FUNDAMENTAL ASPECTS OF THE MIXING

OF PLASTIC MATERIALS

by

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THESIS

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CORRECTION AND NOTE

1. In Tables I, II, III, the sequence of the numbers in the first row should be reversed, in each case :

e.g. Instead of Diam. .86 .69 .52 .36 .20 .04
it should read Diam. .04 .20 .36 .52 .69 .86

2. Spot diameters given in inches, refer to dimensions on the photographic plates. To convert these to dimensions in the original mixture, the numerical values should be divided by the factor 2.3 (the photographic magnification).

When you can measure what you are speaking about,
and can express it in numbers, you know something
about it.

Lord Kelvin

C O N T E N T S

§§§§§§§§§

FIGURES

25. Brabender mixer:- Quantity - mixing energy and $T_{\frac{1}{2}}$.

26. Prong mixer:- Quantity - power

27.   "   " - mixing rate.

28.   "   " - mixing energy and $T_{\frac{1}{2}}$.

29. Morton Duplex mixer - Photograph.

30.   " - Rate of mixing.

§§§§§§§§§§

SECTION 1.

SUMMARY

SUMMARY

1.   The thesis falls into three main sections.   In the first the theoretical aspects of the problem are considered, and a rational basis for analysis of experimental results derived.   The second section describes the development of a new technique for measuring the progress of mixing, and its application to mixing machines.   Findings are reviewed in the final section.

The theoretical ideas developed on the assessment of mixing offer a background, to include less comprehensive but more experimentally convenient measures of this state of mixing.   A concentration distribution spectrum is proposed, as giving fundamental meaning to the ideas of "clumping" of the components which make up a mixture.   Analysis of the influence, on sample composition measures, of sample size, emphasises its association with scale effects and the progress of mixing, and this whole topic is discussed in some detail.

All available evidence on rates of mixing is shown to indicate that, over a substantial range, a first order kinetic mechanism applies.   The influence of sample size on rate determinations is shown to be small, a finding of value in interpreting experimental results and in scaling up from laboratory trials.

Possible measures of efficiency are considered, and

though the fundamental criteria are elusive, practical parameters are suggested and developed.

An experimental method of following the **progress of** mixing of flour doughs was evolved, and is **described in** detail. Analysis is carried out by photographing the **pattern** produced by colour differentiated **components.** The photographic plates are then scanned, using **a photometric** technique, to give a measure of the mixing. **This measure** is shown to be reproducible, self consistent, **and in agree-** ment with such theoretical predictions as can be made.

The method is first applied to investigate the **theoretical** concepts, and then to assess the **performance** characteristics of two types of laboratory mixers. **This** **produces** evidence that the "sigmoid arm" kneading **machines,** **extensively** used in practice, are less efficient than other **types.** **Finally,** it is shown that the method **can be extended** **readily to a commercial scale mixing machine.**

SECTION 2.

INTRODUCTION

INTRODUCTION

2.   Mixing, though its uses are extensive and diversi-
fied, is still an art rather than a science.   The
reasons for this are not its lack of importance for it is
an essential operation of modern chemical industry, but
rather its apparent simplicity, contrasted with the diffi-
culty of an adequate quantitative description.

No comprehensive measure exists to measure the state
of a mixture, nor have the associated problems of predicting,
and measuring, mixing machine performances, been solved.
Outside a few specialised topics, whose urgency has compelled
attention, the experimental data available are limited in
scope and utility.   The bulk of the work remains to be done,
both in formulating the fundamental theory, and in performing
the experiments which must accompany, establish, and apply,
this theory.   The only basis for design at present is
accumulated experience, and better and cheaper mixing equip-
ment could be expected to result from a more rational
approach.

This study is an investigation into some mixing
problems, with particular reference to the mixing of plastic
and semi-solid materials, where natural diffusion plays no
appreciable part, and the mixing is accomplished by cyclic
disturbances which rearrange the components.   An attempt is

made to extend basic knowledge of the mixing process, and also an account of an experimental technique, designed to measure this is given, together with results from its application.

The thesis falls into three main sections. The first is concerned with the fundamental theory. Following a review and discussion of the published literature, extensions to this are proposed particularly on the subject of the state of a mixture. The scope of the treatment is broad, trying to indicate both the extent and the lack of knowledge.

The second section is an account of the experimental work and its results. It is concerned with plastic materials, and arises, in part, from a problem in the baking industry. A technique is evolved to assess such mixtures and applied to practical examples. Details are given of the apparatus, the method, and the results obtained.

Finally there is a section giving a discussion of the results and some conclusions. The experimental work is discussed, appraised critically, and related as far as possible to the theoretical ideas and practical applications.

An index of the notation used, folding out for convenient reference may be found at the back of this volume.

SECTION 3.

FUNDAMENTAL THEORY

3.   FUNDAMENTAL   THEORY

The problems associated with the development of a
theory of mixing fall into three main groups,   a)
the measurement of the state of mixing,   b) the mechanism
and rates by which this state can be changed by external
or internal forces, and   c) the energy and efficiency
considerations involved in these changes.

This section deals with these in turn, presenting for
each a short introduction, a review of the published work,
such new ideas as can be put forward, and finally an attempt
to sum up the position.   The main interest throughout is in
plastic mixing, but much of the discussion is general and
covers broad aspects of the subject.

3.1   The Measurement of State or Degree of Mixing.

3.11   Stated as simply as possible, the problem is to
                characterise, in some way, the distribution of the
different components throughout the mixture.   For any
mixture in which there are distinguishable components, there
are ideas of clumping and grouping of these into various
regions where individual components predominate.   A descrip-
tion of the mixture has to give as briefly as possible, that
is using the fewest parameters, information as to the size
and distribution of these "clumps".   It must inevitably
compromise between the twin limits of, on the one hand vast

FIG. 1.
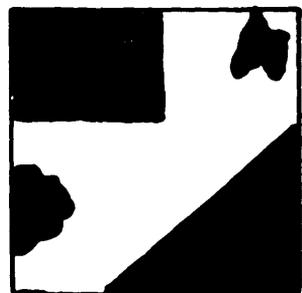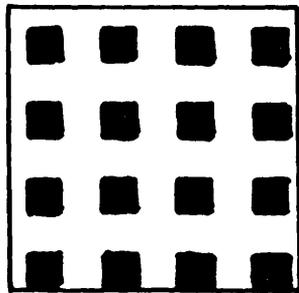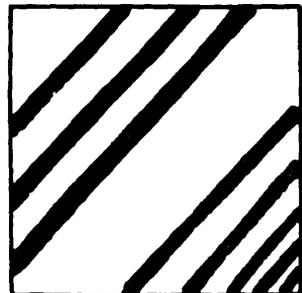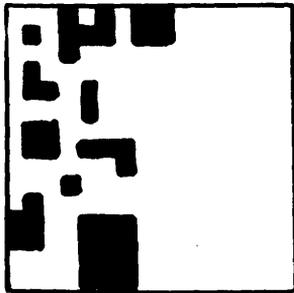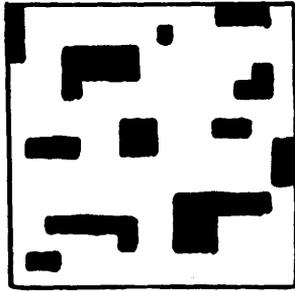
MIXTURE PATTERNS

numbers of terms which will give the position of every particle in the system but are quite unmanageable, and on the other one or two terms which can arise from vast numbers of systems.

The range of dispersion for which the measure must account is very wide, and some idea of its extent is given by the patterns of Fig.1. These range from the wholly regular to the random, with all manner of possibilities in between. It seems unreasonable to condemn any of these, even the regular ones, as being outside the scope of mixing because no ordinary mixing machine will produce them; there is no doubt that they are mixed in at least one sense, and, if possible, must be included. Now comes the problem; of the patterns given, and all the other possible ones, how can it be decided which is the better mixed, and to what extent. In the following discussion several proposed solutions will be examined. It will be seen that they are all based on statistical measurements because, at least from the experimental side, this seems to be the only possible mode of attack, and any theory which cannot be applied to experiment in some way is little more than an imaginative exercise. Beyond this they vary to some extent, though there is much underlying uniformity. To make the treatment more compact only two component systems will be considered.

3.12   Variation in Sample Composition.

Perhaps the most immediately obvious approach to the problem of measuring mixing, is to consider the composition of samples drawn from the mixture.   The overall proportion of the components is usually known, but in a random sample the components present will not in general have this same proportion, though if a large number of them are taken their mean proportions will approach that of the mixture as a whole.   When in a relatively un-mixed state the variation in sample proportions will be considerable, and this variation will diminish as the mixing proceeds. Consequently a measure of this variation would seem to correspond to intuitive concepts of mixing.

3.121   Statistical Measures.

There are two convenient ways of handling this variation:-

3.1211   The Mean Absolute Deviation.

Consider a mixture of proportions $\bar{a}$ of component A , $\bar{b}$ of component B.   Various samples drawn from this $s_1, s_2, s_3 \ldots\ldots s_n$ will have proportions $a_1, a_2, a_3 \ldots\ldots a_n$ of A.   The mean absolute deviation of their proportions is given by:

$$d = \overline{|(a - \bar{a})|} \qquad\qquad \ldots\ldots 1.$$

It may be seen that, if the sample proportions are known, d is quite easily calculated, but it is difficult to handle in a theoretical treatment because of the occurrence of the "absolute value" which makes the algebra very complicated.

3.1212 The Variance and Standard Deviation.

Taking the same notation as above, the standard deviation is

$$\bar{s} = \sqrt{\overline{(a-\bar{a})^2}}$$

.... 2.

the variance being, quite simply, $\bar{s}^2$.

The mean square process in effect treats the absolute values of the deviations, but does not involve the restriction of introducing it explicitly, and the variance, in particular, is convenient to handle theoretically. Because of its dimensions $\bar{s}$ is perhaps to be preferred to $\bar{s}^2$ in practical work, but the transition from one to the other is very direct and simple. From a set of experimental sample proportion figures $\bar{s}$ is a little more tedious to calculate than d , but this is more than compensated for by its other properties. In the review below references i. and ii. use the mean absolute deviation type, while iii-ix. use the standard deviation or a derivative of it.

3.122   Review of the Literature Using These Measures.

i)   Coulson and Maitra[5] effectively use the mean
absolute deviation as the measure of mixing in their
experimental work.   They select samples from a batch of
them, such that they have "approximately" the mean composi-
tion, and, according to the percentage of these in the
batch, define the percentage of mixing.   Presumably this
implies selecting the proportion of samples whose d is
less than some predetermined value, which is not specified
but may depend on the limits of experimental measurement.
Extensive experimental results are given by these workers
using a mixture of sand and coal particles.

ii)   Visman and Van Krevelen[15] again take a similar type
of measure using a percentage, this being, in their
case, estimated by taking the samples un-mixed to be all
those within stated limits of $d > .4$, for $\bar{a} = \bar{b} = .5$.

iii)   The first use of $\bar{s}$ as a measure of mixing, is in a
paper by Lowry[8] on the Mixing of Amatol.   His
interest was mainly experimental for use as a control
measure, and he did not enter into any theoretical argument
nor extend his measure by elaborations.

iv)   Perhaps the most comprehensive discussion of the use
of $\bar{s}$ and $\bar{s}^2$ is that in two papers by Lacey[7], the

later one being much the more extensive.   He postulates
that $\bar{s}^2$ varies between definite limits, proceeding from
the completely un-mixed to the completely mixed states.
His limiting values are:-

a) The initial or non-mixed state, in which each
sample is either A or non-A, and so for this
component he derives the relation:

$$\bar{s}_o^2 \;=\; \bar{a}(\, 1 \,-\, \bar{a}\,) \qquad \text{.... 3.}$$

b) The final state, in which he considers that the
perfect mixture occurs when there is a random
dispersion of one component through the other.   Dealing
with particle mixing, he gives as his criterion of this
random state that the chance of an unbiassed selection of
one particle, from anywhere in the mass, is $\bar{a}$.
Statistically this implies what is termed a Binomial, or
Bernouilli, distribution.   Lacey shows that, in this case:

$$\bar{s}_r^2 \;=\; \frac{\bar{a}(\, 1 \,-\, \bar{a}\,)}{n} \qquad \text{.... 4.}$$

where n is the number of particles in the sample.   To
indicate the form of this type of distribution a proof of
this, though rather briefer than that of Lacey, is given
in Appendix III.

He then proposed the use of the standard deviation
ratio in the form $\dfrac{\bar{s}r}{\bar{s}}$ but in his later paper he proposes

the more elaborate relation which he then terms his
Mixing Index:

$$M_L = \frac{\bar{s}_0^2 - \bar{s}}{\bar{s}_0^2 - \bar{s}_r^2} \qquad \dots\ 5.$$

This has 0 and 1 as the limits, in the un-mixed and
perfectly mixed states respectively. Lacey also gives in
his second paper a very good review of earlier work, some
of it apparently unpublished.

v) Buslik[4] gives an extension of the random state $\bar{s}^2$
    to cover cases of particles which are not uniformly
sized. His problem is rather specialised.

vi) Blumberg and Maritz[2] offer a somewhat different
    statistical treatment though again based on the
measurement of $\bar{s}^2$. They assume the same limiting
conditions as Lacey, but use as their measure of mixing a
statistical test (χ^2) which in effect gives the
probability that, assuming a Normal distribution of $\bar{s}^2$,
their experimental value would be obtained by sampling a
random mixture. This is treated as a statistical hypo-
thesis, which can be tested to a given degree of probability
that increases to a certainty as the mixture tends to the
random state. As an attempt to avoid the dependence of
$\bar{s}^2$ on n they use a transformation $Z = 2\sin^{-1}\sqrt{a}$.

They give the result of one experimental run mixing particles of sand distinguished by colour, in a type of tumbler mixer, the results of which conform reasonably well to their hypothesis.

vii)   Stange[12], in a theoretical paper, deals
        particularly with sampling problems.   He develops the sample composition approach, and then treats the sampling problems on a statistical basis.   The extent of the mixing is measured by assessment of the nature of the results of this sampling, and he goes into the methods of doing this in some detail.

viii)   Adams and Baker[1], in a recent paper again on
        particle mixing, give what is effectively a statistical recipe for handling a mixture in practice, in which $\bar{a} \ll \bar{b}$ and for which a Poisson distribution is applicable, their criteria being based on the properties of this distribution.   They provide the results from experiments in which they mix coloured particles of polythene in a tumbler mixer.

3.1221 Discussion.

There are other papers which deal with mixing state, but they use measures which have, effectively, been considered.   It seems convenient to break this discussion into consideration of papers i-ii , and iii-viii .

3.1222 Papers Using d . (i - ii)

The great handicap of this measure is in the
theoretical treatment of rates etc., and limiting states,
using it.   Perhaps even more important, the adequacy of
sampling cannot be estimated using d .   Coulson and
Maitra relate their percentages mixed to the component
interfacial area but this will be discussed in the section
devoted to this idea;   however it makes no real difference
to the statistical nature of their measure.   On the whole
this statistical difficulty would seem to make the use of
d unattractive,especially when from the data needed to
obtain it $\bar{s}$ or $\bar{s}^2$ can readily be calculated.   Apart
from this it is perfectly consistent, and suffers from the
same disadvantages as $\bar{s}$.

