colourless glass is left. The time is too short for diffusion to reduce the actual intensity of most attenuated cords. Gas bubbles again seem to be playing a part in attenuating cord.

120 r.p.m.(10 min):- The interface is probably not stable. Only a very thin layer of denser glass is left on the bottom. The gas bubbles have distorted the layers considerably. Again the time is too short for much diffusion to occur and much fairly fine detail is seen on the shadow pattern.

The graph (see Figure 55) shows a steady decrease in I as speed increases suggesting that increasing attenuation because of

FIG. 43

EFFECT OF SPEED

DISC STIRRER (CONSTANT REVS.)

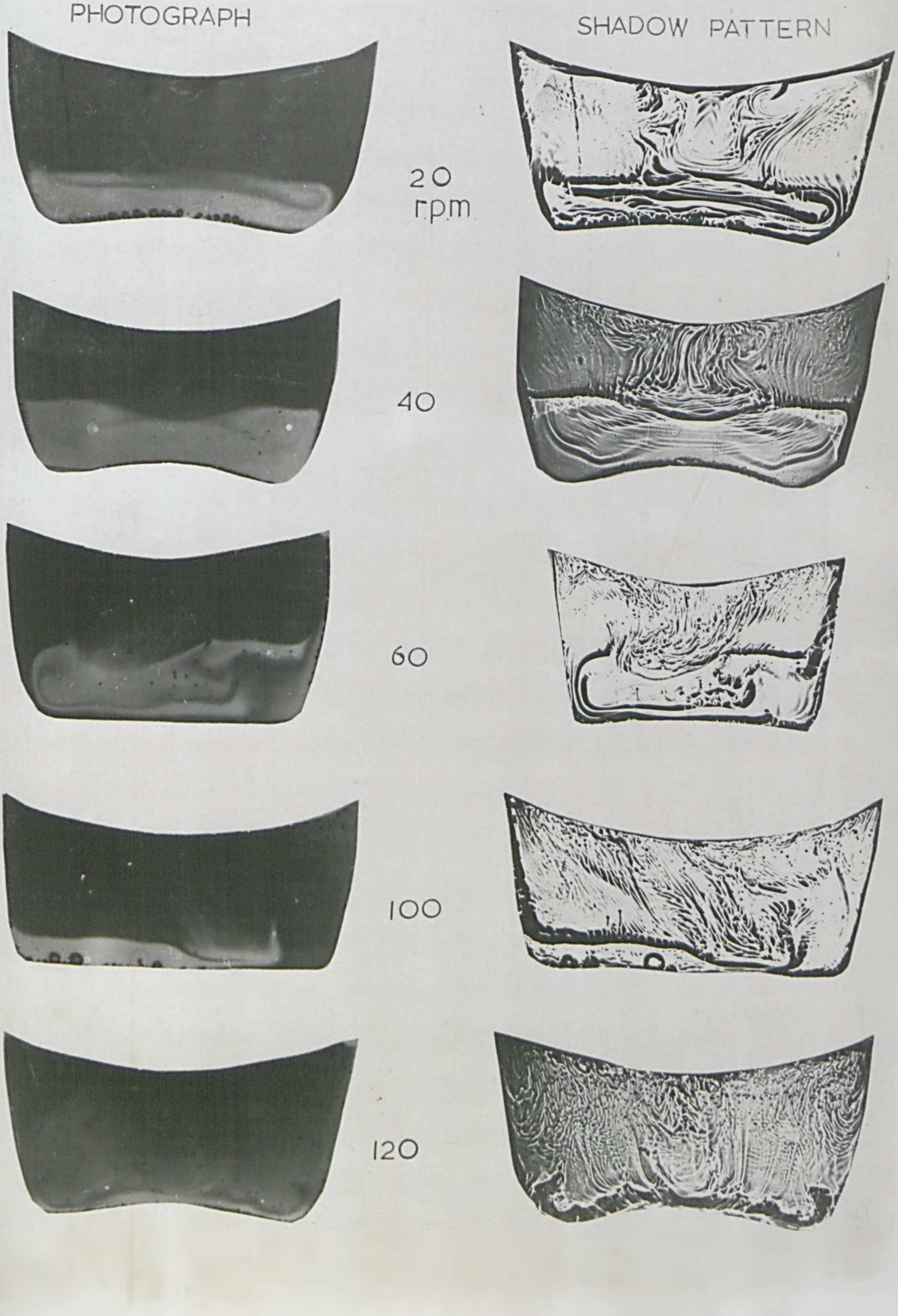
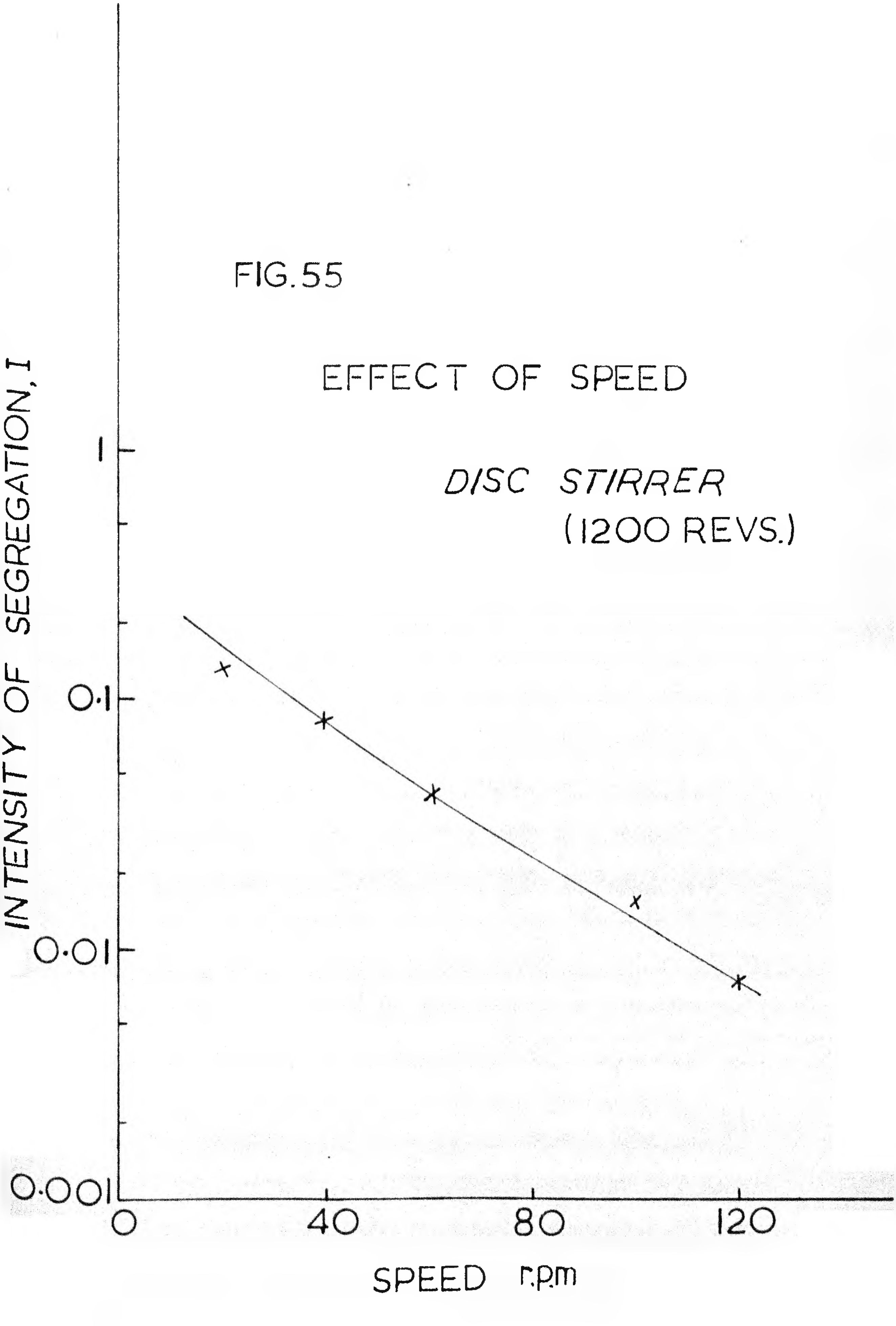


FIG. 55


EFFECT OF SPEED
DISC STIRRER
(1200 REVS.)
INTENSITY OF SEGREGATION, I
1
0·1
0·01
0·001
0
40
80
120
SPEED r.p.m

1) increasing disturbance of interface

2) the possibility that vertical and radial flows become more developed,

is the most important feature in this experiment.

(ii) Disc with blade (denser on top)

Another similar experiment was made with the disc with blade stirrer, stirring for 2000 revolutions when the denser glass was placed on top. The shadow pattern and photographs are shown in Figure 44.

40 r.p.m.(50 min):- The flow pattern seen in the photograph is very curious. Some unmixed dense glass lies very near to the bottom.

60 r.p.m.(33 min):- The interface seems to be stable and is drawn up towards the disc.

80 r.p.m.(25 min):- Central column is drawn up which could be further development of flow seen for 60 and 40 r.p.m.

100 r.p.m.(20 min):- The stable interface is drawn up towards the disc but the bottom layer is much thinner than seen for 60 r.p.m.

The results do not fall into a simple intelligible pattern and there are two obvious reasons:-

1) The denser glass put on top might give different effective distributions at moment when stirring began.