3.1223 Papers Using $\bar{s}$ (or $\bar{s}^2$). (iii - viii)

The major objections seem to be:-
a) It is insufficiently comprehensive.   A great range
of patterns can lead to identical values of $\bar{s}$.
This may not be of practical importance where similar
patterns are being compared, but if more complete or
exhaustive information is required then this statistic
cannot provide it.   It would seem better to choose as
fundamental, a more comprehensive measure, which can then
be simplified where this is adequate for particular cases.

b) Regular patterns, or a tendency to regularity, may

cause difficulties as $\bar{s}^2$ may become less than $\bar{s}_r^2$
the hypothetical value at ultimate mixing.

c) The assumption of a Bernouilli distributed final

state, though plausible, seems to require experi-
mental justification. Many mixers for solids produce quite
a degree of regularity.

d) In general the sample size problem is not dealt

with. In the experiments, the impression is that
a convenient size is chosen and its possible effect on the
results ignored.

To set against these objections there are some
substantial advantages, principally:-

a) It is convenient to measure experimentally.

b) Statistical treatment, for instance of sampling

sufficiency, follows easily and naturally.

c) The idea of sample composition variation seems to

correspond closely to intuitive mixing ideas, and
the measure can easily be visualised and applied, for
example, to quality control of mixtures.

3.123   The Correlogram Treatment.

This approach is in some ways very similar to the

sample composition ones, and uses them in experimental
estimations, but it is a much more sophisticated outlook,
enquiring more deeply into the real nature of the distri-
butions. Though the ideas are borrowed, their application
to mixing is due to Danckwerts[6] and this section will be
a review of his paper.

The basis is still sample composition, but he introduces
a coefficient of correlation defined by:

$$R(r) \quad = \quad \frac{\overline{(a \ - \overline{a})(a_r - \overline{a})}}{\overline{(a - \overline{a})^2}} \qquad \dots \ 6.$$

where a , a_r are point compositions at points r apart.
This will then, in a given mixture, vary with r , and
Danckwerts discusses the nature of this fully in his paper.
He considers the variation, defining what is effectively
the mean value of this i.e. $S = \int_0^\infty R(r)\, dr$ as his mixing
measure. To allow for volume sampling he has to introduce
another measure V which is a different type of average,
i.e. $V = 2\pi \int_0^\infty r^2\, R(r)\, dr$, and which of these is used depends on
the sampling procedure, which is to some extent a difficulty
but one which seems almost unavoidable due, really, to the
fundamental properties of mathematical functions.
Danckwerts also gives another type of measure $I = \dfrac{\overline{(a - \overline{a})^2}}{\overline{a}.\overline{b}}$,
which he proposes to differentiate between systems
in which boundaries are sharp, and those where there is

gradual merging of one component into the other.   He gives quite extensive suggested experimental methods for evaluating his measures, though he does not include any experimental results.

3.1231 Discussion.

This treatment perhaps reflects his interests, which are apparently in diffusive systems for which it is very suitable, but it is still very general, and probes more deeply than the methods previously considered.   It does however seem to have some shortcomings:-

a) Again a given value of the scale of segregation can
   arise from a great number of possible arrangements, though perhaps not so many as with $\bar{s}$.

b) It is not easy to visualise his measures directly.

c) Any degree of regularity upsets the measure badly.
   Some mixing machines do provide this and give rise to a measure of oscillation of $R(r)$ which raises considerable problems e.g. $\int_{0}^{\infty} R(r)dr \neq \int_{0}^{\infty} |R(r)|dr$.   (An actual experimental trial by the present author, though not reported in the experimental section because it has no bearing on the main subject, gave rise to this effect.   The oscillation was quite highly damped disappearing after two or three cycles, but it was nevertheless present.)

d) The sample size difficulty again arises.   In pure
diffusion of liquids or gases point compositions are
reasonably meaningful in something approaching the mathemati-
cal idea, but in other applications this feature seems to need
further investigation.   This applies particularly to the
intensity of segration I , which seems to have little applic-
ability to general mixing problems in any case.

e) To some extent the experimental methods proposed
amount to a measure of $\bar{s}^2$ subject to certain sample
size considerations, so it is only in this latter respect
that it represents a change.

3.13   Interfacial Area Measurement.

3.131   When two components are mixed together the area of
the interface between them increases, and the extent
of this interfacial surface has been suggested as a measure
of mixing.   This is in some ways attractive, but the great
difficulty arises in the determination of this interfacial
area.

3.132   Review of Literature.

i)   Brothman, Wollan and Feldman[3] treat this interfacial
area problem by dividing the whole mixture into cubes,
and they propose, as a measure of the interface, that it is

directly related to the proportion of these cubes which
have "at least one element" of the interface present.

ii) Coulson and Maitra[5] whose "percentage mixed" measure

has been discussed, say that this percentage is propor-
tional to the surface of interface between the components.

iii) Spencer and Wiley[11] propose a theoretical treatment

of flow patterns in terms of this interface using a

visual criterion which appears similar to those in i). and

ii) , but they do not go into any detail as to how it might

actually be measured.

3.1321 Discussion.

i) and ii). Brothman et al. give no experimental
details, but presumably they would take samples and count
the proportion containing one component only.   Thus their
measure, as with Coulson and Maitra, is effectively one of
d as shown previously.

The proportionality between d and the interface
seems to require more attention than it is given.   No
account is apparently taken of the nature of the interface;
presumably the proportionality might hold if the interfacial
surfaces were arranged and distributed in some fixed fashion,
but the statistical problems presented by this are not
considered.   A further difficulty is presented by the size

of the volume elements in the treatment of Brothman <u>et al</u>.,
which is apparently not really considered.   A more general
objection, which applies to the whole interfacial area
concept, is can an adequate meaning be placed on the area
of interface between two components when the boundary is
not sharp, as for example in a diffusing system?   Also
substantial variation in the component proportions, i.e.
the ratio $\bar{a} : \bar{b}$, seems to create fresh troubles for
interfaces as a mixing measure.

iii) Spencer and Wiley propose no way of over-
coming the experimental difficulties.   A further objection
to their treatment is the great complexity of flow patterns
in practical cases.

Although difficult to treat, some extension of the
interfacial area idea might provide very useful information
if a direct measure could be found.   The measure would be
subject to many limitations but within these, for compara-
tive purposes, it could certainly be useful.

3.14   Proposed New Theory.

3.141   This represents an attempt to explore more deeply
        into the fundamental character of the distributions
which occur in mixtures.   As often happens, in work of this
nature, the mathematics can rapidly become very involved,

far out of proportion to the practical advances made.
Every effort has been made to avoid this, but it is necess-
ary to fill in some of the background so that practical
measures can be taken with confidence.   The treatment is
far from rigorous, but it does attempt to deal with some of
the major difficulties which arise without raising too many
new ones.   In particular the sample size question, which
has been mentioned as a difficulty in connection with other
approaches, is taken up in some detail.

3.142   Point Composition and Particles.

Ultimately all matter is, to a very good approxi-
mation, particulate.   In mixing attention is
focussed on such particles, or groups of particles, as are
preserved unchanged throughout mixing operations;   these
may be thought of as mixing particles.   In some systems,
such as liquid and gaseous ones, the mixing particles are
also the fundamental ones and are well below the scrutiny
limit of interest, but this is not always so, as for instance
in most forms of solid particle mixing.

In all cases point compositions can be considered, but
the concept requires some care in its use or the result may
behave as a sample of finite size, and so be subject to the
sample size considerations which are to be discussed.
Obviously at all points, in the mathematical sense, the

composition must be either A or Non-A with nothing between, but in some systems, particularly diffusive ones, it is convenient to speak of point compositions as representing the mean composition in neighbourhoods where this varies only slowly.

By nature, in the mixing sense, is generally implied chemical composition, but in different contexts it can imply other properties such as specific gravity, magnetic susceptibility, radioactivity, and so on. For convenience, in the further discussion, concentration of colour will be the property considered. Mixing can now be said to be the changing of the relative positions of the mixing particles of different natures.

3.143   Scale.

To a considerable extent mixing is a scale effect.

Thus to one scale some system may appear homogeneous, and yet to another the reverse. Perhaps the easiest example of this to look into, is a mixture of similar sized particles in which the two components differ in colour. If the limit of resolution is some distance r , and if, in the mixture, (the particle size being very small compared with r) no particle of one colour is at a distance of more than $r/2$ from the nearest particle of the other, then the mixture appears to scrutiny as homogeneous, that is, fully mixed.

Fig.2
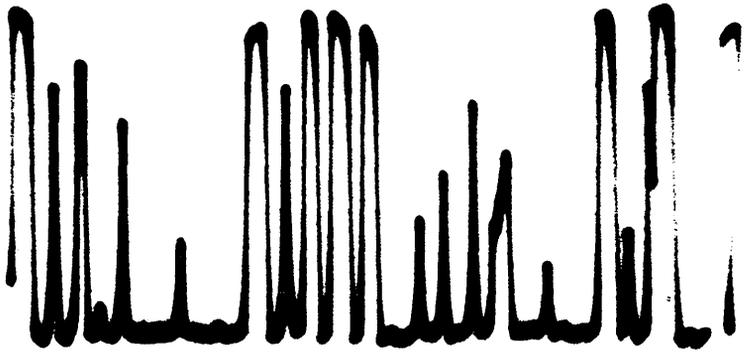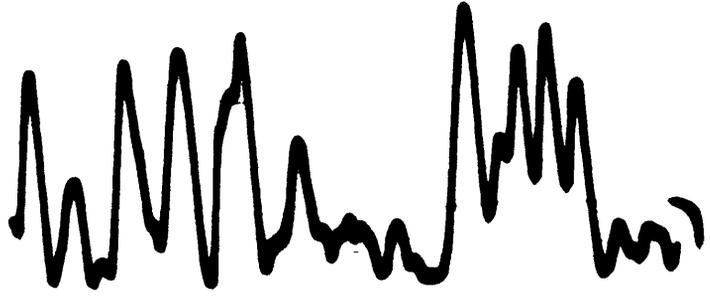
CONCENTRATION VARIATION

SAMPLE SCANS

If now resolution improves to some new limit $r_1 < r$, this same mixture, which was apparently homogeneous, is not necessarily so at all, so that this r , which can be thought of as a limit of scrutiny or interest, has a correspondence with mixing degree and measures something of the "clumping" which is in the mixture.

3.144   Stochastic Processes.

This idea of "clumping", generates through space a distribution of concentrations similar to that arising from what the mathematicians call a stochastic process.   This may be taken to mean, for the present, a sequence of numbers, continuous or discrete, generated in apparently arbitrary and random fashion, but which may reveal some of the properties associated with the idea of periodicity.   In fact, it is only so far as such periodicity is revealed that there can be any quantitative meaning given to the term degree of mixing.

Consider a straight line, drawn at random in a mixture of two components.   Along this line can be plotted concentrations corresponding to each interval or point.   Fig.2 shows possible resulting patterns of variation.   The ordinates oscillate, apparently in arbitrary fashion though limited by pure A and non-A , but there are definite features which are revealed such as the fact that pure A

does not exist over any length greater than say X_c of the line.

If this pattern be thought of as representing the concentrations of component A , written as $C(x)$ for any position x on the line, it can be seen that the mean content of component A , for a sufficiently extensive series of lines, will be given by:

$$\bar{a} = \frac{1}{x} \int_0^x C(x) \, dx \qquad \ldots \text{ 7.}$$

For a short length r this integral gives the mean composition in that length which may be written X_r . All experimental results will be in the form of this over greater or lesser sample sizes, and methods of treating the variation of this have already been mentioned.

Similarly the variance may be written as:

$$\bar{s}^2 = \frac{1}{x} \int_0^x \left[C(x) - \bar{a} \right]^2 dx \qquad \ldots \text{ 8.}$$

and these may be taken as definitions of the measures mentioned previously.

The theory of stochastic processes is one which treats of variations of this sort, in an endeavour to put a quantitative evaluation upon it in terms of periodicity. It

has been developed into a very elaborate mathematical structure particularly in two connections, the statistical theories of Turbulence, in hydromechanics, and of Noise, in electronic circuit studies. The classical treatments are those of Taylor[13] and Rice[10]. Thus the ideas introduced in sections iv-vi are new only in so far as their applications to mixing studies are concerned. In the text only the form of mathematical results is given, derivations of results which are unusual being outlined in Appendix III, or references given to sources of proof.

3.145 Periodicity.

The basic idea is the familiar one of the Fourier series of harmonic components. For $C(x)$ defined for all $0 < x < X_0$, and subject to restrictions as to continuity obeyed by all bounded functions of the type considered,

$$C(x) = \sum_{-\infty}^{\infty} a_n e^{i\omega_n x} \quad \text{where} \quad \omega_n = \frac{2\pi n}{X_0} \qquad \dots \dots 9.$$

taking $x_n = a_n e^{i\omega_n x} + a_{-n} e^{-i\omega_n x}$ i.e. the Fourier component of frequency n it can be postulated that

$$\overline{x_n^2} = 2\,\overline{a_n a_{-n}} = \omega(f_n)\Delta f \to \omega(f_n)df \text{ as } \Delta f \to 0 \qquad \dots \dots 10.$$

The symbol f is used to denote frequency: this is the same idea as a time frequency, but of dimensions $\frac{1}{L}$ and

not $\frac{1}{T}$.

This then leads to the idea of $\omega(f)$ a frequency or distribution spectrum. It implies that, building up these harmonic length components, a distribution, as similar as desired to the actual one, can be synthesised. It is more useful than the Fourier components, because, by suppression of phase angles, it becomes independent of the origin of the measurement.

In the actual mixture sample this distribution can in theory be built up to any desired degree of approximation, and it is only insofar as this periodicity exists, that the mixture can be classified. It is now postulated that this spectrum can be taken as the ultimate characteristic of the mixture. It is called "characteristic" rather than "index" because it is difficult to evaluate, and the latter term is perhaps best reserved for simpler measures which are readily obtained from experimental results. However it is this underlying periodicity which the simpler measures are estimating, albeit it often very roughly.

The physical basis of this characteristic is not at once apparent, but it is closely related to observed features. There will be a maximum value of $\omega(f)$ which can be thought of as giving the mean "clump" diameter $1/f_m$ and the shape of the plot of $\omega(f)$ against f gives the distribution of the clump diameters. Where this distribution is skew it implies

a broader spread of sizes on the one side or the other of the mean, and the presence of un-mixed regions in a mixture would appear to create this effect.

The spectrum, which is not directly measurable, is related to the concentration distribution through the Fourier transformation. The transformation from the distribution function to the spectrum can always be performed in practice, though the process may be very tedious, e.g. by approximating to the function using a series of Hermite Polynomials. The converse operation does not lead to a unique result because of the phase suppression. The spectrum seems important however, not because of its immediately practical value which is perhaps small, but because it enables so many of the other measures to be put into unified perspective.

3.146   The Autocorrelation Function.

This function is defined by:

$$R_r = \overline{c(x)\, c(x + r)} = \bar{a}^2\, R(r) \qquad \dots\dots 11.$$

and directly related to the spectral function by

$$\omega\,(f) = 4 \int_0^\infty R_r \cos \omega r\; dr \qquad \dots\dots 12.$$

It is of considerable practical interest as well as theoretical, and as mentioned previously its connection with

the mixing process has been suggested by Danckwerts, though
he did not investigate some of its implications.   Using
the relations above it can be determined from actual concen-
tration distribution measurements.   Danckwerts also gives
methods for the evaluation of certain mean values of it in
his paper.   The present purpose is served by emphasising
its relation to the general pattern, and showing that its
existence implies that of the spectral function.

3.147   Finite Sample Averages.

All real measurements of sample compositions in a
mixture take the form of concentration averages
over finite sized samples.   On the model of the present
discussion the process may be defined as

$$X_r = \frac{1}{r} \int_x^{x+r} C(x)\ dx \qquad \dots 13.$$

This is the value of the concentration of component A in
a sample of size r and it is this measure which will be
treated most fully because of its widespread practical
occurrence.   The variance of X_r is written $\overline{X}_r^2$.

There is a relation between $\overline{X}_r^2$ and the spectral
function given by

$$\frac{d}{dr}(r^2 \overline{X}_r^2) = 2 \int_0^\infty \frac{\omega(f)}{f} \sin fr\, df \qquad \dots 14.$$

so that theoretically, knowing the way in which $\overline{X}_r^2$ varies

with r , the spectral function can be computed.

Also there is a close connection with the autocorrelation function, which may be written in the general form

$$\overline{X}_r^2 = \frac{2}{\overline{X}_1^2} \int_0^{x_1} \int_0^{x_1-r} \overline{C(x)\ C(x+r)}\ dx\ dr \qquad \dots 15.$$

An idea which Danckwerts mentions, and very necessary to his particular treatment, is that of the value of r for which the autocorrelation is zero for all values of r greater than r_0 . Using this idea then there follow the simpler relationships for what may be regarded in a sense as limiting values,

$$\text{for }\ r \ll r_0 \qquad \overline{X}_r = C(x)\ \overline{X}_r^2 = \overline{s}^2$$

$$\text{and }\ \text{for }\ r \gg r_0 \qquad \overline{X}_r = \frac{K}{2r} = \frac{2}{r} \int_0^{r_0} \overline{C(x)\ C(x+r)}\ dr$$

$$\dots 16.$$

3.148   Dimensional Considerations.

A difficulty which arises with these more fundamental measures stems from dimensional considerations. Though it is perfectly consistent and meaningful to define the basis of a mixture in terms of what, for want of a better name, has been called "length frequencies", the experimental determinations which can lead to these can strictly only arise from line sample contents. By this is meant, in the

practical sense, samples in which one dimension greatly
predominates, and it is this dimension which is varied.
If however sampling is on a volume, or area basis, the
analysis of the effect on sample composition variance of
the changing of sample sizes will lead not to a length
spectrum, but to some other form which is difficult to
conceive except possibly in terms of some spherical
harmonics.

Danckwerts avoids this issue, as has been mentioned,
by defining separate linear and volume measures; he did
not need a two dimensional one, but it could be easily
developed if needed.   This necessity to have several
measures is very unfortunate, but there seems to be no easy
way from the difficulty if the treatment is to be rigorous.
It is the problem of the relation between moments of various
orders, and unless a distribution is assumed, and there seems
no point in doing this, there is no necessary connection
between them.   However the aim of the present treatment is
to bring the periodic ideas forward, and to show the patterns
which exist, rather than strict values, and these are not
affected by the dimensional problem.   The discussion speaks
of sample size when what is strictly meant is the length of
line samples, but the ideas and the patterns are applicable
to both and it is these which are of present interest,
particularly in the sample size problem which will now be

considered in some detail.

3.149   The Sample Size Problem.

This section is concerned with an investigation of the behaviour of $\overline{X}_r^2$ as r varies. This variation is of the greatest practical importance, because all experimental work has involved the taking of samples of apparently arbitrary sizes at the various stages of mixing. The problem is whether this arbitrary size factor will influence the results of this work, and there is also interest in the general behaviour of this statistic. It is immediately obvious that, for a given mixture, the larger the samples are the less will be the variation in their composition; if the sample grows to the size of the whole mixture, as a limit, then the sample composition is the mean composition and the variation zero. At the other limit the variation is given by Equation 3 , that is when all samples are either pure A , or non-A .

One very interesting point, which makes this problem the more important, is the interrelationship between sample and "clump" size. In fact the value of $\overline{X}_r^2$ will depend on the ratio of r to "clump" size. Consequently it may be seen that a curve showing the relationship of $\overline{X}_r^2$ to r at constant "clump" size is the same curve, though to a different scale, as that showing the change of $\overline{X}_{r_1}^2$ with "clump"

size i.e. with mixing.   This is of importance in consider-
ing mixing rates, and the behaviour of these clumps or
groupings on mixing.   The problem will now be developed
analytically.

3.1491   Space Averages for Discrete Values.

Consider the series $C(x) = x_1, x_2, x_3, \ldots\ldots x_n$

It may be thought of as representing values of x
taken at equally spaced intervals $\triangle x$ along a sample line
or lines.   Then as is shown in Appendix III if:

$$\overline{X}_r = \frac{\overline{x_1 + x_2 + \ldots + x_r}}{r} \quad \text{and} \quad R(s) = \frac{\overline{x_r\, x_{r+s}}}{\overline{x}^2}$$

then

$$\overline{X}_r^2 = \overline{X}^2 \left\{ \frac{1}{r}\left[1 + 2\sum_{1}^{r-1} R(s) \right] - \frac{2}{r^2}\sum_{1}^{r-1} sR(s) \right\} \quad \ldots. 17.$$

This is the fundamental equation for the variation of $\overline{X}_r^2$,
in terms of r , and the autocorrelation coefficients for
the terms in the series, and shows the way in which these
coefficients influence this variation.

For the limiting case when the sample is only one term:

$$\overline{X}_r^2 = \overline{X}^2 \qquad \ldots. 18.$$

and for the other limit, when the number in the sample r is
much greater than the greatest length over which the auto-
correlation is significant, i.e. r_0

FIG. 3

THE EFFECT OF SAMPLE SIZE (GROUPING) ON THE VARIANCE

$\odot$ $R_1 = \cdot 9$, $R_2 = \cdot 5$, $R_3 = \cdot 1$, $R_4 = R_5 = \cdots = 0$

$\times$ $R_1 = \cdot 7$, $R_2 = \cdot 2$ $R_3 = R_4 = \cdots = 0$

— $R_1 = R_2 = \cdots = 0$
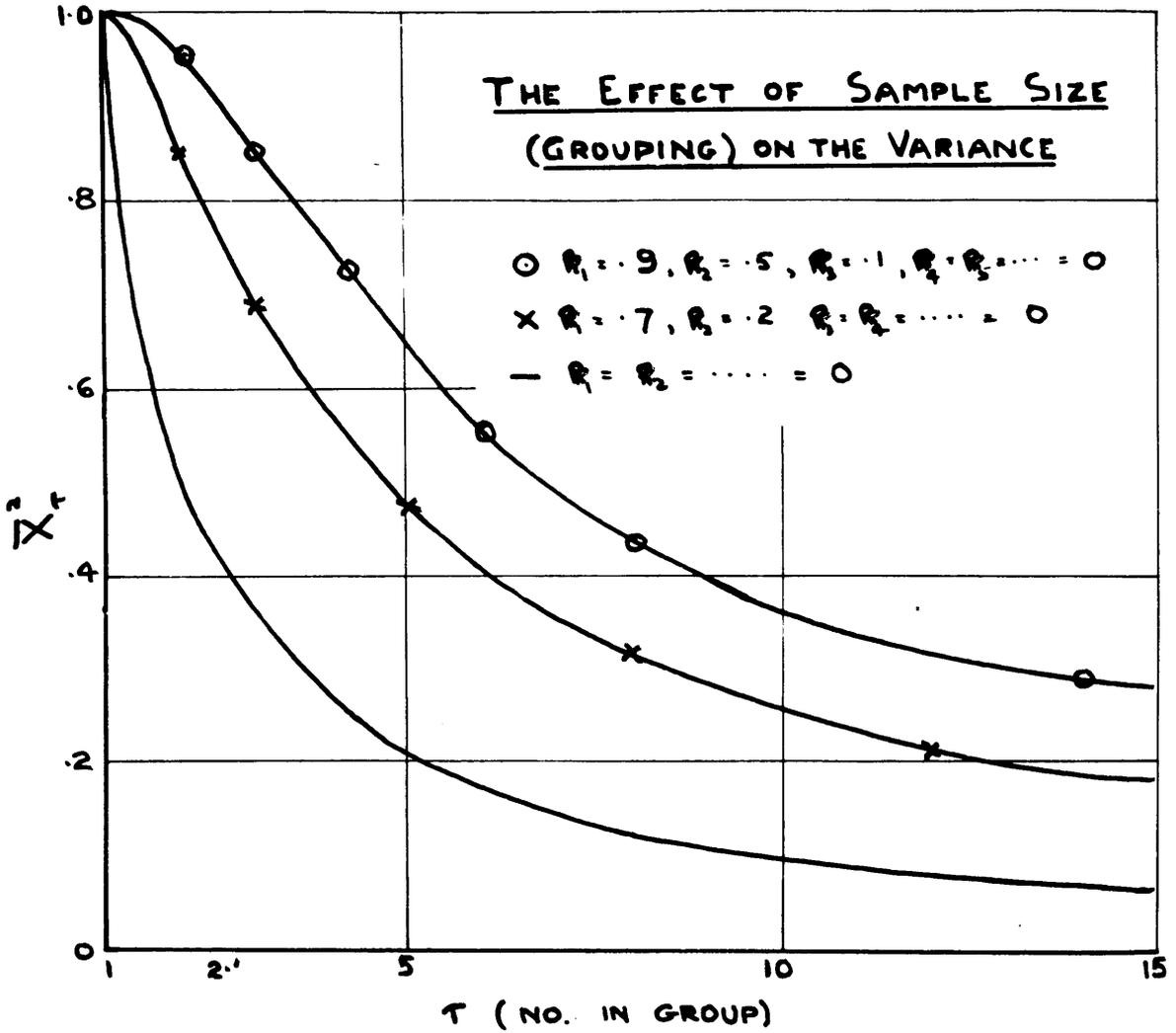
then $\qquad \bar{X}_r^2 = \dfrac{\omega_0}{2r} = \dfrac{K}{2r} \qquad$ .... 19.

where $\qquad \omega_0 = 2\displaystyle\int_0^\infty R_s \, dk = $ a constant

Thus the curve of $\bar{X}_r^2$ against r starts off at a fixed value which represents no-mixing, and at large values of r it becomes a reciprocal type of relation. Between these limiting conditions the shape will depend on the autocorrelation coefficients and thus on the spectrum, in the particular case under consideration. Figure 3 shows the shape of the curve for some selected values of the R_s. Strictly it should not be a curve but only a series of point values between which the function has no existence, but, as will be seen in the next section, the treatment can be extended to the continuous case. The plotting has been done for the discrete case for it is easier to see the influences of the coefficients of R_s in this. Experimental values of $\bar{X}_r^2$ for a range of values of r will show this shape of curve, because the arrangement is virtually the same.

3.1492 Space Averages for Continuous Values.

From Equation 17 above, or directly as shown in

Appendix III this idea can be extended to continuous values in which the Δx of the interval between the points tends to zero, giving

FIG. 4

PLOT OF $\dfrac{\sin^2 x}{x^2}$
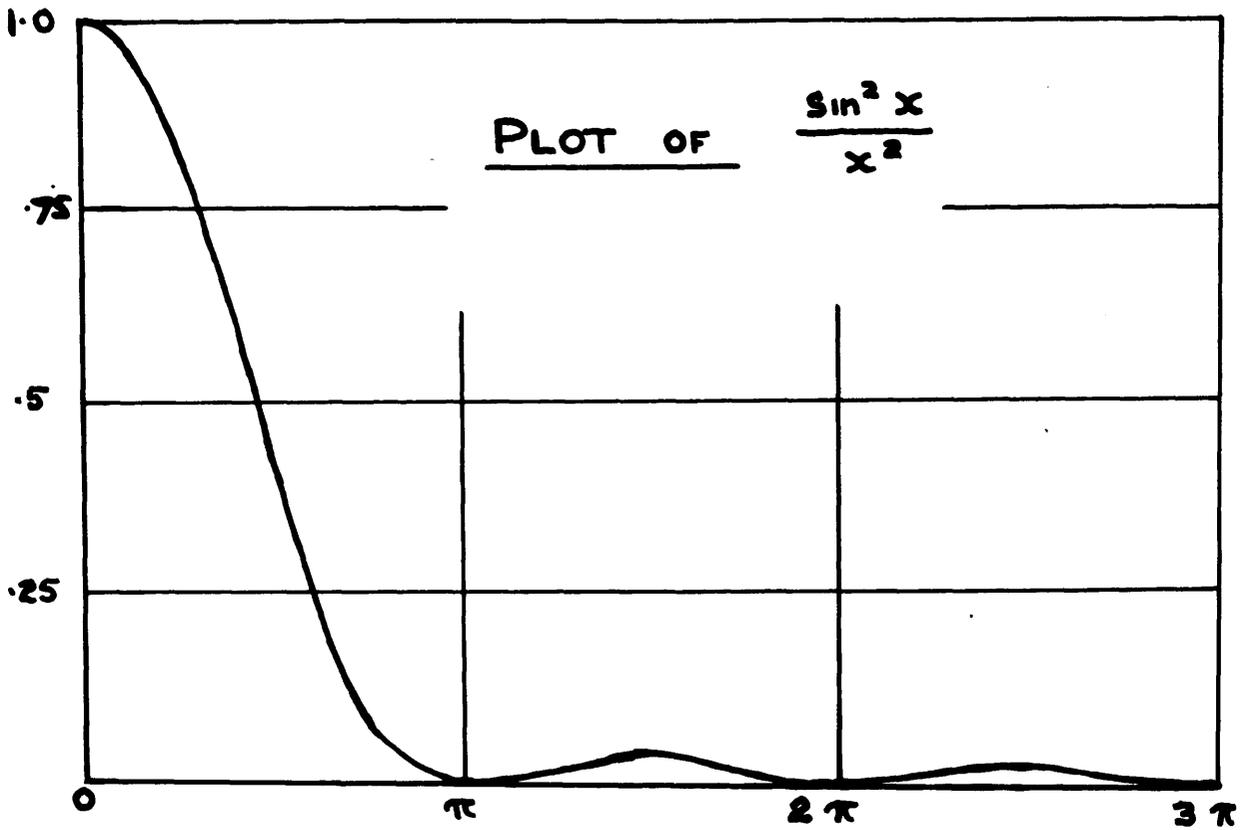
$$\overline{X}^2_{r_s} = \frac{2}{r_s}\int_0^{r_s} R_r \, dr - \frac{2}{r_s^2}\int_0^{r_s} rR_r \, dr \qquad \ldots \text{ 20.}$$

This is actually the equation which will give **continuous** curves as the type shown in Fig. 3 , **and it can of course** handle the continuous distribution of autocorrelation coefficients which actually occurs in practice.