2) A possible effect of depth of immersion of stirrer.

Unfortunately these experiments were done before effect of density was fully realized and no further information likely to help interpret them is available.

FIG. 44 EFFECT OF SPEED (CONSTANT TIME)

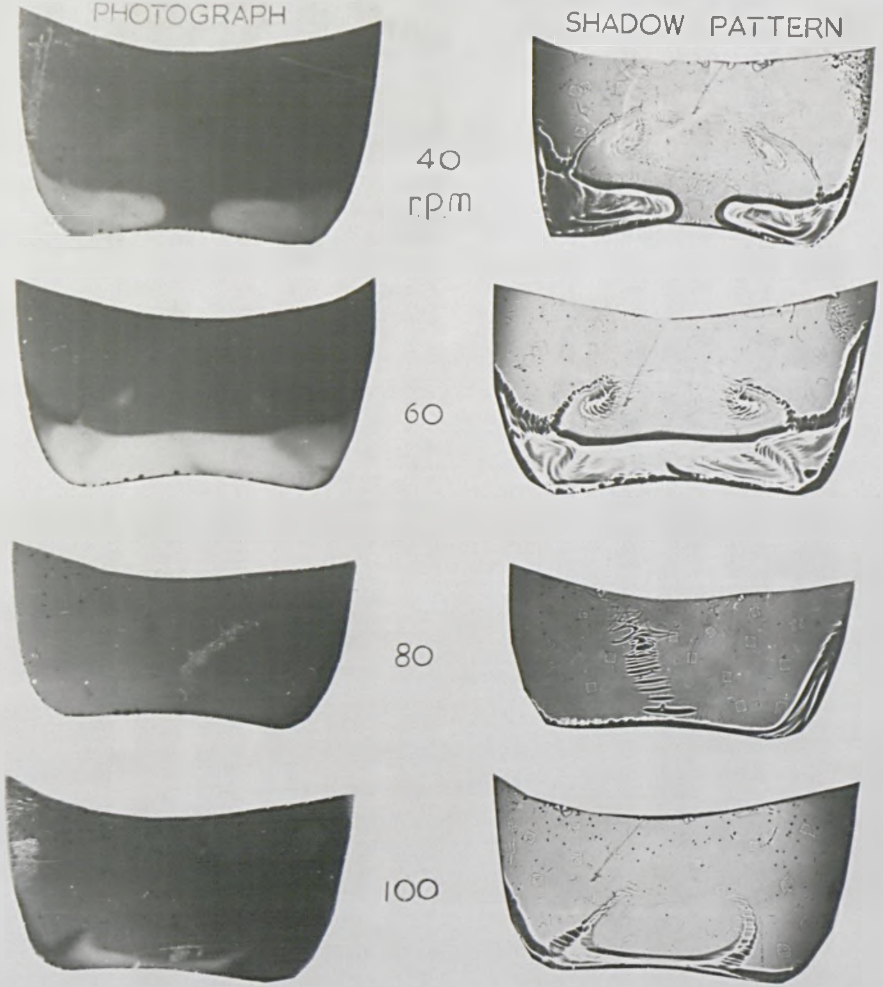
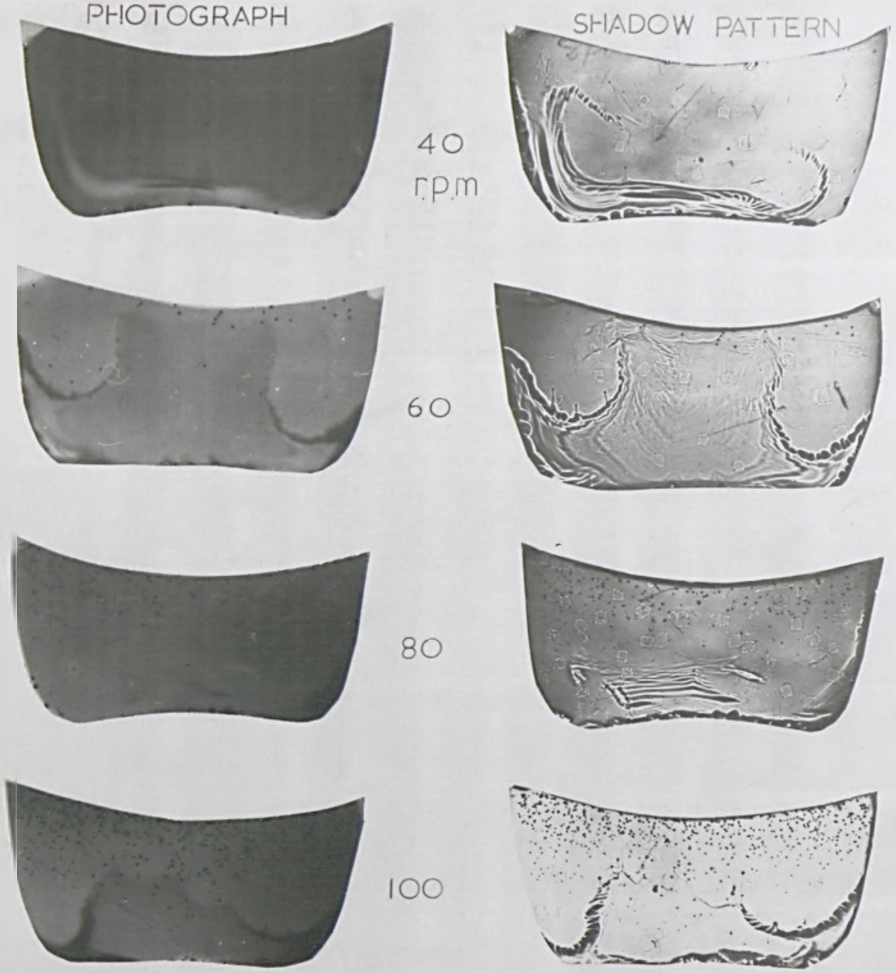


FIG. 45 EFFECT OF SPEED (CONSTANT REVS)



DISC WITH BLADE

(iii) For constant time (60 minutes)(see Figure 45)

40 r.p.m.(2400 revs):- A hole in the middle of layer is very curious. A thin dome shape is seen drawn up towards the stirrer.

60 r.p.m.(3600 revs):- The vertical and radial circulation is beginning to develop. A thick layer of unmixed glass is at the bottom. A very thin dome shape was seen drawn up towards the stirrer at 40 r.p.m. and a similar feature occurs here but its upper part shows evidence of vertical and radial flow.

80 r.p.m.(5400 revs):- A central column is drawn upwards. A very thin layer can be seen on the bottom.

100 r.p.m.(6000 revs):- The flow pattern looks like further development of that seen at 60 r.p.m.

6 EFFECT OF STIRRING

A few glasses were melted from batch and stirred with disc at 20 r.p.m. for different lengths of time. The flow patterns and mixing are compared with glasses not stirred, but melted for the same length of time. The flow patterns of stirred and unstirred melts are given in the Figure 46.

(i) Unstirred melts

1 hour:- Vertical attenuation of cords can be seen which is probably due to gas bubbles.

2 hours:- A complex flow pattern has been developed probably the flow is under the influence of density differences. If the flow were mainly caused by thermal convection a more regular circulation would probably be seen.

4 hours:- A slight bulk inhomogeneity can be seen. A layer presumably denser on the bottom is very distinct.