3.1493 Averages for Regular Functions.

If $C(x)$ can be written as a Fourier series then it can be shown that

$$\overline{X}^2_r = \sum_{n=1}^{\infty} K_n^2 \frac{\sin^2 nr}{n^2 r^2} \qquad \ldots \text{ 21.}$$

This cannot be plotted without assuming values for the Fourier coefficients, but the basic function, that of $\frac{\sin^2 nr}{(nr)^2}$ is plotted and shown in Fig. 4 . This curve has the same shape as those of Fig. 3 but the ordinates diminish much more rapidly, the envelope of the maxima being $\frac{1}{r^2}$ instead of $\frac{1}{r}$. This arises from the regularity and does not occur in real mixtures. Similarly real mixtures will **not give the** minima since they have a continuous spectrum of periods. The solution does however give a clue as to the way the real distributions are built up. (The real cases may be considered as having the fundamental period tending to infinity and a complete spectrum of harmonics within this.)

3.1494   The Chessboard Problem.

As an attempt to deal with the sample size problem in two dimensions, the scanning of a chessboard type of concentration distribution was considered.   This implies that the components are distributed regularly in a two dimensional array like the squares of a chessboard, and this pattern can be represented analytically by a double Fourier series of the form

$$f(x,y) = K' \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} K_m K_n \sin \frac{m \pi x}{a} \sin \frac{n \pi y}{a} \quad .. \; 22.$$

The scanning of this by a square spot of side r leads to a mean square composition variation given by

$$\overline{X}_r^2 = K' \sum_{m=1}^{\infty} \frac{K_m^2 \sin^2 \frac{m r \pi}{a}}{\left(\frac{m r \pi}{a}\right)^2} . \sum_{n=1}^{\infty} \frac{K_n^2 \sin^2 \frac{n r \pi}{a}}{\left(\frac{n r \pi}{a}\right)^2} \quad .. \; 23.$$

This is the product of two terms each like that in Equation 21 .   It is considered that, in real systems, the zero values of this will not occur for the same reasons as mentioned in section c) above, and thus that the overall result of scanning on ordered lines will be again of the form shown in Figure 3 , but falling off much more rapidly.

The chessboard is too highly idealised an arrangement to be of practical importance, but it reveals the complexity of working in more than one dimension.   For a pattern of this type the extension to three dimensions would be

straightforward, and would result in the variation of $\overline{X}_r^2$ with size of the cube used for scanning, being given by the product of three terms each of the form

$$\sum_{1}^{\infty} K_n^2 \left(\sin^2 \frac{nr\pi}{a} \right) \frac{1}{\left(\frac{nr\pi}{a}\right)^2}$$

and again leaves the fundamental shape unaltered. Only the simplest of arrangements, which will allow analytical equations for the distribution to be written in the form

$$f(x,y,z) = X(x)\ Y(y)\ Z(z) \qquad \dots 24.$$

can be treated by this method, and these are so far removed from practice that further analytical development seems futile.

3.150   Application in the Analysis of Experimental Results of the Spectral and Associated Functions.

Almost all experimental methods used in the study of mixing involve the taking of samples of finite size, and the measurement of their composition in terms of one of the components. This then allows the computation of $\overline{X}_r^2$. If the variation of $\overline{X}_r^2$ with r is measured, then a good deal of additional information may be available. In such cases it is possible, at least in theory, to estimate the spectral or autocorrelation functions. If the $\overline{X}_r^2 - r$ relation is approximately reciprocal, then this indicates

that the sample size is larger than the correlation lengths, and this may give added confidence to the use of this size. It may also be possible, by observing the effect of mixing on the curves, to see whether the spectrum distribution remains of the same shape on mixing. In some cases there may also be the possibility that a Fourier series may be fitted directly to the experimental data, and from this the spectrum can be estimated.

3.16   Summary of the Measurement of the State of Mixing.

The most complete measure of this seems to be the distribution spectrum. When this is of regular shape it could be characterised by measures such as $\int_{max}^{}f_{max}$ or $\bar{f}^2$ and such concepts as kurtosis, developed for statistical distributions, can be applied. In other cases the complete distribution is necessary to characterise the mixture fully.

In practice the information obtained by experiment is in the form of sample compositions. Unless the additional knowledge is needed the sample sizes will be effectively constant, and so the statistic which it seems best to calculate is the variance $\bar{S}^2$. The subsequent treatment of this does not seem critical: such measures as Lacey's standard deviation ratio of his Mixing Index M_L, or Danckwerts S , embody all the available information for they amount to the

same thing basically, and so far as rate measurements based on them are concerned, simple transformations will have no effect.   Consequently it seems a matter of personal convenience and preference which is used, but there seems no real objection, at least for comparative work, in using the standard deviation directly without any further fuss.

3.2   The Rate of Mixing.

3.21   Once some measure has been given to the degree of mixing, then the discussion of quantitative rates becomes possible.   It must be emphasised however that these are interdependent, consequently it is very difficult to consider any absolute rate of mixing.   There may be intuitive ideas as to how rate measurements should behave, and, in fact, these influence the selection of measures of mixing state for their behaviour on mixing must not contradict what common sense proclaims as to mixing and non-mixing.

Discussion to be useful must be confined to real processes, or at least to very near approximations.   Flow patterns in mixing machines are always complex and some simplification is essential, but this has to be carefully watched lest the practical considerations are lost in mathematical fantasy.

3.22   First Order Kinetics.

The most popular approach in the literature is from the assumption that, at any time, the rate of mixing is proportional to the amount of mixing remaining to be done, that is to the difference between the value of the mixing index or measure at that time, and the value of that index at ultimate equilibrium.   This gives rise to the type of equation spoken of as "First Order" in the theories of rate processes.   The detail of the equation will obviously depend on the nature of the mixing measure and the ultimate state, but a general equation of the form:

$$\frac{dM}{dt} = k \left| M - M_m \right| \qquad \dots 25.$$

can be written whenever a single mixing index figure is used.

3.23   Review of the Literature.

i)   Lacey[7] does not derive any rate equation, but simply states that it is likely to be of the form

$$M = 1 - e^{-kt} \qquad \dots 26.$$

where M is his mixing index at time t , and k is the rate constant.   This is effectively only a rearrangement of the first order type, and he demonstrates its applicability to some particle mixing results from other people's experiments.   He does also give some attention to diffusive

systems but that is outside the present scope.

ii) Brothman et al.[3] using the interfacial surface

derive, invoking the Law of Mass Action, an equation

of the form

$$S = S_m (1 - e^{-kt}) \qquad \dots 27.$$

where S is the surface area at time t and S_m the

maximum possible interfacial surface.   From this, relating

as mentioned earlier this surface area to the volume propor-

tion containing an element of interface, they arrive at a

complicated exponential equation which may be found in their

paper.

iii) Coulson and Maitra[5] start with much the same basic

premises as Brothman et al., but making slightly

different assumptions, reach the equation

$$\frac{dS}{dt} = k (S_o - S)$$

and thence   .... 28.

$$\ln \frac{100}{X} = kt$$

where X is their percentage mixing measure.   These workers

give extensive and interesting data from runs in a drum mixer

containing particles of coal and salt, and show that their

equation is quite closely followed by these results.

iv) Michaels and Puzinauskas[9], using as their measure the

ratio $\frac{\overline{S}}{\overline{S}_o}$, plot results of a series of experiments,

using clay sand and water in a kneading mixer, on logarithmic paper against time.   Their results show an initial straight portion, followed by a falling off of the rate over a longer mixing period.

v)   Weidenbaum and Bonilla[16], again using a variance ratio
        for their measure, give the same form of equation as Lacey, assuming first order rates.   Their experimental results, using sand and salt in a drum mixer, show that this equation holds over the initial stages but deviations appear after prolonged mixing.

vi)   Spencer and Wiley[11] make a novel and interesting
        approach.   They give as their measure of state what is really a geometrical description in the form of a position matrix.   (This was not mentioned in the section on these, because for experimental purposes such a measure seems hopelessly difficult to evaluate and cumbersome to handle.) This matrix involves dividing the material into a conveniently large, depending on the distribution geometry, number of cells, numbering these 1,2,3.....N .   This then defines a 1 x N row matrix, $\left[a_i^o \right]$.   They then consider the result of operating on this with a distribution matrix $\left[D_{ij} \right]$ which is an N x N square matrix.   They postulate that, after m distribution operations, the final position matrix is given by

$$\left[a_i^m \right] = \left[a_i^o \right] \left[D_{ij} \right]^m$$

.... 29.

This is illustrated by a very simple deformation using a
6 x 6 matrix, and this shows the effect on the proportions
of the components in the various cells before and after the
deformation process.

3.231   Discussion.

Most of the workers are content merely to postulate
first order mixing rates, rationalising their choice
on intuitive grounds.

The derivations offered by Brothman et al., and by
Coulson and Maitra, seem in some respects on shaky ground.
The authors leave themselves very open to criticism by saying
that the Law of Mass Action is applicable to an interface,
expanding in a mixing operation.   They also postulate a
proportionality between the mean absolute deviation of their
sample compositions and the interfacial surface area, in
order to arrive at their result, and, as explained, this
needs very careful consideration.   If these contentions are
rejected, then Coulson and Maitra effectively join the
majority ranks who postulate first order rates from the start,
while the complicated equation of Brothman et al., for which
there seems no experimental confirmation, is left unsupported.

Spencer and Wiley's paper presents the most interesting
theory, but its possible applications suffer from the very
cumbersome matrices necessary for the simplest of operations,

and from extreme experimental inconvenience.   They propose
the use of a punched card machine to obviate the former
objection, and complete flow theory to care for the latter,
which could then be checked by the usual sample composition
methods.   However no experimental results on the basis of
their work are available.

3.24   A Proposed Treatment.

In view of the complicated nature and lack of know-
ledge of mixing flow patterns, there seems no point
in considering the behaviour of elaborate measures of the
state of mixing in rate discussions.   Consequently most
attention will be given to the measure $\bar{s}$ or its derivatives.

3.241   Mechanisms of Mixing.

There seem to be two fundamentally different mixing
operations.   These can be called:-

a) Shear Mixing.   This implies the movement of individual
   particles of one component, relative to those of the
   other.

b) Convective Mixing.   By this is meant a displacement acting
   on a group of particles, and the relative motion is
   between groups, which may themselves of course be mixed.

Most, if not all, real mixing operations proceed by a
combination of these.   In some cases it may be useful to

subdivide or classify mechanism further, for example shear mixing could be divided into, pure shear in which the relative particle movement is ordered, and diffusion in which it is random, but there does not seem any fundamental need for these distinctions.

Both of these mechanisms would tend to give increased disorder on disturbance, proportional both to the extent of the disorder already existing, and to the degree of the disturbance. This leads to first order rates and, on the assumption that the sample composition standard deviation is a measure of this disorder, which is highly probable on statistical grounds, then this standard deviation should obey a rate equation of the type of Equation 25 . Further theoretical treatment must depend on flow patterns, and these are too arbitrary and varied for a general attack.

The idea of deformation matrices gives additional support to the first order kinetic theory. The cell sizes may be set very small and then, with the deformation operating at a definite rate, the effect per unit time will depend on the state at the beginning of that time, and on the deformation matrix which is, from the postulate, constant.

This all seems to agree with intuition. The experimental results also show this type of law to be followed, at least over the initial stages. There is perhaps an apparent difficulty, to which attention has not been previously drawn,

that in these rate considerations no distinction is made
between d and $\bar{s}$, and the experimental results of both
seem to obey first order laws.   However it is shown in
Appendix III that if the system from which they are drawn is
normally distributed with respect to sampling, and there
seems no reason why mixtures should not be, then $d = \bar{s}\sqrt{\frac{2}{\pi}}$
and so $d(d) = kd(\bar{s})$ showing that no inconsistency is
involved.

3.242   Competing Rates.

Some explanation for the observed departures from
the first order law when mixing has been proceeding
for some time, may arise from the existence of competing
processes.   While at first the forces tending to promote
increasing disorder are predominant, these later diminish,
according to the first order law, and other tendencies which
decrease the degree of mixing may become of comparable impor-
tance.   This would then lead at first to a falling off from
the first order rates, and eventually to the steady state
conditions,which occur frequently in chemical reaction
kinetics,where alternative and opposing alternatives contest
with one another.   In particle mixing especially, gravita-
tional forces tend to un-mix by separating particles of
different sizes or specific gravities.

3.243　　Some Observations on the Spectrum Distribution

in Mixing.

As mentioned earlier there is a correspondence

between the variation of $\overline{X}_r^2$ with r and that of

$\overline{X}_{r_1}^2$ with t . If the distribution spectrum shape remains

constant throughout the mixing, though of course the numeri-

cal values will change, then these are the same curve.

Consequently this assumption that it does remain constant

may be made and postulating some regular change in r

observe its effect on $\overline{X}_r^2$, which is the same thing as observ-

ing the effect of mixing on $\overline{X}_{r_1}^2$ with the same sort of

changes in r .

There is no justification for treating this other than

in qualitative fashion, but it does show some interesting

points. For instance if r decreases linearly with time

it may be seen, looking at Equation 17 or at the curves of

Figure 3 , that $\overline{X}_r$ will not decay logarithmically. On

the other hand, assuming that the rate of change in r is

proportional to r itself, would lead to a roughly logarith-

mic decrement relation, though with the rate falling off as

the time increases considerably which is the experimentally

observed effect. This of course does not prove anything

because of uncertainties, both in the shape of the curves

and in the behaviour of the spectrum on mixing, but it does

show that, from plausible assumptions, something similar to

the experimental form appears.

3.25   Summary of Rate Measurements.

The best description of mixing rates seems implicit
in the Equation   25   though this has been demonstra-
ted, rather than proved.   Whether M_m is finite or zero
affects the final form, and in the experimental work of this
study the ultimate standard deviation is taken as indis-
tinguishable from zero, so that the equation takes the simpler
form

$$\frac{dm}{dt} = -km \qquad \qquad \dots\, 30.$$

3.3   <u>Energy Requirements for Mixing.</u>

3.31   A popularly held belief was that the power require-
ments of a mixer could be used as a measure of the
rate of its mixing.   It is not difficult to see that this
is in general untrue, but it does show the widespread lack
of knowledge on the subject of the power requirements and
efficiencies of mixing machines, which are nevertheless of
substantial practical importance.   Dealing with mixers of
widely different geometry, and materials of varying proper-
ties, makes it appear however that any general treatment
will be very difficult and complicated.

Linked with power is the question of theoretical

rearrangements which will require the least energy to transform one distribution, e.g. completely separated components, into another, e.g. when the components are randomly distributed throughout each other. There may be some minimum work required for this in any given case, and intuitively this would certainly seem to be so and,if this could be evaluated,it would give a fundamental measure on which could be based mixer efficiencies. However the mathematical difficulties of this problem in geometry appear formidable, and no solution has appeared.

Another type of efficiency which might be envisaged would be a machine efficiency, based on the idealised operation of some set deformation pattern, i.e. mixing machine type. In terms of this the performances of actual mixing machines could be compared. This efficiency could be compared with the hydraulic efficiency of a pump, where the theoretical energy-throughput relationships can be calculated. Then, on measuring the actual ones, there is a discrepancy due to internal friction and other losses, and from this the performance of the pump, as a member of a class of pumps, can be assessed. In the gaseous state the free energy changes on mixing can be calculated, but this does not seem applicable to solid systems.

3.32   Review of Literature.

There is almost nothing available.   The only
mentions of the subject seem to be:-

i)   Spencer and Wiley[11] in continuous mixers define a
    type of efficiency as the ratio of power used for
mixing, to that spent in transportation of the material
being mixed through the mixer.

ii)   van der Vusse[14] in a two liquid system in which his
    liquids are of different densities, proposes as the
idealised energy of mixing that necessary for the change in
potential energies from the un-mixed to the mixed states.

iii) Weidenbaum and Bonilla[16] mention the relationship of
    entropy and probability, and suggest the possibility
of testing this in relation to mixing using statistical
methods.

3.321   Discussion.

The efficiency suggested by Spencer and Wiley, seems
    an ad hoc derivation for their particular problem.
That of van der Vusse does not seem to be very realistic at
all;   presumably, if the mixture were inverted the energy
required for mixing would be negative from this theory.
The ideas of Weidenbaum and Bonilla are interesting, but
they do not make any practical use of them.

3.33   Some Suggested Efficiency Ideas.

In the present state of knowledge, the most promising

attack seems to be via ad hoc measures of efficiency

designed for specific tasks but which, as the volume of data

grows, may become of much wider application.

For instance a study might be concerned with the use of

fundamental mixing operations, and, for a given set of

material properties, trying to discover which operations

perform most mixing for the least amount of work.   This is

a possible practical line, though hardly for theory in its

present state.

Another approach is that used in the experimental work

of this study.   From the mixing rates, it seems a logical

extension to characterise the performance of a mixer, under

given conditions, in terms of a mixing "half life".   This

gives in effect the time required to diminish the mixing

measure to one half of its initial value, and this time will

be a constant independent of the initial state if the rate

is first order.   It has been seen, in the rates section,

that experimental results show this latter supposition to be

true, at least over the earlier stages of mixing, so from

these $T_{\frac{1}{2}}$ values the performances of mixers can be compared.

Furthermore, measuring the actual energy required to

reach $T_{\frac{1}{2}}$, gives a value expressing the work required, in a

given mixer, to perform a standard mixing operation. This
has been used to compare operating conditions, and to arrive
at what might be called a maximum operating efficiency.
Admittedly this is a rather specialised and perhaps crude
approach, but it does provide operating data, and information
about machine performance, which can then be arranged so as
to provide maximum rate of mixing, or minimum energy,
whichever is required in the particular application considered.

The actual factor in repetitive mixing machines which is
determining is the mixing cycles, generally revolutions of the
mixer blades, and not strictly the time of mixing. In the
discussion speeds are taken as constant, but these may be
either reduced to a standard speed or mixing cycles can be
considered for comparative purposes. For most practical
purposes however it is the time which matters, quite irrespec-
tive of blade speed, and it was this consideration which
caused its adoption.

3.34   Summary of Energy Requirements in Mixing.

Overall, there is not very much comfort in the answers
available to questions concerning the power require-
ments and efficiency of mixing machines. Individual ad hoc
efficiencies may be used, and very useful, but the general
problem, which is of great concern to the designer, still
awaits solution.

S E C T I O N   4.

EXPERIMENTAL   INVESTIGATIONS

4.   EXPERIMENTAL   INVESTIGATIONS

4.1   Introduction.

The basic problem was to find a method of following,
quantitatively, the progress of mixing of flour
doughs.   If possible the results would be suitable for
theoretical analysis.   Thus it was determined to use the
sample composition standard deviation approach, if experi-
mental methods could be found for this, as offering the
prospect of the most useful information, and also to observe
the effect of variation in the sizes of samples considered.

4.11   Review of the Literature.

When this study was commenced there was no published
account of any investigation into plastic mixing
systems.   However, when much of the preliminary work had
been completed, a paper appeared by Michaels and Puzinauskas[9]
which seemed, at first sight, to cover some of the same
ground.   In their work however they used different materials,
clay, sand, and water, paid little attention to the theoreti-
cal side using standard deviation measures without elaboration,
and with straightforward methods of analysis available had a
less complicated methodological task.   Thus what originally
appeared to be a similar investigation became, on closer
examination, a different approach to a rather different
problem.

4.12   The Selection of Experimental Material.

A number of difficulties arose from the use of flour dough.   It would have been possible to have obtained results much sooner, and more easily, using other materials, but dough was not selected on grounds of experimental convenience but on account of other factors, outside the subject of mixing, which are given briefly in Appendix II.   It was decided, though, to simplify the problem to the extent of treating only the blending of homogeneous doughs.

The nature of flour dough precluded any chemical sampling and analytical method because, due to adsorption on the protein present, it was found impossible to recover quantitatively anything which was added, unless it was something of the nature of, say, iron filings which would disturb the dough, giving it different physical properties.   Also, the plastic nature of the dough made any theoretical treatment of the forces required for deformation impossible on present knowledge.   One definite advantage which did accrue from these difficulties was that a method, found to work in this case, should do the same, both for materials easier to handle, and for others equally difficult.

4.13   Experimental Requirements.

i)   To establish a method of measuring the degree of mixing of two colour differentiated dough masses;   this to be

done by measuring the composition of samples in terms of one of the components, with provision made for varying the sample size.

ii) To measure the power used in the mixing process.

iii) To establish that the method could yield consistent results related to mixing states, rates, and efficiencies, by investigating the performance of laboratory mixing machines.

iv) To show that the method could be applied to plant scale mixers.

4.14   The Principles of the Experimental Method Adopted.

The distribution pattern of the components was transferred, by the photographic process, on to plates where the components, originally differentiated by colour, now, by affecting the emulsion to different degrees, appeared as silver deposits of varying densities. Thus a record of the mixture was prepared in convenient form for measurement, an adequate number of plates to fulfil sampling requirements being taken.

The evaluation of this distribution was effected by the modulation of a light beam, passing through the plate and on to the cathode of a photo-tube. By scanning, at a suitable speed, a proportionately modulated current was produced in the photo-tube output circuit, and this could be measured

electrically. The fluctuations of the photocurrent, which represented the variation in colour composition of the original mixture, may be broken up into an A.C. and a D.C. component, which could be separated electrically by a condenser. The A.C. was measured as a steady reading on a suitably damped thermo-microammeter, which gave directly the root-mean-square value irrespective of frequency or wave form. The scale of the A.C. was governed by the mean light flux falling on the photo-tube, and so that had to be measured by passing the total output through a D.C. microammeter, and then the A.C. readings could be corrected to a standard mean flux figure. The sample size was controlled using an iris diaphragm to alter the diameter of the scanning spot on the plate.

4.15   Arrangement of the Experimental Section.

Apart from the introduction, the first three sections deal with the experimental method, giving a description of the apparatus, of the procedure for using it, and of the results of calibration runs.

Then follow the actual results which fall into two broad groups. The first describes the results of runs of an exploratory character designed to test out the method. Much of this section has a bearing on the theoretical ideas developed earlier. The second section gives the results of

runs testing the performances of commercial machines.   The
first runs, using laboratory mixers with two different types
of mixing blades, measure the effect on rates and efficiency
of the quantity in the mixing bowl, while the second shows
that the method is applicable to the measurement of commer-
cial scale mixing, using a full sized machine.

4.16   Note on an Alternative Measuring Method.

Some preliminary work was carried out on an alter-
native method of measuring mixing which will be
mentioned briefly.   The basic idea was to incorporate into
the two components under investigation chemical compounds,
one into each, such that when mixing takes place some
distinctive reaction producing colour, occurs at the inter-
face.   Dough properties made the choice of reagent extremely
complicated, for strong oxidising agents, acids, alkalis,
etc., were out of the question because of their effects on
the nature of the dough.   Reagents finally found to work
were $\alpha\alpha'$ dipyridyl, and ferrous iron.   Both can be colour-
less or nearly so initially, and when mixed a bright pink
colouration is produced.   If this could then be estimated,
it would give a measure of the effective component interface.
Photographic methods for this were tried, but many difficul-
ties were apparent and the work was given up in favour of the
method actually used which seemed to promise results more
easily.   This interfacial colour scheme would appear to have

FIG. 5

OPTICAL ARRANGEMENT

Dimensions: 9" | 33" | 12"

1½" LENSES PLATE — L_3, L_2

DIFFUSING SCREEN — 931A

8" LENS — L_1

IRIS, CONDENSER FILTERS, LAMP

½ PLATE CAMERA

21.5"

4 x 100 WATT BULBS

13"

6.5"

SAMPLE PLATFORM
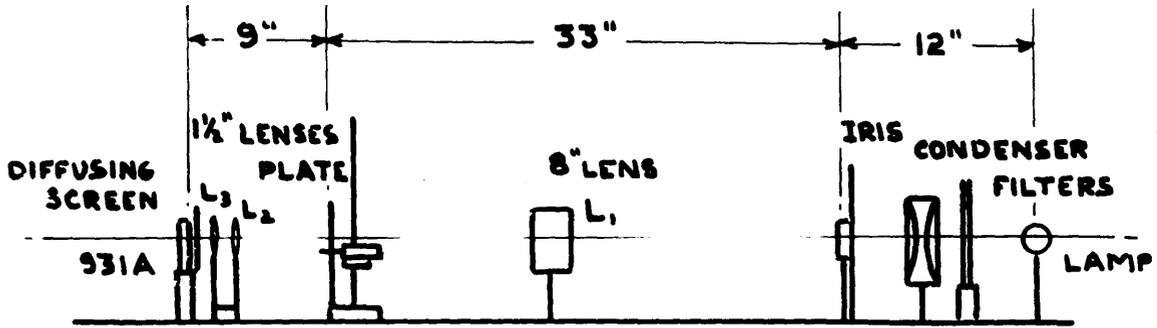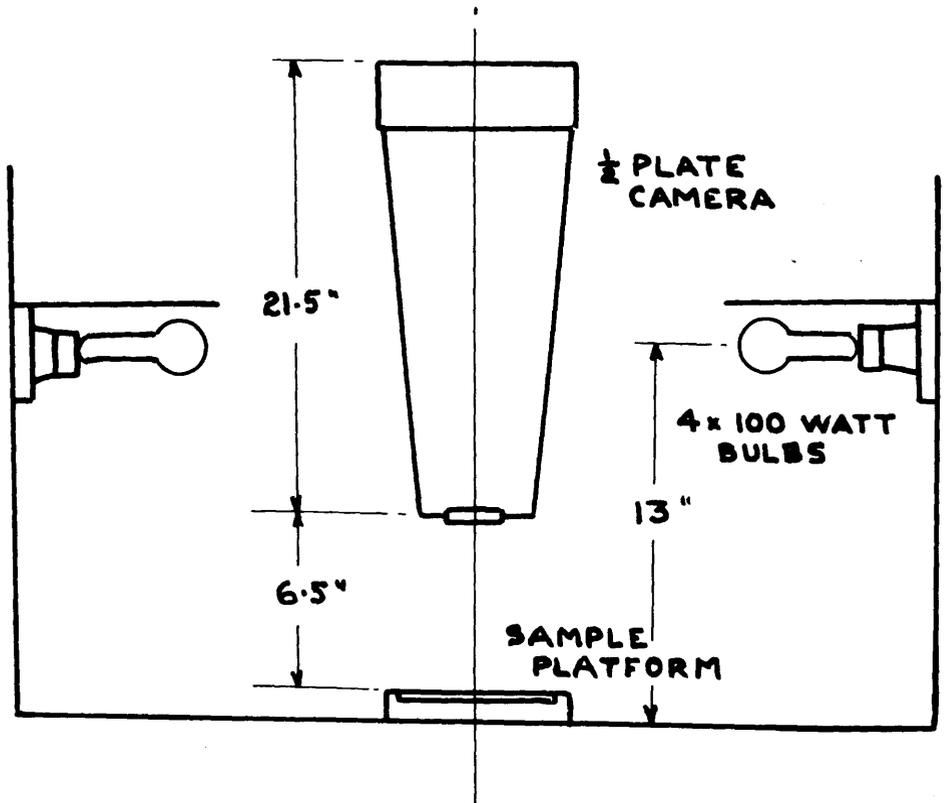
PHOTOGRAPHIC STAND

possibilities, once the necessary development work has been done.

4.17   Note on Experimental Conditions.

Only such experimental details as are pertinent to the purpose of the runs are given.   Many runs were for comparison only; in such cases convenient quantities were selected for the operation of the mixer, but these are not recorded in detail since there is little practical interest in miscellaneous data for small laboratory mixers except when some particular point is demonstrated.   In these cases all relevant figures are supplied.

The greatest impediment to the carrying out of large numbers of experimental runs was the time and labour involved, a single run taking nearly a fortnight to carry right through to the final plotting of results, and the estimation of each rate value required a full run.

4.2   The Apparatus.

4.21   Optical.

The optical arrangements are shown in the diagram, Fig.5.   A 36 watt bulb provided the light source, and from this the light passed through a condenser lens to the adjustable iris diaphragm.   Following the iris, an 8" focal length lens formed an image of the iris aperture on the

plate itself.   Modulated by the plate the light then was
focussed by two 1.5" lenses, through a diffusing screen, on
to the cathode of the photo-tube.

The iris diaphragm was a 13 leaf photographic one,
adjustable from .04" to 1.28" aperture, the diameter
being measured by mounting the iris in a protractor.   The
lever which altered the setting moved round the circular
scale of this protractor, and by calibration a very sensitive
measure of the aperture diameter could be taken.   This
calibration curve is given in Fig.8.   It was assumed that
the leaves were sufficiently closely spaced to give a good
approximation to a circle.

The focal length of the lens L_1 was chosen to give a
suitable range of spot sizes on the plate, and the actual
relation between diaphragm and spot diameters was calculated
as 1.42 : 1   (see Appendix IV).

The lenses L_2 L_3 were of short focal length, 1.5",
since the window of the photo-tube, which was small, had to
receive the whole of the light coming from the plate.   The
light from the filament source, as modulated by iris and
plate, was focussed on to a diffusing screen over the glass
window to avoid effects from the varying sensitivity of
different portions of the cathode surface.   The overall
arrangement, after some trial and error adjustment, worked
very well and calibrations are discussed in the electrical

section.

The total light flux passing through the plate was held constant at all scanning spot sizes, and so involved large reductions in light intensity as the spot diameter increased. This was done by a filter, using uniformly exposed plates, placed between the source and the condenser.   Fine control was obtained through adjustment of a rheostat inserted into the battery feed leads to the bulb.   This arrangement was a later refinement, as it had previously been suspected that the spectral distribution of the light might be important. It was found to have no effect, so this method of controlling the light was used in addition to the exposed plate series.