FIG. 46
COMPARISON OF STIRRED & UNSTIRRED MELTS

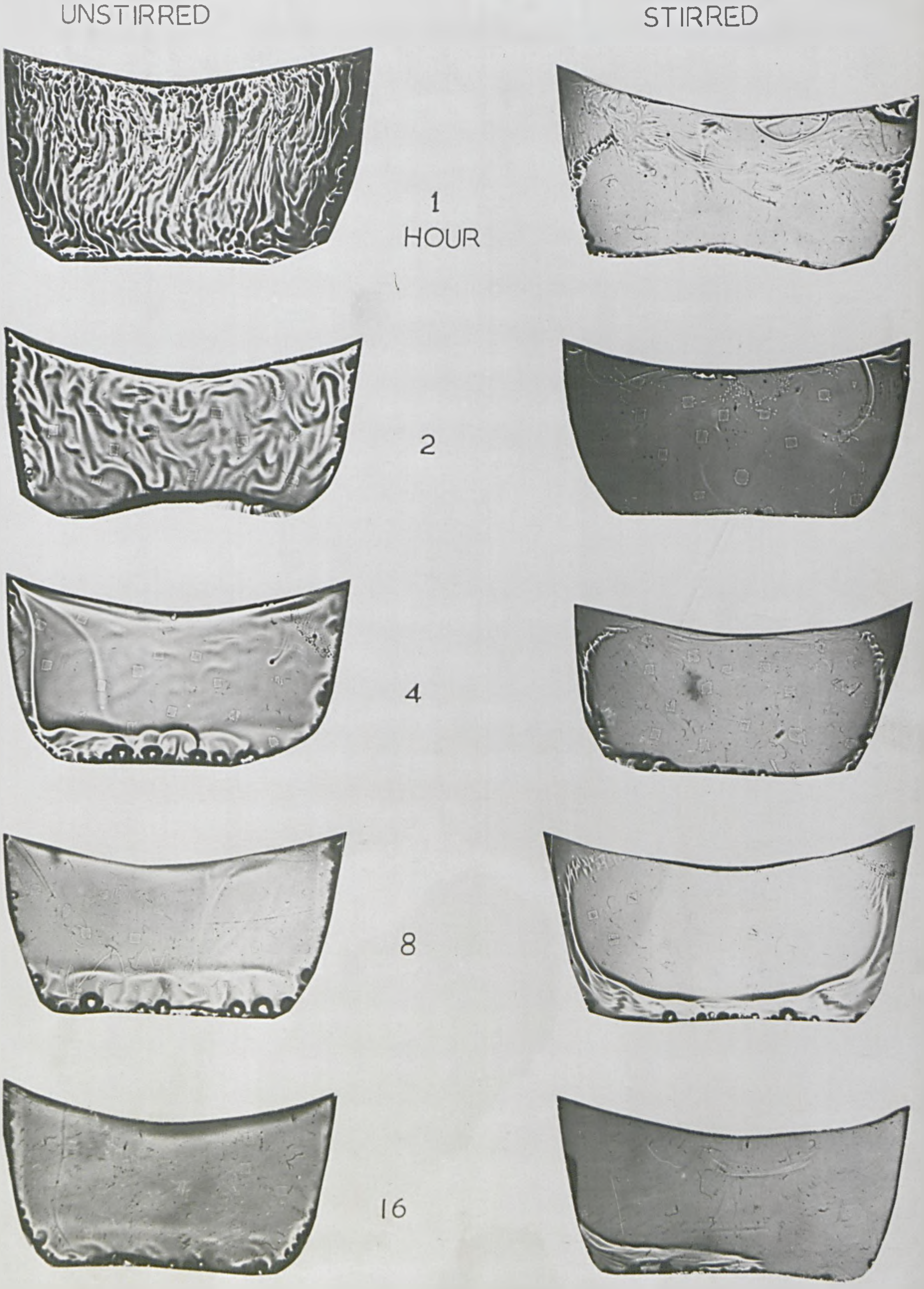
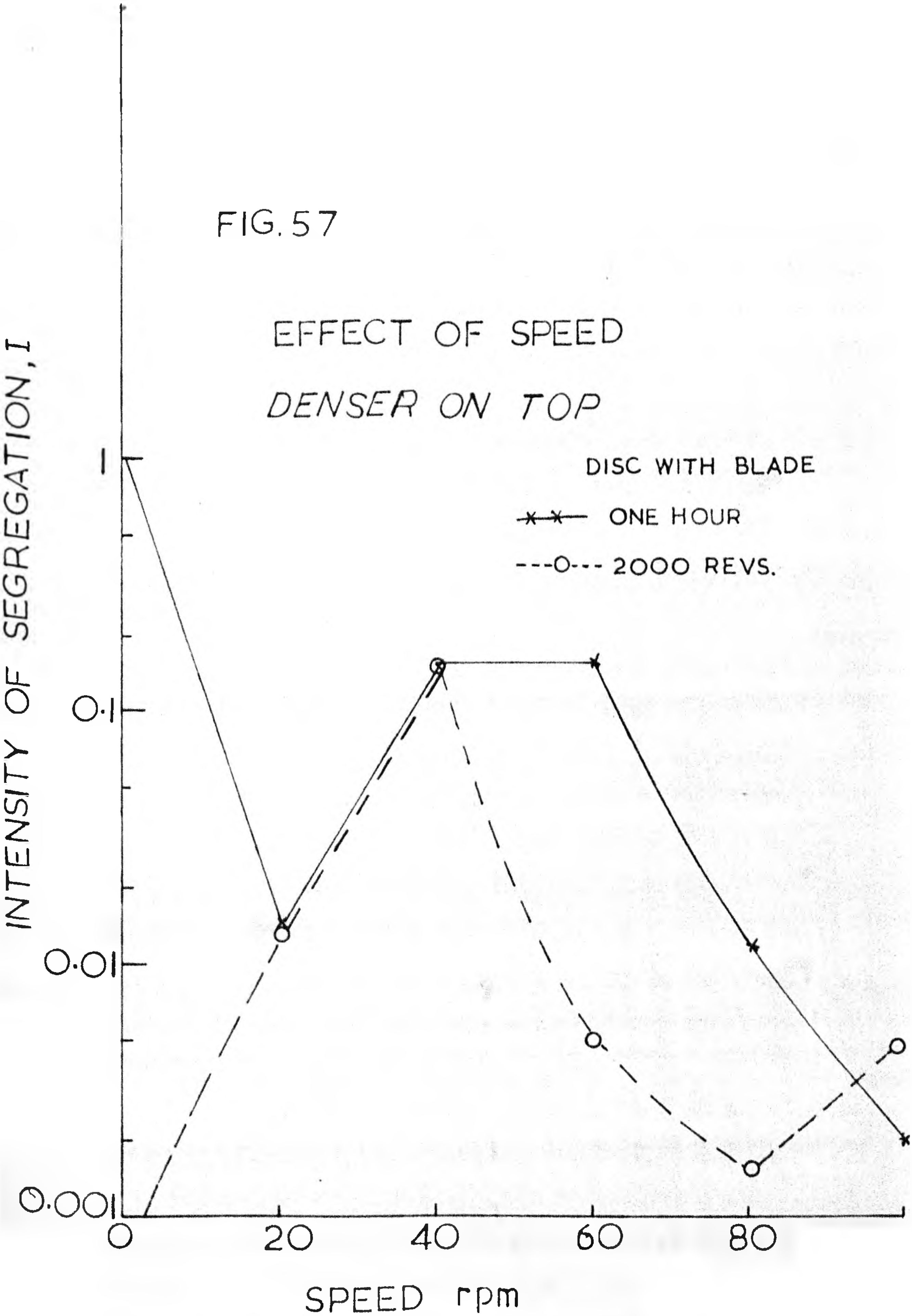


FIG. 57



EFFECT OF SPEED

DENSER ON TOP

8 hours:- The bulk inhomogeneity is not serious. A fairly thick layer still lies on the bottom; it looks thicker but more diffuse than at 4 hours.

16 hours:- The layer on the bottom is still there. This is relatively thick but becoming much more diffused. No cords are seen in the rest of the melt.

(ii) Stirred melts

1 hour:- This is much more homogeneous than the unstirred melt at 1 hour. An interface has appeared half way down around the edge and there is evidence of well developed rotation about the axis but little sign of vertical or radial flow.

2 hours:- From the shadow pattern this seems to show fairly good mixing. There is hardly any fine detail visible but the features that are seen suggest vertical and radial flow as well as rotation about the axis.

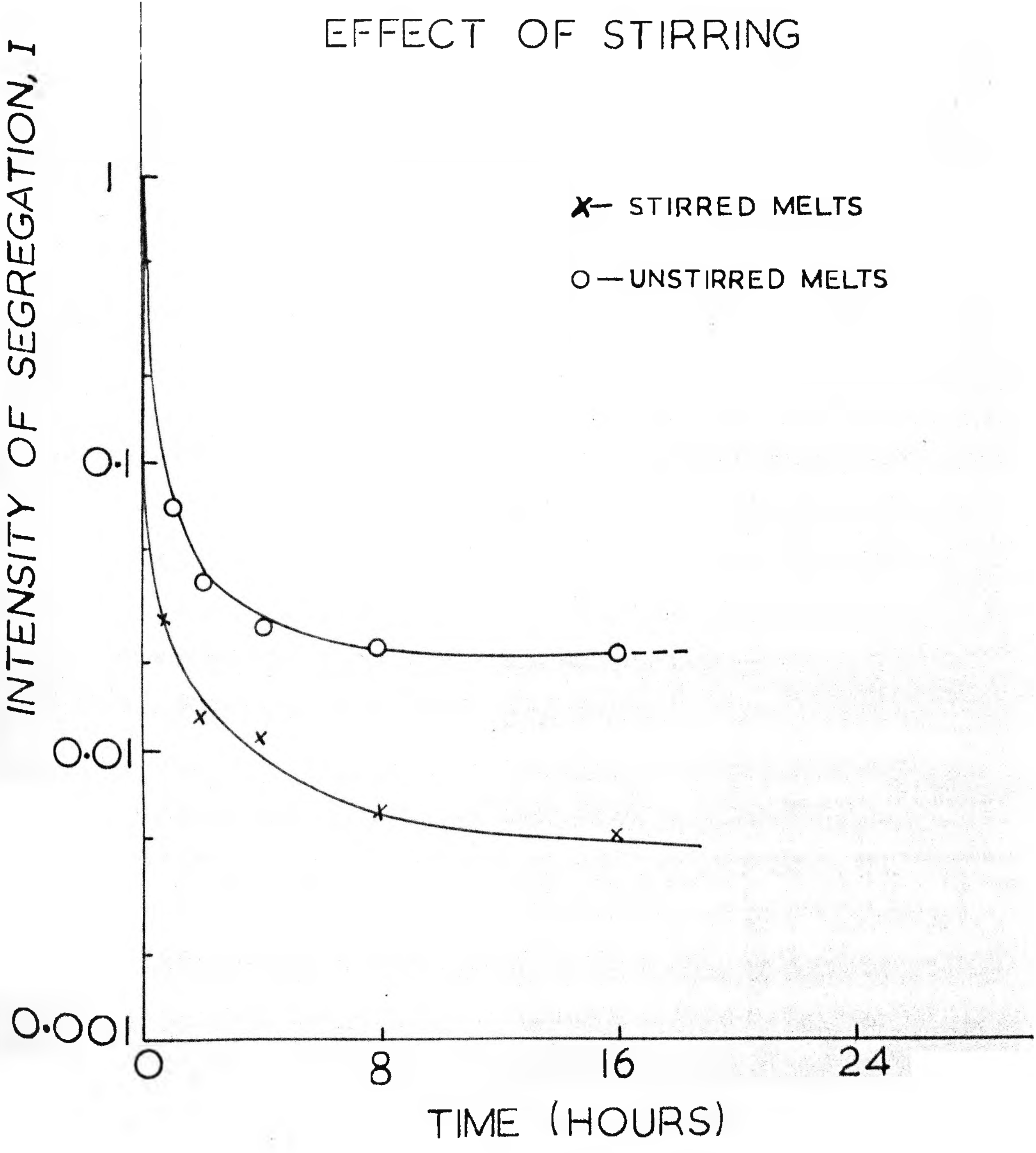
4 hours:- The interface near the walls is unexpected. It might be a later stage of that seen at one hour but does not seem to follow from the pattern seen at one hour.