4.22   Electrical.

4.221   The Photocell.

It was desirable that the response of this should be linear with the light flux, and also that the sensitivity should be as high as possible.   The only one suitable seemed to be of the photomultiplier type, and a 931 A tube was used.   The H.T. supply to this came from a stabilised power pack, and the tube showed very satisfactory stability from a relatively simple power source.

4.222   The Measuring Circuit.

The load resistor for the photomultiplier was one

FIG. 6.

CIRCUIT DIAGRAM

250 V A.C.

MOTOR

+ 215 V

6 SN 7

1 µF.

BATT. CHARGER

BATTERY

LAMP

GALVO.

THERMO-
AMMETER
A.C.

1·5 K.   1·5K.   ·25 M

C.R.O.

POWER PACK II

STABILISER

HEATERS

SPOT LIGHT

6 V.

− 1100 V.

931 A

POWER PACK I

AMMETER
D.C.

·5 M
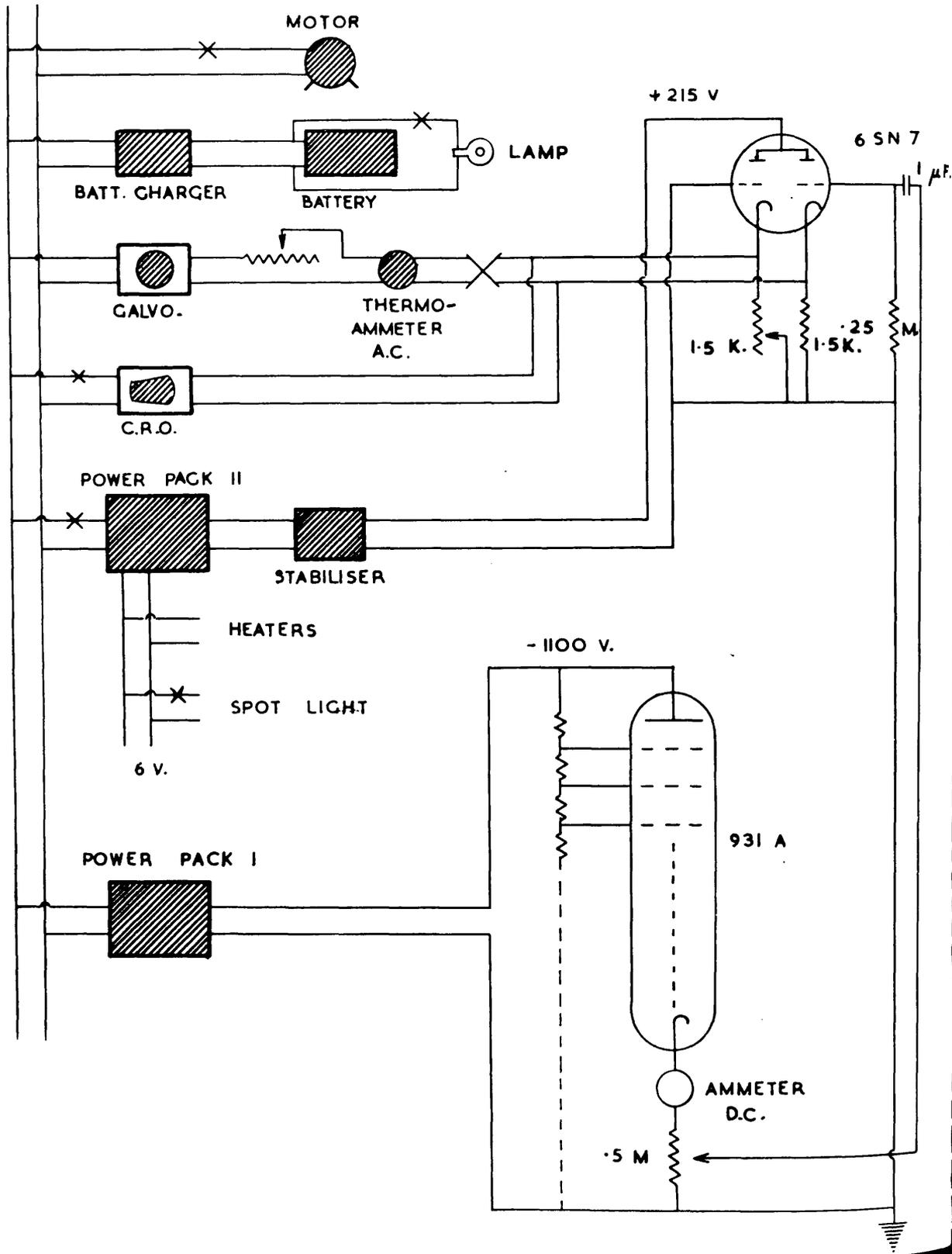
of .25 megohms , connected directly between the anode and earth, and the current passing through this, that is the total output from the 931 A , was measured by a D.C. microammeter. (A multi-range spot galvanometer). The A.C. component of this, arising from the modulation caused by the rotating plate, was fed off through a 1$/$uF. paper condenser and thence to the grid of a double triode. The final measurement was made between live and dummy anodes of this double triode using a thermo-microammeter, the circuit being shown in Fig.6.

This latter consisted of a heater wire in close proximity to a thermocouple, both being enclosed in an evacuated bulb. The range was from about 100$/$ua. up to 1.5 ma. and over this it gave consistent readings. Extensive calibration of this was carried out, and curves plotted since the thermo-microammeter is non-linear in its response. The e.m.f. developed across the thermocouple was dropped by a variable resistor box, and finally provided current to operate a sensitive spot galvanometer. The calibration of the thermoammeter was carried out using both sinusoidal and square waves, and over a wide range of frequencies. It appeared from this to be surprisingly reliable, and to be independent of frequency over a range from 20 cps. to 50 Kc. Further calibration was accomplished by applying sinusoidal voltages to the photomultiplier load resistor,

and thus measuring the response of the circuit as a whole.
Results are given in Fig. 9 .

To monitor the signal an A.C. cathode ray oscilloscope
was connected in parallel with the thermo-microammeter:
this enabled the operator to follow the effects of the
sample size alteration, and gave a qualitative picture of
the process.

H.T. supplies for the valves were from a power pack,
and to overcome mains fluctuations two neon tubes were
connected across the output to give uniform voltage.

4.223   The Light Source.

Originally bulbs fed from the stabilised mains were
tried, but the 50 cps. ripple made them quite
useless.   It was necessary to obtain stability over consid-
erable periods of time (some hours), and if possible high
intensity, but this did not seem easy unless discharge tubes
were employed.   It was found that enough light came from a
36 watt car bulb though the time stability, when fed from a
simple battery, was not adequate.   This was cured by continu-
ously charging the 12 volt heavy duty battery at the same
rate as the bulb draining it, so that the battery was main-
tained at the same state of charge, being in effect a swamp
reservoir between the mains-fed rectifier charger and the
bulb.   This gave very steady light, with high stability

and scarcely perceptible ripple.

4.23   Mechanical.

4.231   Scanning.

The problem was to provide for movement of the
scanning spot over the plate surface.   Also this
movement must be at a relatively high speed, to avoid diffi-
culties associated with low frequencies (i.e. less than 20
cps.) in the measuring equipment.   Methods of moving the
light beam were considered, but finally rejected in favour
of the simpler system of spinning the plate so that the light
beam, with its lenses and photo-tube, could be left
stationary.

The original mounting of the plate was using a suction
cup mounted on a rotating spindle.   When the speed was high
operational hazards were considerable, so the final solution
was to drill the plate and bolt it between 3/4" diameter
brass washers,with rubber spacers,directly on to the spindle.
These limited the area available for scanning, but not
seriously.

Drilling the plates was time consuming, using a copper
tube, and a drilling paste of carborundum and emery suspended
in camphor and turpentine, which was both aromatic and effic-
ient.   The resultant mounting was rigid and reasonably safe.
Driving the spindle through a flexible cable allowed for

Fig. 7

BRABENDER FARINOGRAPH
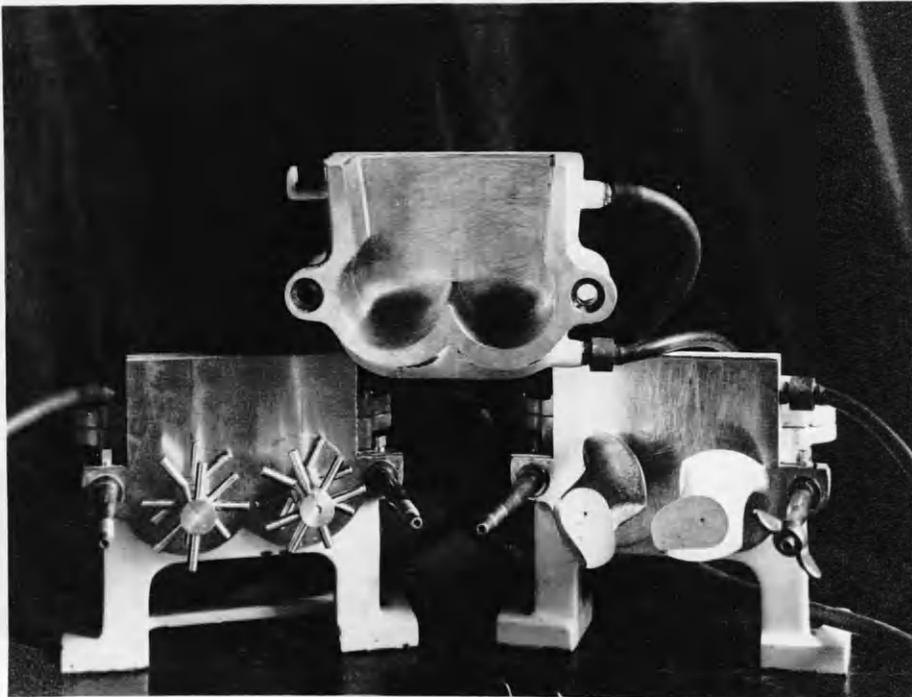
MIXING BOWLS

movement of the centre of rotation relative to the light beam: thought was given to the provision of some regular reciprocating motion for this, but it seemed too much of a complication and scarcely necessary. The drive was from a 1/6 H.P. induction motor at 1500 rpm., this speed being virtually constant.

4.232   The Mixing Machines.

The laboratory mixer used was a commercial Brabender Farinograph. This instrument is a standard piece of flour testing equipment, but its use for this purpose does not concern the present study. This mixer uses two "sigmoid arms" in a bowl with a dough capacity of about 600 grams in all. The overall machine, and also detail of the mixing bowl and blades, is shown in Fig.7. The dimensions of the bowl were $5\frac{1}{4}$" x $3\frac{1}{2}$" x $4\frac{1}{2}$" deep.

The machine is provided with means of continuously measuring and recording the mixing torque by a system of levers, actuated by the reaction torque of the driving motor. Also the mixing bowl is provided with a thermostatted jacket, and throughout the experimental runs this was maintained at 25°C.

To provide comparison with the "sigmoid arms", peg type mixing arms were made up, and fitted into a spare Brabender bowl. No particular design could be used for this, but the

pegs were fitted at 45 and $^{11}/_{16}$" intervals on the mixing shafts, the arrangement being illustrated in Fig.7. The two mixers will be termed, to differentiate them, the Brabender and the Prong mixers. The two shafts in both types rotated at differential speeds in the ratio of 2 : 3 . In all cases where speeds are given this refers to the slower, which was the speed of the motor drive shaft.

For the large scale test a "Morton Duplex" mixer with a capacity of up to 100 lb. of dough was used. This machine is shown in Fig.29. It also employs the "sigmoid arm" type of blades with differential speeds of 45 : 73 . There was no provision for thermostatting or for measuring the power consumed.

4.24   Photographic.

4.241   Material.

A great deal of investigation was necessary to obtain suitable materials for this part of the work. Details are of no general interest, so only the final choice will be given. The colours used were ordinary white dough, and dough otherwise identical, but mixed with water containing 1/5 % of anatto, an orange dye whose colour derives from the carotenoid bixin. In effect the mixing process, from the colour viewpoint, amounts to a dilution of this dye intensity, and over the range of this dilution the photographic process

had to provide a silver deposit proportional to the dye concentration.   A blue filter (Wratten 39) over the taking lens was found to assist this.

4.242   Equipment.

The actual photograph was taken with camera and

lights in a permanent mounting, the sample being illuminated by eight 100-watt bulbs.   The photographic apparatus is shown on Fig.5.   The exposure was   10   seconds at   f9   taken through a   120 mm.   lens.

Development was found to be critical also, and was done using a dilute metol hydroquinone developer in a tank holding 20   plates.   Agitation was important for reproducibility and was on a standard, intermittent but regular, pattern.   This gave rather a low γ,(.8),   but apparently the best results. The camera gave a magnified image,(linear dimensions x 2.3), focussing being by a ground glass screen using a standard half-plate camera, and the photograph was taken on to slow orthochromatic process plates (Ilford N20, Ordinary). Overall the photography provided many difficulties some of which were not entirely solved - the results are discussed further under "calibration".

4.3   The Experimental Procedure.

4.31   The Mixture.

4.311   Proportions.

In all of the work reported in this discussion the
proportion of the components was orange 1 , to
white 4 .   This may seem arbitrary, but the reasons were:-

i)   It was possible to make the "artificial" mixtures much
more easily in proportions such as these.

ii)   Most of the reported work on mixing had been on   1 : 1
proportions and it seemed of interest to diverge from
this.

iii) The supply of anatto dye was limited and there was doubt
if further supplies would duplicate it.   These propor-
tions made for its conservation.

The theoretical effect on the mixing measurement of these
proportions would be small, and there seems no special virtue
in the 1 : 1 mixture over any other, so long as the amounts
of the two components are comparable: when one is present in
much greater quantity than the other, then new problems are
certainly raised.   This question is one which remains to be
investigated.

4.312   Texture.

The initial preparations involved the making up of
two homogeneous masses of dough, one white the other
orange.   These were made up under standard conditions, the

flour being in all cases mixed with 50% of its weight of water into a uniform dough, unless otherwise stated. This result in a stiff plastic mass which will scarcely flow under its own weight. The elastic properties of dough are such that it cannot really be much further characterised, except by empirical comparisons or by using very elaborate apparatus which, even then, gives results of dubious objective value. (See Appendix II).

4.313   Mixing.

The method of loading was standardised as far as possible by putting the more bulky component, white, into the mixer, and turning it over for six revolutions. Then the other component was spread out evenly over the top, and actual mixing commenced from this point. All sampling was done at intervals of six revolutions or multiples thereof, which meant that the blades were in the same relative positions at the beginning and end of runs. Torque measurements were taken during the running, but it was found more satisfactory to do this independently, for record purposes. The flour used in all runs was National Spring 80% extraction.