8 hours:- The flow pattern is very like that at four hours but a distinct layer is seen on the bottom and this is considerably thicker than the earlier results suggest.

16 hours:- The curious interface seen at 1,4 and 8 hours stirring is absent. A distinct layer thinner than that at 8 hours is still seen. This result could be the natural successor to that obtained at 8 hours.

The stirred melts are always more homogeneous than the unstirred (see Figure 56). The difference is very obvious early in the process on the shadow patterns. The formation and

FIG. 56



EFFECT OF STIRRING

persistence of the thin layer on the bottom with the simple disc was not expected. To remove this a better stirrer is needed. It is not clear whether the presence of the thin bottom layer in the stirred melts resulted from a slow settling under gravity or to accidentral differences in effective initial distribution in the different melts.

7 EFFECT OF TIME ON AMOUNT OF DIFFUSION

A few experiments were done in which the melt was left in the furnace for half an hour after stirring stopped. A comparison of these results with these removed from the furnace as soon as stirring ceased is shown in Figure 47. The glasses used were 1 and 2 with a vertical interface in the initial distribution. The stirrer was the plain disc.

200 revs:- After 200 revolutions the flow pattern is not well developed. The shadow pattern of the melt removed at once shows very fine detail. After leaving for half an hour a considerable amount of fine detail has disappeared and the flow pattern appears to result from local differences in density.

400 revs:- When removed as soon as stirring had stopped a fairly well developed flow pattern is seen.

After leaving for an additional half hour two important effects are seen.

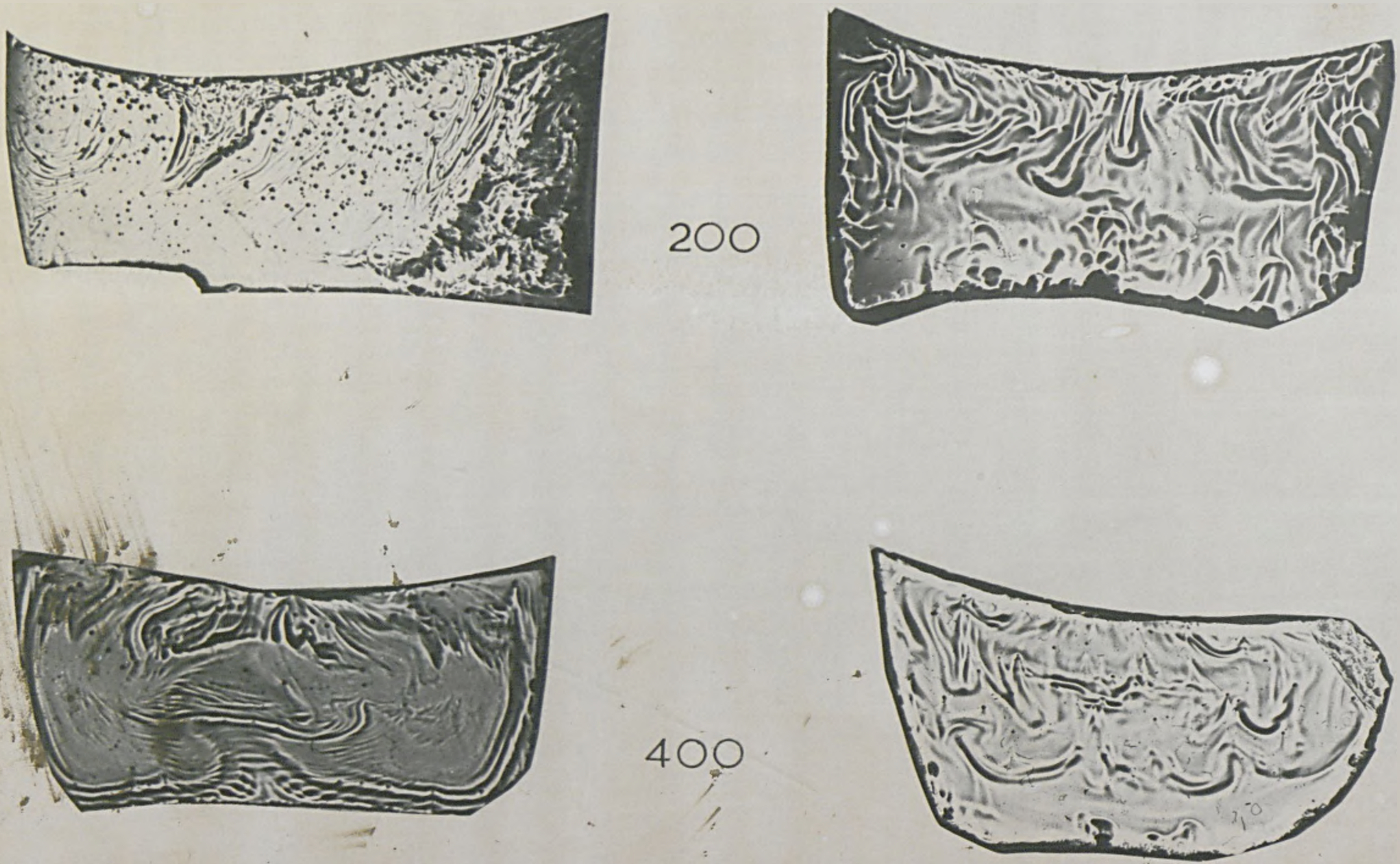
1) There is a distinct tendency to flow giving horizontal layers but these layers are deformed in some places by rising gas bubbles.

2) Disappearance of much fine detail presumably because in half an hour $\frac{Dt}{\delta^2}$ approaches or exceeds unity.

FIG. 47

REMOVED AT-ONCE

LEFT FOR 1/2 HOUR



EFFECT OF FLOW & DIFFUSION ON LEAVING THE MELT IN THE FURNACE

THE EFFECT OF LEAVING IN THE FURNACE AFTER STIRRING HAD STOPPED

Both pairs of shadow patterns show significant difference in general flow after leaving for half hour. This suggests that better mixing might possibly be obtained by several intermittent periods of stirring than by continuous stirring.

The disappearance of fine detail on leaving half hour shows that this time is sufficient for diffusion to greatly reduce the concentration differences between adjacent thin layers of cord. Considering a simple static model, a parallel sided slab of thickness 2δ, the condition for diffusion to be almost complete is

$$\frac{Dt}{\delta^2} = 1{\cdot}5$$

This gives reduction of maximum concentration difference, at the centre of the slab, to about 3% of the initial value.

Measurements made on the shadow pattern of the melt stirred for 400 revs and removed at once shows that the finer layers seen were actually about 0·08 cm thick. It can therefore be seen that these layers would be effectively removed by diffusion alone in another half hour if the diffusivity were given by

$$D \geqslant \frac{1{\cdot}5\delta^2}{t} = \frac{1{\cdot}5 \times 16 \times 10^{-4}}{1800} = 1{\cdot}4 \times 10^{-6}\,\text{cm}^2\,\text{sec}^{-1}$$

No accurate values of effective diffusivity of these glasses are available but Becker[36] estimated a diffusivity of about $6 \times 10^{-8}\,\text{cm}^2\,\text{sec}^{-1}$ for the mixing of two soda-lime-silica glasses at 1400°C. If this diffusivity applied to the present glasses, half hour would give $Dt/\delta^2 \simeq 6 \times 10^{-8} \times 1{\cdot}8 \times 10^3/1{\cdot}6 \times 10^{-3} = 0{\cdot}07$ which would be just sufficient to affect the maximum concentration difference.

If flow reduced δ by a factor of two or more after stirring stopped; then half hour would clearly be sufficient time for the fine detail to become considerably more diffuse on the shadow pattern. If the true effective diffusivity were somewhat higher the complete disappearance of fine detail in half hour would be expected when some attenuation also happened.

USE OF THE ETCHING METHOD TO MEASURE HOMOGENEITY

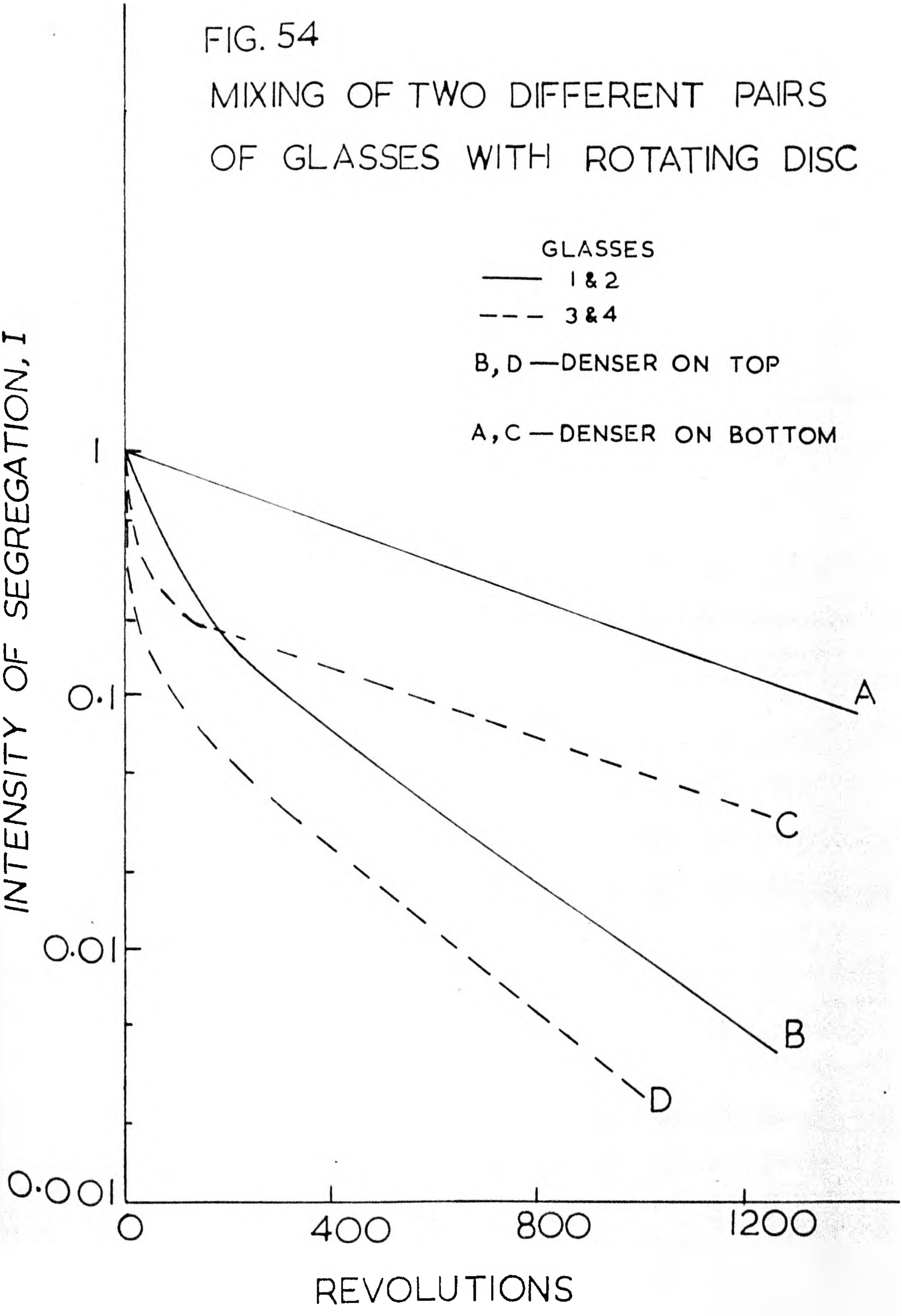
The figure 54 shows the results obtained for two different pairs of glasses, curves A and B for one pair, C and D for the other. In curves A and C the denser glass was on the bottom and in curves B and D the denser glass was on the top. The curves show a steady improvement in homogeneity with time in every case and that one can distinguish easily the difference in the rate of homogenising between the two pairs of glasses and also the greater efficiency of homogenisation when glasses flow under buoyancy forces at the beginning. From these results one can see that values of I calculated from the etching data have a quantitative significance in these experiments both for following improvement in homogeneity with time and for distinguishing different behaviour.

Similarly the efficiency of different types of stirrers can be compared when they are used under identical conditions as shown in Figure 52.

When logarithm of intensity of segregation, I, is plotted against time the results nearly always lie on a smooth curve and there is a very small scatter, showing that the measurements are reasonably precise. In some cases duplicate experiments were performed. For example in one case intensity, I, was calculated to be $1{\cdot}1 \times 10^{-2}$ and $1{\cdot}6 \times 10^{-2}$ in two different experiments.

FIG. 54

MIXING OF TWO DIFFERENT PAIRS OF GLASSES WITH ROTATING DISC



Though the difference between these results is about 40%, when I is represented on a logarithmic scale the difference becomes very small and this again confirms that the procedure used to calculate I gave sufficiently precise results, at least in the earlier stages of mixing.

This technique also gives the position of inhomogeneities and one can say, for example, whether the inhomogeneities lie on the bottom or in the centre of the melt. This information is not used when one only considers how I varies but it is always available for use in interpreting flow patterns or for any other purpose.

There are many methods which might be used to determine the homogeneity of any system including a glass melt. The etching method developed in this work has been found to be very convenient for the derivation of quantitative results and investigation of efficiency of stirrers, effect of time and so on. However, it may not always be the best method to use with glass.

Significance of intensity of segregation

In determining the intensity of segregation, I, it is necessary to specify the variance before mixing has taken place. This is very easy in the mixing of only two different phases. In this work the mixing was started with a known initial distribution of two glasses with striation thickness much greater than sample size so that the variance before mixing began was a maximum and this value was assumed to be 1. The other important assumption made was that there is a linear relation between depth of etching and composition in the region between the two glasses used.

In melting of batch it is not possible to state the initial distribution because more than two components are involved and neither composition nor quantities nor spatial distribution can be specified. This means that it is by no means easy to specify intensity, I, for freshly melted glass. This was the reason for starting with previously melted and homogenised glasses. The difficulty of defining the maximum variance and hence defining I does not affect the present work but it does complicate the extension of studies of this kind to the melting of batch. However, in this case, comparison of actual variance would be useful when studying differences between melts made from similar batches which can be assumed to produce the same maximum (but unknown) variance.

Actual glasses are usually multicomponent and equal depths of etching are given by a range of compositions not one specific composition. In the present work the glasses could be chosen to lie on a line almost perpendicular to the contours of equal depth of etching, so this was of little importance. In other systems, where regions of considerably different composition but almost the same depth of etching could exist, measurements of this kind would not give a good evaluation of homogeneity. Mass transfer and both definition and measurement of affective diffusivity are complex and difficult to evaluate in multicomponent systems which makes interpretation of results difficult.

LINEAR RELATION BETWEEN COMPOSITION AND DEPTH OF ETCHING

A small departure from a linear relation is not serious if the line joining the glass composition is almost perpendicular to lines of equal depth of etching. If this angle is very different departures from linearity or the curvature of the actual diffusion path could be serious and might give misleading values of intensity, I.

In soda-lime-silica glasses, the depth of etching is predominantly controlled by the silica content of the glass, so that depth of etching is a more sensitive measurement of variation in silica than in soda or lime content. In the present work the difference in depth of etching of the original two glasses was 16 fringes and intermediate values in the partly mixed melts were recorded only to the nearest fringe making an error of up to $\frac{1}{2}$ fringe possible. Since the difference in silica content was 5·5%, $\frac{1}{2}$ fringe difference would be equivalent to about 5·5/32 = 0·17 SiO_2. Many glasses require that difference in composition be much smaller than this but it would be possible to measure depth of etching much more accurately and detect difference in SiO_2 content at least 10 times smaller by using a high quality interferometer. The present method therefore could be made more precise.

Löffler[26], in his original work on etching of glasses, showed that other reagents (e-g HPO_3, 10% Na OH etc.) gave a different relation between depth of etching and composition. It is therefore possible to determine compositions more precisely if two etching experiments are done with different etching solutions and this would aid investigations made in multi-component systems.

SIZE OF THE SAMPLE

It has already been mentioned that the size of the individual samples required to give a reliable estimate of intensity, I, depends upon the size of the inhomogeneities present. The sample size should be no bigger than the actual size of inhomogeneities and is best rather smaller. Another problem is that if the size of the melt is increased, how should the size and number of the individual samples be increased. To get sufficiently precise results it is necessary that the sum of individual samples represents a certain proportion of the whole body. If the total sample is too small and therefore not representative, the result is inaccurate and not reproducible; if the total sample is unnecessarily big, the result is accurate but too much work is involved and time is wasted. In general it is difficult to specify beforehand how large a fraction of the whole body must be taken and this is best found by checking the reproducibility.

If it were desired to scale up the present work to investigate the mixing of larger melts one would have to consider how to change the size of the etch pits and the number of etch pits.

Initially the striation thickness was considerably greater than the size of the etch pit so that in nearly all cases the several measurements made on each pit would necessarily give the same result and 20 etch pits would really give only 20 independent values. However, in most cases average striation thickness soon became appreciably smaller than the size of the etch pit and each of the measurements made on one pit becomes an independent observation. When 3 measurements were made on each pit this gives 60 independent observations and gives a more representative sample. Using larger etch pits would not affect the true scale of examination but would make the measurements at different places on the same pit more independent of each other and this could be an advantage.

In scaling up it seems likely that the etch pits should be larger but when it is not at present known whether striation thickness would remain the same or also be scaled up in approximately the same ratio of the linear dimensions of the system, it is not clear how much larger they should be. It may be suggested that, to give rather better sampling of the body, they should be scaled up rather more than the linear scale of the melt. It is also likely that a larger number of etch pits should be used because the volume of the system increases with the cube of linear dimensions. To make the total sample the same volume fraction would mean making the etch pits very much larger unless the number is considerably increased. No simple rule can be given about how to change both number and size of etch pits.