4.314   Sampling.

Procedure for this varied, being improved slightly in the later runs though there was no substantial difference in the results. The final method was; at the end

of a run the whole mass was removed from the mixer as carefully as possible to avoid disturbance, though some was inevitable. The mass, then in the shape of a rough ball, was cut by a wire into sections, one or two samples being taken out each an approximate cylinder $5/8$" thick and $3 - 4$" in "diameter". These samples were then gently squeezed between two sheets of plate glass in a frame to a thickness of $1/2$", and both the top and bottom surfaces were photographed. The section planes were selected at random, as was the portion chosen from the samples for photography. The squeezing, besides being small, did not affect the cut surfaces merely splaying out the sides which were outside the photographed region.

After being photographed the material was removed from the plates and returned, with the remainder of the mixture, to the machine, and the mixing proceeded.

4.32   Scanning.

The equipment for this was housed in a dark room, so that there was no necessity to shield the light sensitive portions. This meant that access to all parts of the apparatus was virtually unrestricted.

The procedure for taking the results was: with the plate spinning, and the iris set to its smallest diameter, the light intensity was adjusted, using filters and the

rheostat, to give a reasonably large reading on the thermo-microammeter. Readings both of this and the D.C. were recorded, and then additional filters were placed in the light path and the iris altered to the next larger setting, these being taken at regular intervals on the protractor scale. At this,the light was then adjusted to give approximately the same D.C. reading, i.e. the same mean light flux, and both instruments again read, the A.C. having decreased because of the averaging effect of the larger sample size. This was then repeated over the range of sample sizes, and again, having moved the plate centre, over the whole range for another position of the scanning annulus on the plate. The two positions taken were at mean radii of 1.3" and 1.8" from the spindle axis.

The D.C. was kept at the same figure over the run to maintain the highest degree of comparability for all the sample sizes at a fixed degree of mixing. When moving to higher degrees of mixing, this D.C. figure had to be raised to obtain reasonable values of the A.C., for the total fluctuation fell off with mixing as predicted in the theory. A feature, quite noticeable at high mean current value, was the charge on the blocking condenser which became large and when the light was altered suddenly, moving to a larger sample size, there was a surge in the A.C. This meant that considerable care had to be exercised to make changes grad-ually, to avoid overloading the thermo-microammeter which

was without any protection.

4.33   Calculations.

The non-linearity of the thermal instrument necessi-
tated the use of a calibration chart, which converted
its readings into the root-mean-square voltage across the
931 A load resistor.   This reading was directly propor-
tional to the mean flux given by the D.C. instrument reading,
so, to compare values with the different fluxes necessary for
reasonable A.C. figures, they were converted to a standard
mean flux arbitrarily set at a scale reading of 100 units
(actually corresponding to 42.5 microamperes) D.C.   This
value for each sample size, is then averaged over all the
plates at the same mixing stage, (usually four, with two
readings on each plate making eight in all) and this provides
the figure, for that sample size, given as m (volts) on the
graphs and in the tables.

In the rate plots a further averaging process over the
six size samples is performed, and the resulting single
figure is given for the stage of mixing as m' (volts).

No attempt is made to convert these figures into concen-
trations.   The reasons for this are given more fully in the
discussion, but briefly there seems no point in making the
conversion since m or m' are proportional to the compar-
able values of $\bar{s}$ and conversion procedure might conceal

Fig. 8

Calibration Curves

OPTICAL SYSTEM

IRIS AREA - PHOTOCURRENT
(CONST. LIGHT INTENSITY.)

MICROAMPERES

(IRIS DIAM.)^2 × 10

IRIS CALIBRATION

IRIS SCALE READING (DEG.)

SCANNING SPOT DIAM. (IN.)
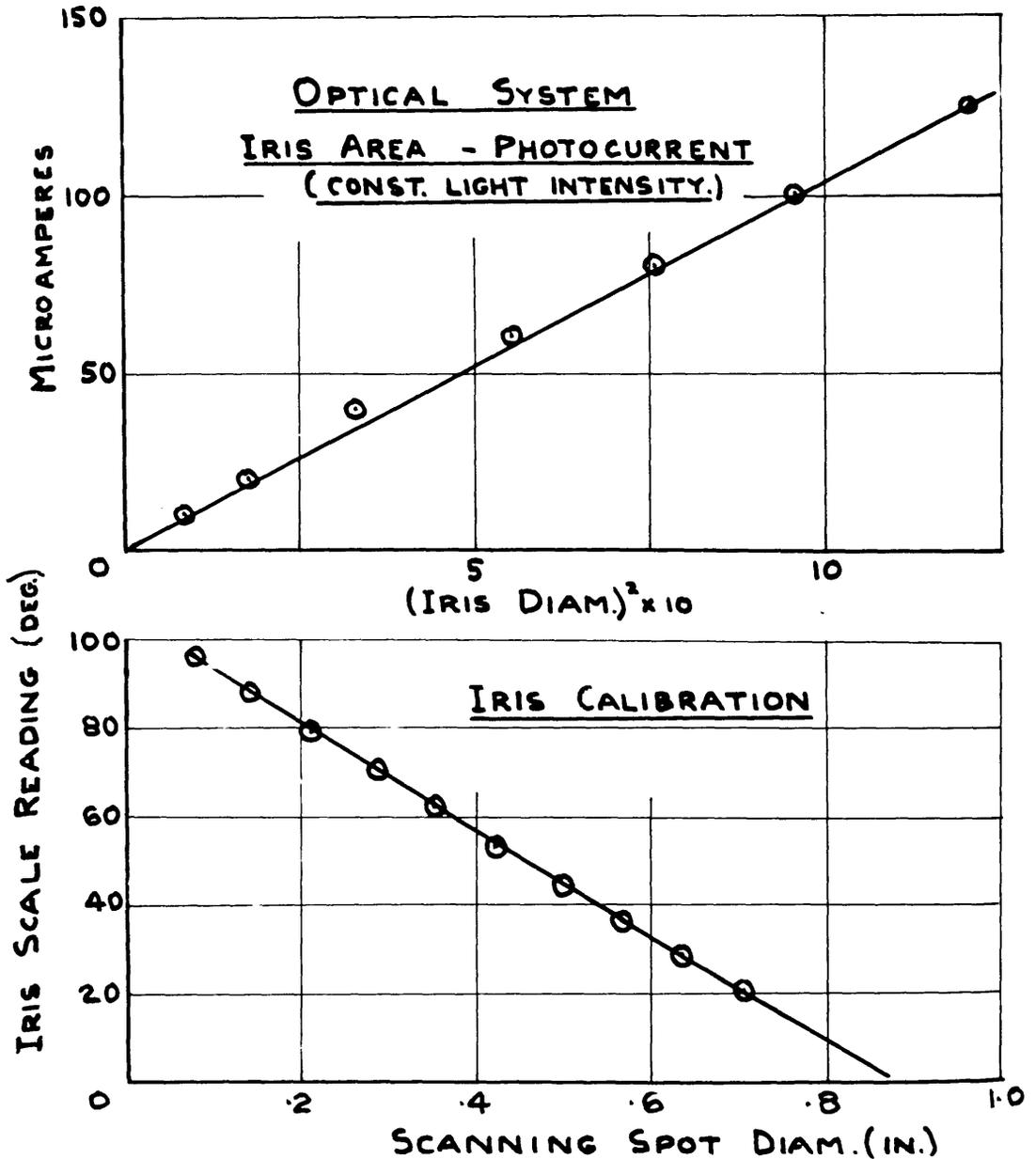
some of the sample variation.

It is possible to estimate the initial value of m at
no-mixing, (see Appendix IV) and on some of the rate plots
this point has been included.   The values chosen for the
sample sizes may appear arbitrary, but result from regular
20° intervals on the protractor measuring the iris aperture;
when converted into inches they do not appear at particularly
convenient intervals.

4.4   Calibration Work.

4.41   Optical.

The aperture of the iris diaphragm was calibrated,
using a series of plug gauges to give a relation
between the angular reading on the protractor and the actual
diameter.   This actually gave the diameter of the inscribed
circle, but the iris was a good approximation to a circle and
the error in taking it as one would be small.   The ratio of
the iris diameter to that of its image on the plate was
calculated as being 1.42 : 1 and details are given of the
computation in Appendix IV.

4.42   Power.

The Brabender mixer was equipped with its own driving
motor, freely mounted on bearings so that the reaction
torque could be measured through a lever system to a scale,

Fig. 9

CALIBRATION
CURVES

MEAN CURRENT - VOLTS
(R.M.S) FOR DIFFERENT
INPUT FORMS.

VOLTS (R.M.S.)

INPUT MICROAMPERES (D.C.)

BRABENDER MIXER
POWER.

POWER (H.P. × 10²)

SCALE READING
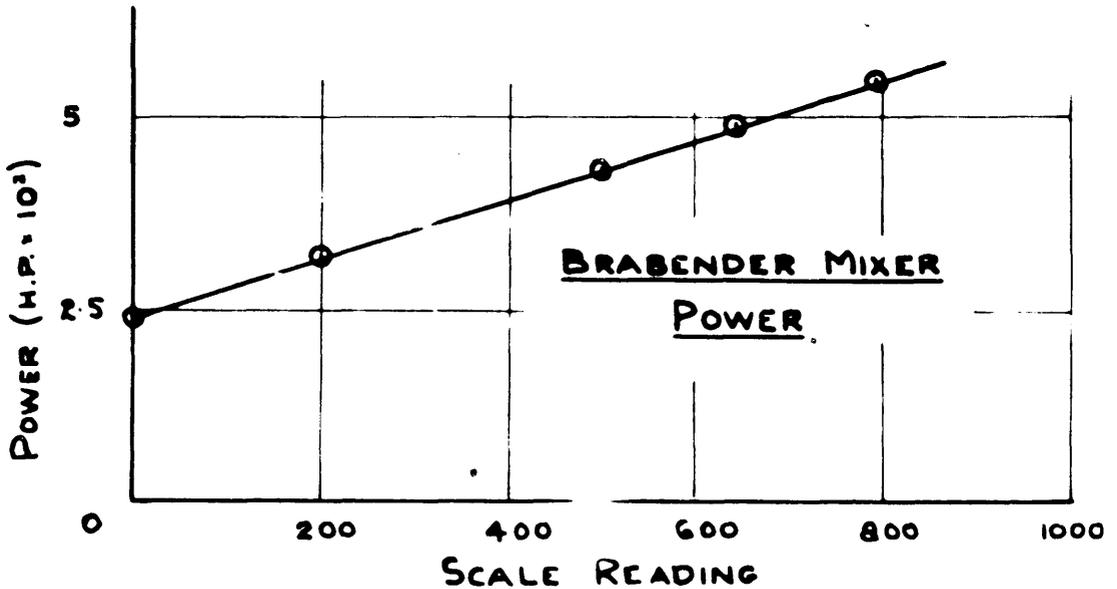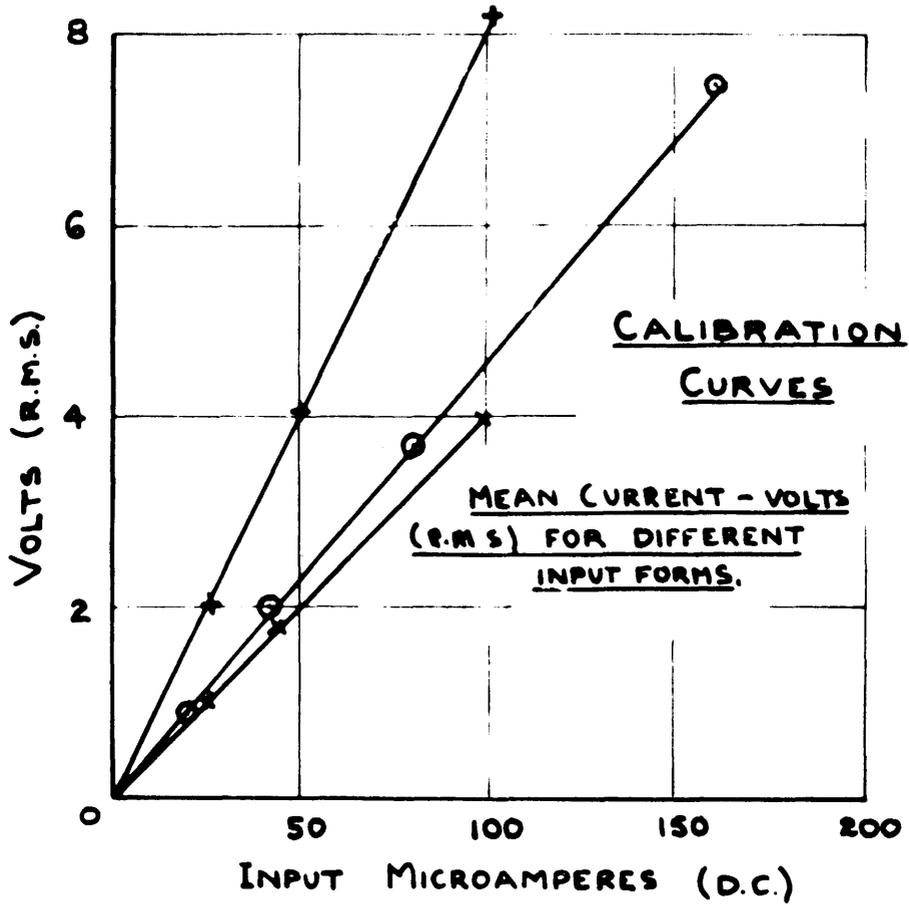
and also recorded against a time base.   Static calibration
was effected by hanging weights on a lever arm and taking
corresponding deflections.   The no-load friction could be
determined by observing the torque needed to rotate the
blades of the empty mixer, and it was assumed that the
additional losses in friction and gearing under load would
be small compared with the power used for the mixing itself.
Graph   9   shows the power calibration obtained.   Since the
power consumed was not dependent on the dough colour the
actual readings were taken on special runs for this only,
during which conditions could be better controlled.   Since
dough changes in properties with working it was very diffi-
cult to obtain reliable figures even under the most careful
control, but the figures quoted are obtained from the results
of many runs and give at least a very good idea of the power
taken.   This point about dough properties is discussed in
Appendix II.