Goodness of sampling and precision of intensity of segregation, I, should be tested by finding the reproducibility.

COMPARISON OF FLOW IN MELTS AND ROOM TEMPERATURE MODELS

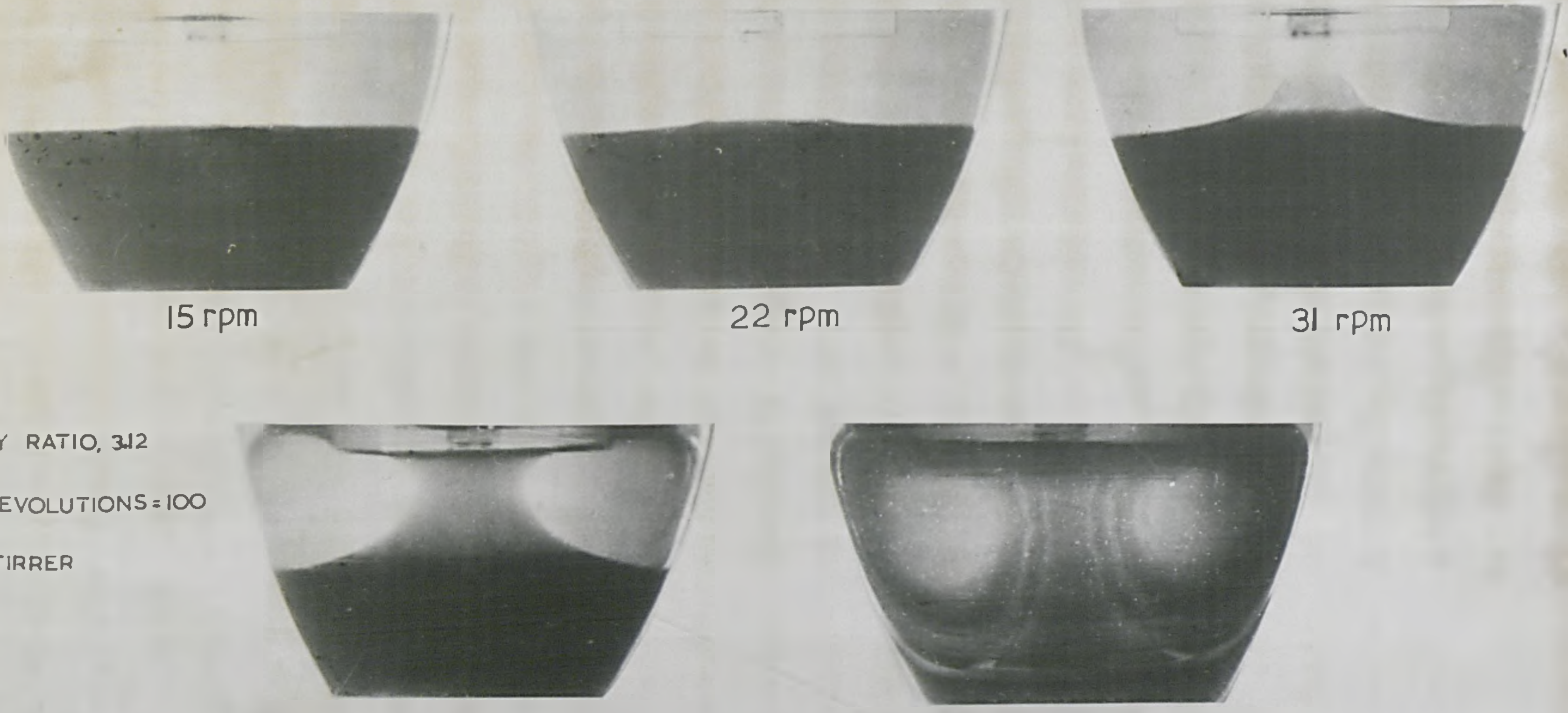
The flow patterns observed in the glass melts are completely different from those observed in the room temperature model. This may be in part due to the difference in Re number of the two systems which differ by a factor of 10. But of primary importance are the density and viscosity of the two phases to be mixed. The model, which mixed liquids of equal density and viscosity, can bear little resemblance to the glass melts, which mixed liquids of different density and viscosity. If the denser liquid is on the bottom mixing obviously more difficult as was shown by experiments with glasses, see Figures 52 and 53. However, even if the densities are identical but the viscosities different, the two liquids may not mix. When the viscosities are different, the interface between the layers may be deformed but remain stable giving very inefficient mixing. Yih[37] has shown that even for a stratified liquid flowing over a plane surface the interface may or may not be stable even at very low Re. He also showed that the ratios of the viscosities and the thicknesses of the two layers have a very important influence on stability of interface. Recent experiments by Moore[38] have confirmed that density and viscosity differences affect mixing. In the closed system used, flow pattern is much affected by speed of stirrer. Figure 58 shows how the stability of interface varies with speed of stirring for a particular viscosity ratio. There is a particular critical speed that is needed to make the liquid-liquid interface unstable, at lower speeds mixing is by diffusion aided by convection and at higher speed by attenuation and diffusion which is much more rapid.

EFFICIENCY OF STIRRERS

The efficiency of a stirrer often depends upon the initial distribution. This is clearly shown by the data in Figure 52 in which there is not much difference between the two differnnt stirrers when the denser glass is placed on the top but a big difference when the denser glass is on the bottom. The best

FIG. 58

EFFECT OF SPEED ON STABILITY OF INTERFACE



15 rpm

22 rpm

31 rpm

55 rpm

67 rpm

VISCOSITY RATIO, 3.12

TOTAL REVOLUTIONS = 100

DISC STIRRER

stirrer to use in any particular system therefore must depend on the properties and initial distribution. The stirrers studied were not very efficient mixing devices but they were originally chosen to produce simple flow patterns (in a system of equal density and viscosity) which would aid understanding of the experimental results, rather than for maximum efficiency. The stirrers used all left a thin layer of glass of different composition at the bottom of the crucible but the necessary condition that velocity is zero in contact with the metal wall makes mixing of such a layer difficult in any case.

The disc is not an efficient mixer but it is a convenient standard for comparison of the performance of other stirrers.

The addition of a blade to the disc breaks up the interface and increases the mixing efficiency particularly when the denser glass is on the bottom, but the homogeneity obtained is not of optical quality.

The complex disc stirrer is only efficient when the lower disc is above the liquid-liquid interface. This stirrer can be used to remove the thin layer on the bottom of the melt, rather quicker than either of the others but does not mix the bulk of the liquid so well.

MEAN DEPTH OF ETCHING

The original homogenised glasses 1 and 2 were etched in the standard conditions, that is for ten minutes at 20°C, and gave depth of etching 10 and 26 fringes respectively. After mixing the two glasses for different number of revolutions, for one set of experiments all the specimen were etched together at the same time. Differences in mean depth of etching in any set therefore could not be due to differences in etching conditions. But as the different sets were not etched together, they could differ slightly from each other. This can happen with a very slight difference of experimental conditions, for example a $\frac{1}{2}$°C difference in temperature can vary the depth of etching by three to four fringes, small differences in time of etching have much less effect.

The depth of etching can also vary for individual samples if the photoresist is not properly washed away from the etch pits but care was taken in preparing the sections to avoid this. Differences in mean depth of etching in any one set of experiments might be due to sampling errors or a non-linear relation between depth of etching and composition. The former would be random but the latter would probably change steadily as mixing improved.

To examine the way in which depth of etching varied the results for each set of melts were treated as if mean depth was to be used for a control chart and the probability of the various values being statistically significant estimated from the ranges. Some of the results are shown in Table XIV. Out of 44 results, 14 lie outside the limit that the probability of the differences is significant is 5% and 6 beyond the 0·1% probability limit. The data do not suggest a general trend of mean depth with increased mixing and therefore do not suggest distinct non-linear relation between composition and depth of etching. The number of observations beyond the 5% or 0·1% probability limits suggests that the total sample taken in each melt was not quite large enough to be truly representative. The variation in grand means between sets of results shows some small difference in etching conditions.

CONCLUSIONS

Most of the detailed conclusions drawn in the case of experiments with different stirrers, development of etching technique and different flow patterns have already been given at the appropriate places in the text. Figures 48 to 53 show the main results of the behaviour of different types of stirrers. However, some important conclusions drawn during the present work can be summerised here.

1) The etching and interferometery technique developed in this work gives a useful quantitative description of homogeneity, and information about the position and intensity of the cord. It is however, too lengthy a method to use in industry for the daily or more frequent estimation of the homogeneity of glass. However, any technique suitable for use when rates of production are 100 or more tons a day will be difficult to find.

2) The technique can be used to distinguish between systems that behave differently and to compare the efficiency of different types of stirrers.

3) The results obtained for intensity of segregation and flow patterns showed that the behaviour of the glass melts was not similar to that of room temperature systems. This might partly be due to Reynolds number not being properly matched but was largely due to differences in viscosity and density of the two glasses used.

4) Of the three different stirrers used, the disc with blade is the best mixing device, especially when the denser glass is put on the bottom.

5) In melts that are not stirred the homogeneity improves rapidly with time up to 2-4 hours melting and then more slowly

up to 8 hours. Beyond 8 hours, there is very little further improvement. Plots of I vs time were of rather similar shape for melts which were stirred but the homogeneity of stirred melts was considerably better than of unstirred melts.

FURTHER WORK

From the present work we know that density and viscosity have important effects on the flow pattern and extensive work should be done on model at room temperature with different liquids of different properties as well as further experiments at higher temperature, to show that behaviour is similar when Reynolds number, viscosities and densities are properly matched. To match these properly more accurate values for density and viscosity of the glasses used will be necessary.

In this investigation batch was not sintered, but it is believed that sintering the batch material before melting gives a more homogeneous product than one in which the raw batch is melted directly and so this should be investigated in future.

In these experiments 90 gms of glass was melted. To see the effect of scaling up, experiments should be done with melts considerably larger scale, for example about 1500 gms.

When very homogeneous glasses are needed the etching and interferometry method may not be sufficiently sensitive and other techniques of measuring intensity of segregation may need to be developed.

TABLE I

THE EFFECT OF CHANGE IN GLASS COMPOSITION ON DENSITY OF A CONTAINER GLASS

	Substituting one glass forming oxide for another				Change in Density g/cc
	SiO_2	Na_2O	CaO	Al_2O_3	
+ 1% SiO_2	-	- 0·0075	- 0·00127	- 0·0043	- 0·0085
+ 1% Na_2O	+ 0·0075	-	- 0·0053	+ 0·0033	+ 0·0065
+ 1% CaO	+ 0·0127	+ 0·0053	-	+ 0·0085	+ 0·0120
+ 1% Al_2O_3	+ 0·0043	- 0·0033	- 0·0085	-	+ 0·0020

TABLE II

COMPOSITIONS OF GLASSES USED (wt. %)

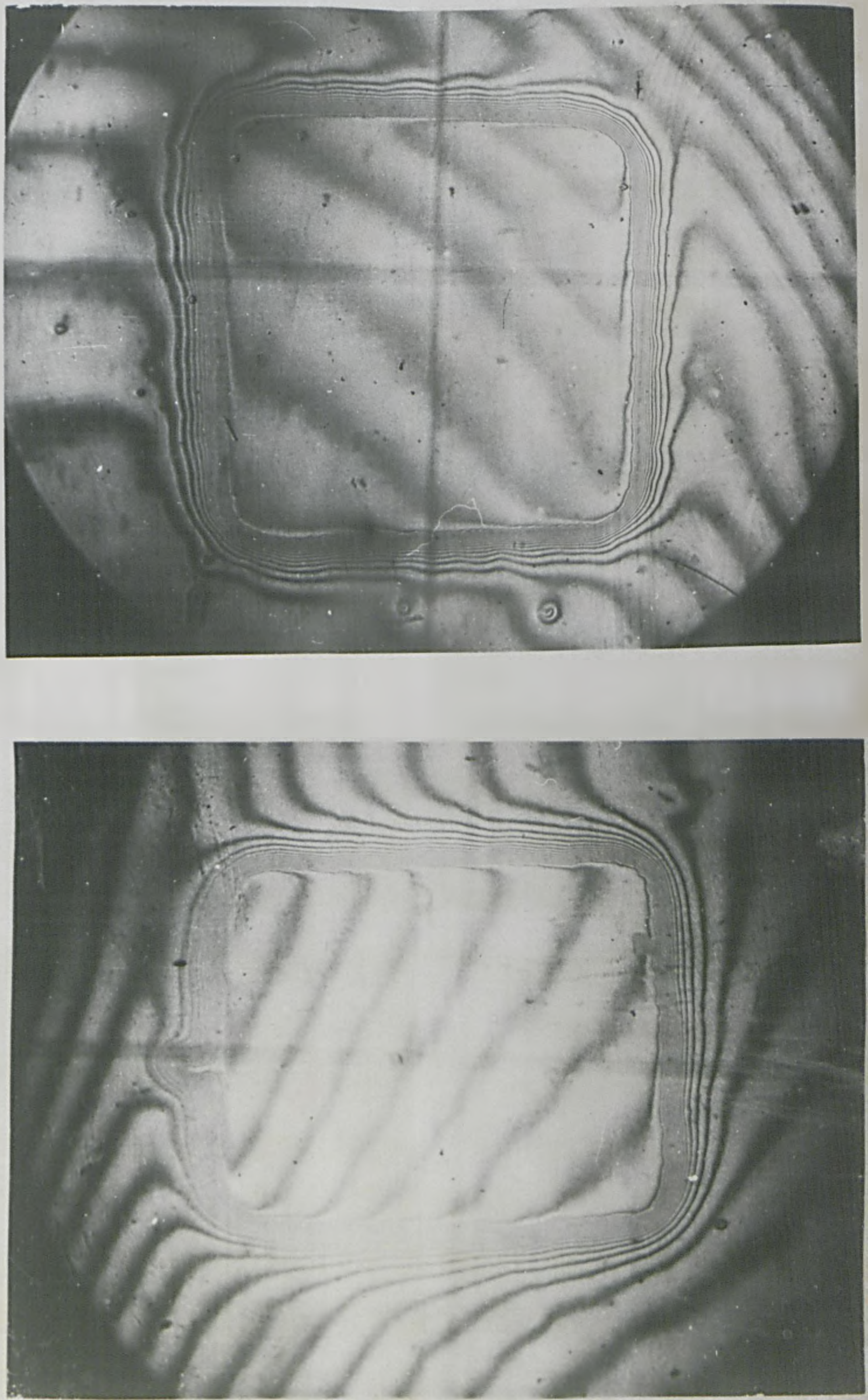
Glass	SiO_2	Na_2O	CaO	CoO
1	73·50	16·50	10·0	0·025% of total batch
2	68·0	17·0	15·0	-
3	70·0	10·0	20·0	0·025% of total batch
4	72·25	15·15	12·15	-

TABLE III

B.S.Mesh No.	Aperture mm	Sand grain size mm
25	0·599	0·510
36	0·422	0·337
60	0·251	0·220
85	0·178	0·150
120	0·124	0·114
150	0·104	0·096
170	0·089	0·071
240	0·066	

FIG.59

TYPICAL ETCH PITS



APPENDIX

INDIVIDUAL EXPERIMENTAL DATA

In each set of experiments, the mean depth of etching, variance and intensity of segregation was calculated separately. The data for each set is given in tables IV to XIII.

TABLE IV

GLASSES 1 AND 2

Initial Distribution - Denser glass on the top

Stirrer - Plain Disc

Speed - 20 r.p.m.

Depth of etching in fringes	Frequency					
	50 revs	100 revs	200 revs	400 revs	800 revs	1200 revs
10	-	5	-	2	-	-
11	7	-	-	-	-	-
12	15	7	-	2	-	-
13	3	3	6	3	2	-
14	-	7	5	5	7	-
15	-	5	10	16	16	33
16	-	5	7	9	11	13
17	-	2	5	6	13	7
18	1	1	2	-	7	-
19	-	2	5	10	-	-
20	1	7	6	4	-	-
21	1	3	1	-	-	-
22	2	1	4	-	-	-
23	8	1	2	-	-	-
24	7	-	3	-	-	-
25	2	-	-	-	-	-
26	-	-	-	-	-	-
Mean Depth	17·05	15·54	17·0	16·08	15·84	15·50
Variance	32·1	14·40	11·44	5·52	1·8	0·52
Intensity	0·47	0·21	0·16	0·079	0·020	0·0043

TABLE V

GLASSES 1 AND 2

Initial Distribution - Denser glass on the bottom

Stirrer - Plain Disc

Speed - 20 r.p.m.

Depth of etching in fringes	Frequency					
	50 revs	200 revs	400 revs	800 revs	1000 revs	1200 revs
10	10	-	-	-	-	-
11	12	-	-	-	-	-
12	8	10	-	-	-	-
13	7	23	12	-	-	-
14	-	2	13	13	14	-
15	-	-	-	-	-	15
16	-	4	12	10	8	-
17	-	-	-	6	9	-
18	-	-	-	3	3	25
19	-	-	8	-	-	-
20	-	-	7	5	7	12
21	-	-	-	7	7	-
22	-	5	-	-	-	-
23	4	-	-	-	-	-
24	12	-	-	-	-	10
25	13	17	15	7	7	-
26	-	-	-	-	-	-
Mean depth	19·1	16·5	17·8	17·03	18·02	18·61
Variance	56·44	43·23	23·97	16·67	13·7	8·7
Intensity	0·85	0·65	0·36	0·25	0·20	0·13

TABLE VI

GLASSES 3 AND 4

Initial Distribution - Denser glass on top

Stirrer - Plain Disc

Speed - 20 r.p.m.

Depth of etching in fringes	Frequency 50 revs	100 revs	200 revs	400 revs	800 revs	1000 revs.	1200 revs.
10	-	-	-	-	-	-	-
11	-	2	-	-	-	-	-
12	-	5	-	7	2	-	-
13	-	7	-	7	-	-	-
14	-	10	-	14	10	-	-
15	-	12	-	14	43	-	-
16	-	10	-	18	13	-	-
17	-	3	-	4	-	-	-
18	-	2	-	2	-	-	-
19	-	2	-	-	-	-	-
20	-	4	-	-	-	-	-
21	-	1	-	-	-	-	-
Mean depth	-	16·1	-	14·5	15·1	-	-
Variance	-	5·87	-	2·21	0·60	-	-
Intensity	-	0·0835	-	0·029	0·0053	-	-

TABLE VII

GLASSES 3 AND 4

Initial Distribution - Denser glass on the bottom

Stirrer - Plain Disc

Speed - 20 r.p.m.

	Frequency						
Depth of etching in fringes	50 revs.	100 revs	200 revs	400 revs	800 revs	1000 revs	1200 revs
10	6	-	1	-	-	-	-
11	12	-	7	-	-	-	-
12	3	-	10	-	-	-	5
13	7	-	16	-	-	-	11
14	3	-	11	-	-	-	29
15	-	-	10	-	-	-	8
16	2	-	2	-	-	-	3
17	4	-	3	-	-	-	8
18	4	-	2	-	-	-	6
19	2	-	2	-	-	-	1
20	11	-	-	-	-	-	-
21	2	-	-	-	-	-	-
22	2	-	-	-	-	-	-
Mean depth	17•0	-	14•1	-	-	-	14•7
Variance	16•60	-	4•0	-	-	-	2•86
Intensity	0•246	-	0•19	-	-	-	0•0394

TABLE VIII

GLASSES 1 AND 2

Initial Distribution - Denser glass on the top

Stirrer - Disc with blade

Speed - 20 r.p.m.

Depth of etching in fringes	Frequency							
	100 revs	200 revs	400 revs	600 revs	800 revs	1000 revs	1200 revs	1500 revs
10	2	-	-	-	-	-	-	-
11	3	-	-	-	-	-	-	-
12	5	13	-	-	-	-	-	-
13	3	-	8	-	-	-	-	-
14	-	15	4	5	-	-	-	-
15	-	9	13	8	10	-	10	-
16	6	-	6	30	28	-	15	16
17	3	3	4	13	8	-	20	40
18	4	4	6	3	3	13	14	-
19	-	3	7	5	2	-	-	-
20	10	4	4	-	2	19	-	-
21	10	3	-	-	-	8	-	-
22	-	-	5	-	-	6	-	-
23	-	-	-	-	-	-	-	-
24	-	-	-	-	-	-	-	-
25	-	-	-	-	-	-	-	-
26	-	-	-	-	-	-	-	-
Mean Depth	17·13	15·70	16·66	16·32	16·36	19·62	16·71	16·66
Variance	13·78	13·31	7·31	1·74	1·47	1·39	1·04	0·23
Intensity	0·204	0·179	0·107	0·026	0·020	0·018	0·012	0·0024

TABLE IX

GLASSES 1 AND 2

Initial Distribution - Denser glass on the bottom

Stirrer - Disc with blade

Speed - 20 r.p.m.

	Frequency				
Depth of etching in fringes	100 revs	400 revs	800 revs	1000 revs	1200 revs
10	-	-	-	-	-
11	1	-	-	-	-
12	11	-	-	-	-
13	23	6	-	-	-
14	3	5	6	-	-
15	-	10	9	-	-
16	4	8	29	-	-
17	-	4	13	-	4
18	9	3	1	6	28
19	-	5	-	10	35
20	8	6	-	27	-
21	-	-	-	20	-
22	-	5	-	-	-
23	-	2	-	-	-
24	-	3	-	-	-
25	16	-	-	-	-
26	-	-	-	-	-
Mean depth	18·19	17·0	16·80	19·97	18·46
Variance	43·1	11·60	1·80	0·85	0·38
Intensity	0·62	0·17	0·027	0·011	0·0046

TABLE X

GLASSES 1 AND 2

Initial Distribution - Denser glass on the bottom

Stirrer - Complex Disc

Speed - 20 r.p.m.

Depth of etching in fringe	Frequency				
	100 revs	400 revs	800 revs	1000 revs	1500 revs
10	6	-	-	-	-
11	2	-	-	-	-
12	7	-	-	-	-
13	3	-	-	-	-
14	-	-	-	-	-
15	-	-	-	-	-
16	-	-	-	-	-
17	5	17	10	7	9
18	2	13	30	29	25
19	1	6	-	-	-
20	10	4	8	12	10
21	10	4	-	-	-
22	3	-	-	-	-
23	1	-	-	-	-
24	-	6	5	-	-
25	-	10	7	12	12
26	-	-	-	-	-
Mean depth	17·10	19·71	19·50	19 70	19·50
Variance	13·72	9·80	7·54	7·32	7·20
Intensity	0·20	0·14	0·11	0·105	0·10

TABLE XI

EFFECT OF SPEED
(Constant Revolutions)

GLASSES 1 AND 2

Initial distribution - Denser glass on the bottom

Total revolutions - 1200

Stirrer - Plain Disc

Depth of etching in fringes	Frequency 20 r.p.m.	40 r.p.m.	60 r.p.m.	100 r.p.m.	120 r.p.m.
10	-	-	-	-	-
11	-	-	-	-	-
12	-	-	-	-	-
13	-	-	-	-	-
14	-	-	-	-	-
15	15	-	-	-	-
16	-	5	-	-	-
17	-	3	5	-	-
18	25	15	20	-	-
19	-	5	13	-	-
20	12	20	10	16	23
21	-	-	-	25	20
22	-	-	12	14	10
23	-	-	-	-	-
24	10	10	-	-	-
25	-	-	-	2	-
26	-	-	-	-	-
Mean Depth	18·61	19·7	19·34	21·0	20·7
Variance	8·7	5·38	2·65	1·06	0·55
Intensity	0·13	0·080	0·040	0·015	0·0075

TABLE XII

EFFECT OF SPEED
(constant time)

GLASSES 1 AND 2

Initial distribution - Denser glass on the top

Stirrer - Disc with blade

Total time - one hour

Depth of etching in fringes	Frequency				
	20 r.p.m.	40 r.p.m.	60 r.p.m.	80 r.p.m.	100 r.p.m.
10	-	-	-	-	-
11	-	-	-	-	-
12	-	-	-	-	-
13	-	-	-	-	-
14	-	-	11	-	-
15	10	-	41	-	-
16	15	8	-	6	5
17	20	39	-	10	42
18	14	3	-	12	6
19	-	-	-	3	-
20	-	-	-	-	-
21	-	-	-	-	-
22	-	1	-	-	-
23	-	-	-	-	-
24	-	-	-	-	-
25	-	10	6	-	-
26	-	-	-	-	-
Mean Depth	16•71	18•31	15•84	17•38	17•02
Variance	1•04	9•37	9•48	0•82	0•20
Intensity	0•014	0•140	0•141	0•0112	0•0019

TABLE XIII

EFFECT OF SPEED
(Constant Revolutions)

GLASSES 1 AND 2

Initial distribution - Denser glass on the top

Stirrer - Disc with blade

Total revolutions - 2000

Depth of etching in fringes	Frequency 20 r.p.m.	40 r.p.m.	60 r.p.m.	80 r.p.m.	100 r.p.m.
10	-	-	-	-	-
11	-	-	-	-	-
12	-	-	-	-	-
13	-	-	-	-	-
14	-	-	-	-	-
15	-	-	-	-	-
16	-	8	7	10	-
17	50	39	37	42	-
18	-	3	11	2	5
19	8	-	-	-	30
20	6	-	-	-	20
21	-	-	-	-	-
22	-	-	-	-	-
23	-	-	-	-	-
24	-	-	-	-	-
25	-	11	-	-	-
26	-	-	-	-	-
Mean Depth	17·48	18·36	17·07	16·89	19·27
Variance	0·99	9·88	0·32	0·18	0·40
Intensity	0·0138	0·147	0·0039	0·0015	0·0049

TABLE XIV

	Revolutions	Mean Depth	Standard Deviation	Group Mean	Mean Standard Deviation	Notes
Glasses - 1 & 2 Denser glass on top Stirrer - Plain Disc	50	17·05	5·65	16·17	2·91	Outside 5%Limit
	100	15·54	3·94			-
	200	17·00	3·51			Outside 5%limit
	400	16·08	2·34			-
	800	15·84	1·34			-
	1200	15·50	0·72			Outside 0·1%limit
Glasses - 1 & 2 Denser glass on bottom Stirrer - Plain Disc	50	19·10	7·51	17·84	4·93	Outside 5%limit
	200	16·50	6·50			Outside 5%limit
	400	17·80	4·88			-
	800	17·03	4·07			-
	1000	18·02	3·70			-
	1200	18·61	2·94			-
Glasses - 1 & 2 Denser glass on top Stirrer - Disc with blade	100	17·13	3·70	16·89	1·98	-
	200	15·70	3·64			Outside 0·1%limit
	400	16·66	2·70			-
	600	16·32	1·31			Outside 5%limit
	800	16·36	1·21			Outside 5%limit
	1000	19·62	1·79			Outside 0·1%limit
	1200	16·71	1·01			-
	1500	16·66	0·48			-
Glasses - 1&2 Denser glass on bottom Stirrer - Disc with blade	100	18·19	6·56	18·10	2·57	-
	400	17·0	3·40			Outside 0·1% limit
	800	16·80	1·34			Outside 0·1%limit
	1000	19·97	0·92			Outside 0·1%limit
	1200	18·46	0·62			-
Glasses - 1 & 2 Denser on bottom Complex Disc stirrer	100	17·10	3·70	19·10	2·99	Outside 5%limit
	400	19·71	3·13			-
	800	19·50	2·74			-
	1000	19·70	2·70			-
	1500	19·50	2·68			-

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