4.43   Photographic.

        A great deal of trial and error work was done on this
        and even the final results were not particularly
satisfactory.   However an approximately linear relation
between the colour dilution, i.e. concentration, and silver
deposit was obtained.   This is perhaps best shown by Fig.10.
It shows the result of mounting eight dough samples in a
frame, each sample in rotation having half the concentration

Fig. 10

TRANSMISSION OF
LIGHT THROUGH PLATE.
STAGES ARE AT CONCENTRATIONS
EACH HALF THAT OF THE PRECEDING ONE
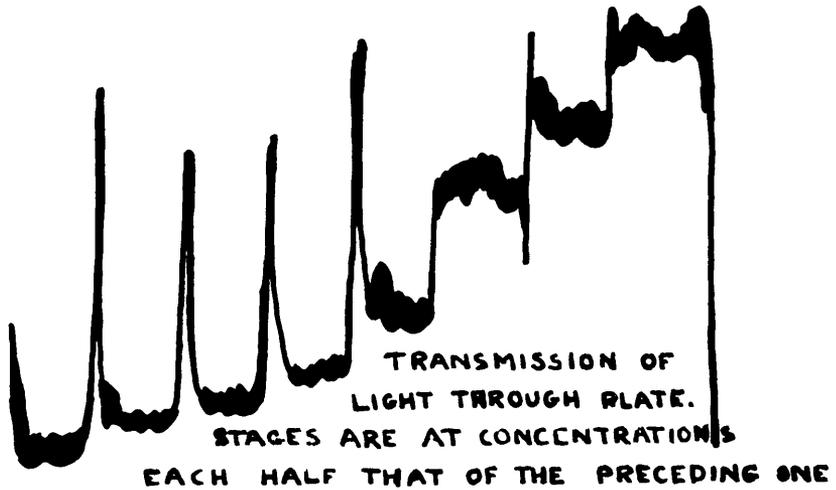
PHOTOGRAPHIC CALIBRATION

CALIBRATION OF
ELECTRICAL CIRCUIT
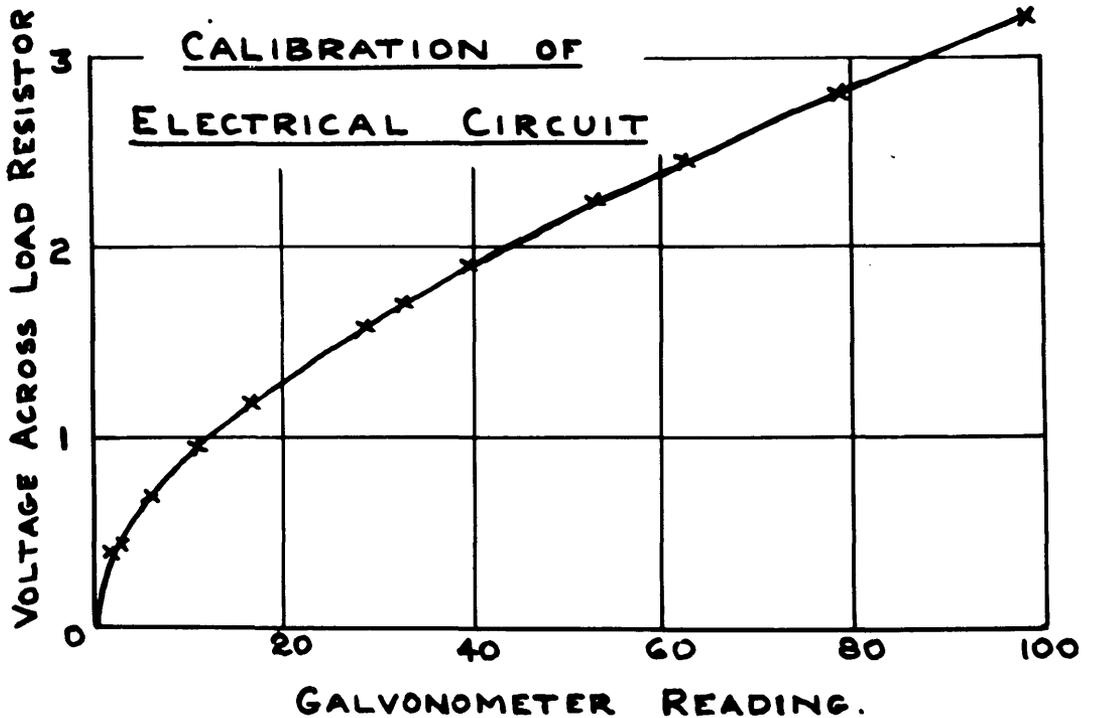
of the one before it, (the beginning and end points being obvious) photographing this, scanning with a small spot, and photographing the resulting trace on the C.R.O.   It may be seen that the curve is very nearly parabolic, though it does depart from this at the extremities.'   This however was the best result that could be obtained over a wide range of dyes, filters, concentrations, and development conditions.

The actual reproducibility of the photography, so far as development and exposure are concerned, was checked by taking two plates of one particular mixture, and putting them independently through the processing.   The results are shown in Table III.

4.44   Electrical.

4.441   Aperture Diameter against Mean Current.

It was necessary to check that the response of the 931 A was linear with the increase in light flux. Fig.8 , a plot of area against microamperes, shows this to be so.   It indicates linearity, at least in the sum, of the collection of the light by the window of the tube through the various lenses and of the tube response itself.

4.442   Calibration of the Measuring Circuit.

Two methods were used.

a)   One was a check of the thermo-microammeter itself

against input, from a signal generator.   This showed, as expected, non-linear but reproducible response, and no frequency dependence.   This latter was essential because, as explained in the theoretical section, though no immediately obvious frequency components exist in the scanner output nevertheless there is a frequency spectrum and, for a constant scanning speed, it will change with mixing so the measuring instrument must be independent of this.   Independence of wave form, also and equally essential, was established by comparing the results of inputs of various wave shapes e.g. square.

b)   The other check was an overall one.   A.C. (50 cps) was applied to the 931 A load resistor and the response of the thermo-microammeter to this was measured, at various current loadings.   Fig.10 gives the results and was used as the calibration curve of the measuring apparatus in the calculations, though replotted as an alignment chart for convenient use.

Further investigation, which is in a sense calibration, may be found under the section on the results from "Artificial" mixtures.

FIG. 11
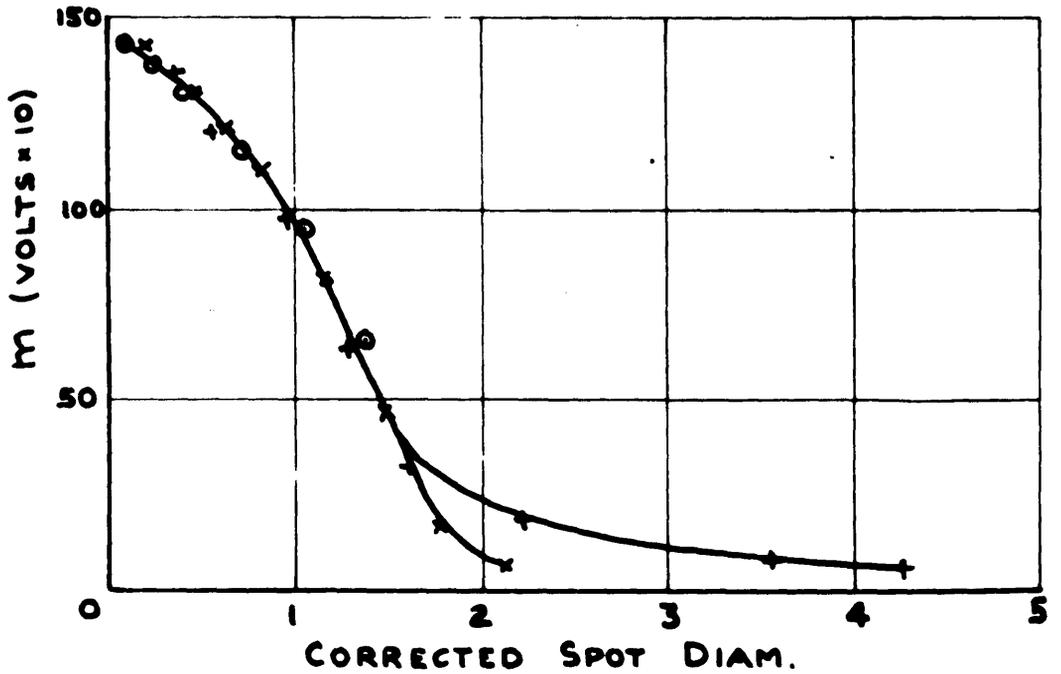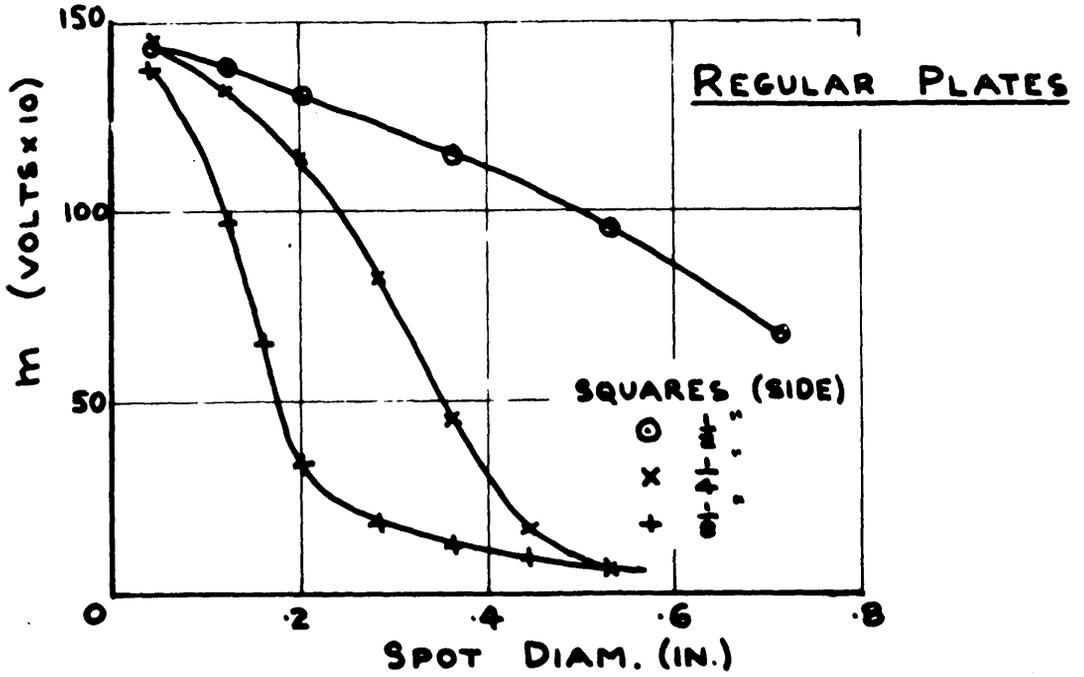
4.5   Results.

4.51   Artificial Mixtures.

By this term is meant plates which were prepared synthetically and systemmatically, rather than photographs of actual mixtures.

4.511   Regular Patterns.

Plates were prepared in which squares of black paper were pasted on to the glass in regular array covering 25% of the total surface, and three sizes of squares were used, one size to each plate, of sides $1/2"$, $1/4"$, and $1/8"$. These were then scanned and the results, plotting m against spot diameter, are shown on Fig.11 for the three plates. These curves are of the expected shape, and should in fact all be the same curve but to a different horizontal scale. This is demonstrated also on Fig.11 in which the curves are replotted to give substantially the same line, the abscissae being in the ratios 4 : 2 : 1   though, since it is taken between fixed scanning limits, the range of the three curves will alter. Discrepancies for the lower values, in particular the relatively high values for the 'smallest spot' curve, may be explained by the difficulty of preparing the pattern of $1/8"$ side squares, when the leaving of traces of glue on the clear portions of the plate could not be helped giving rise to additional fluctuation components.

Fig. 12
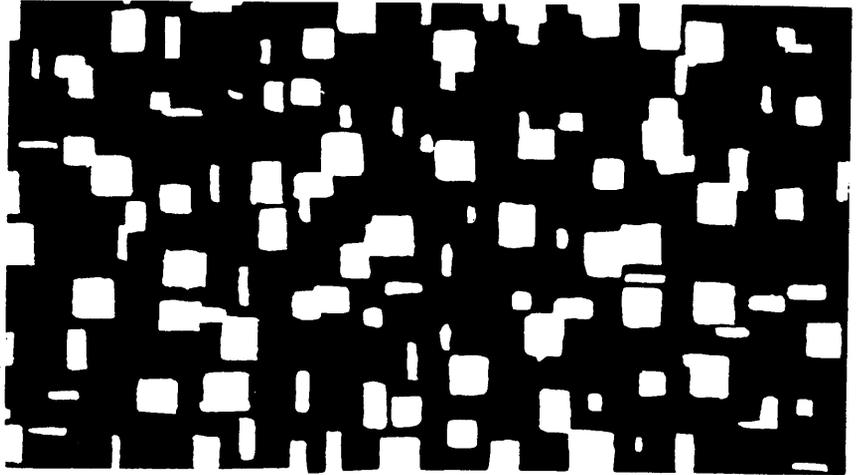
SAMPLE OF RANDOM PLATE

FIG. 13

RANDOM PLATES

CORRECTED DIAM. RATIOS

ORIGINAL SIZE RATIOS
⊙ 1·0
× 1·75
+ 2·4

CORRECTED SPOT DIAM.
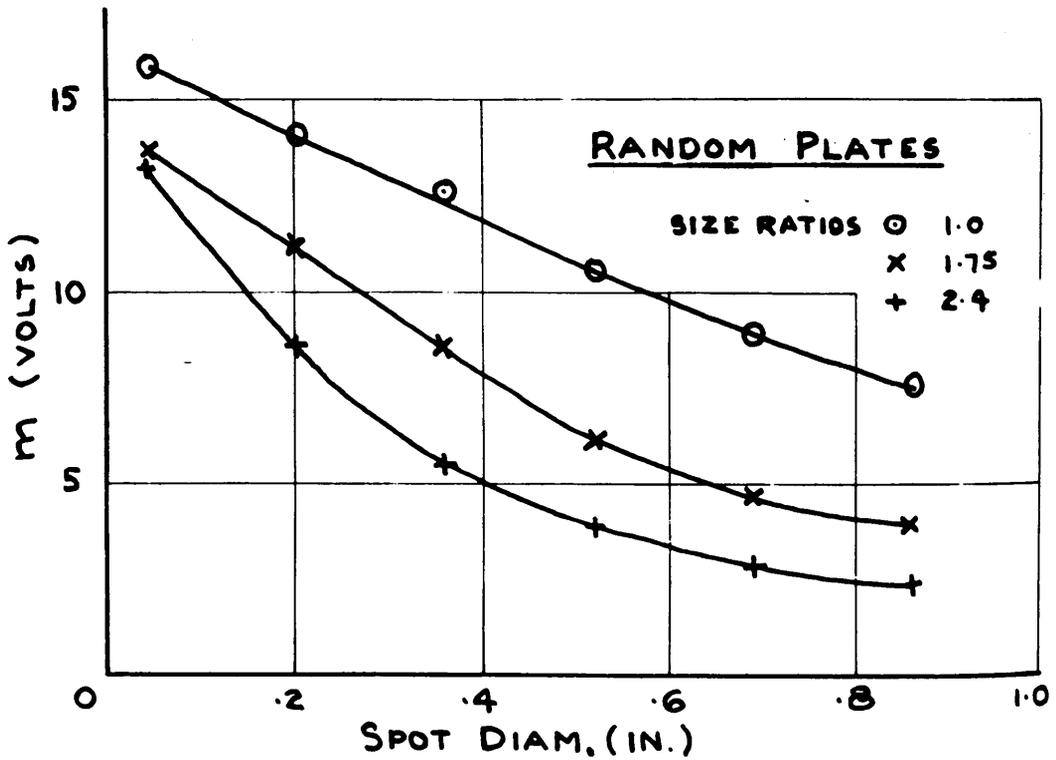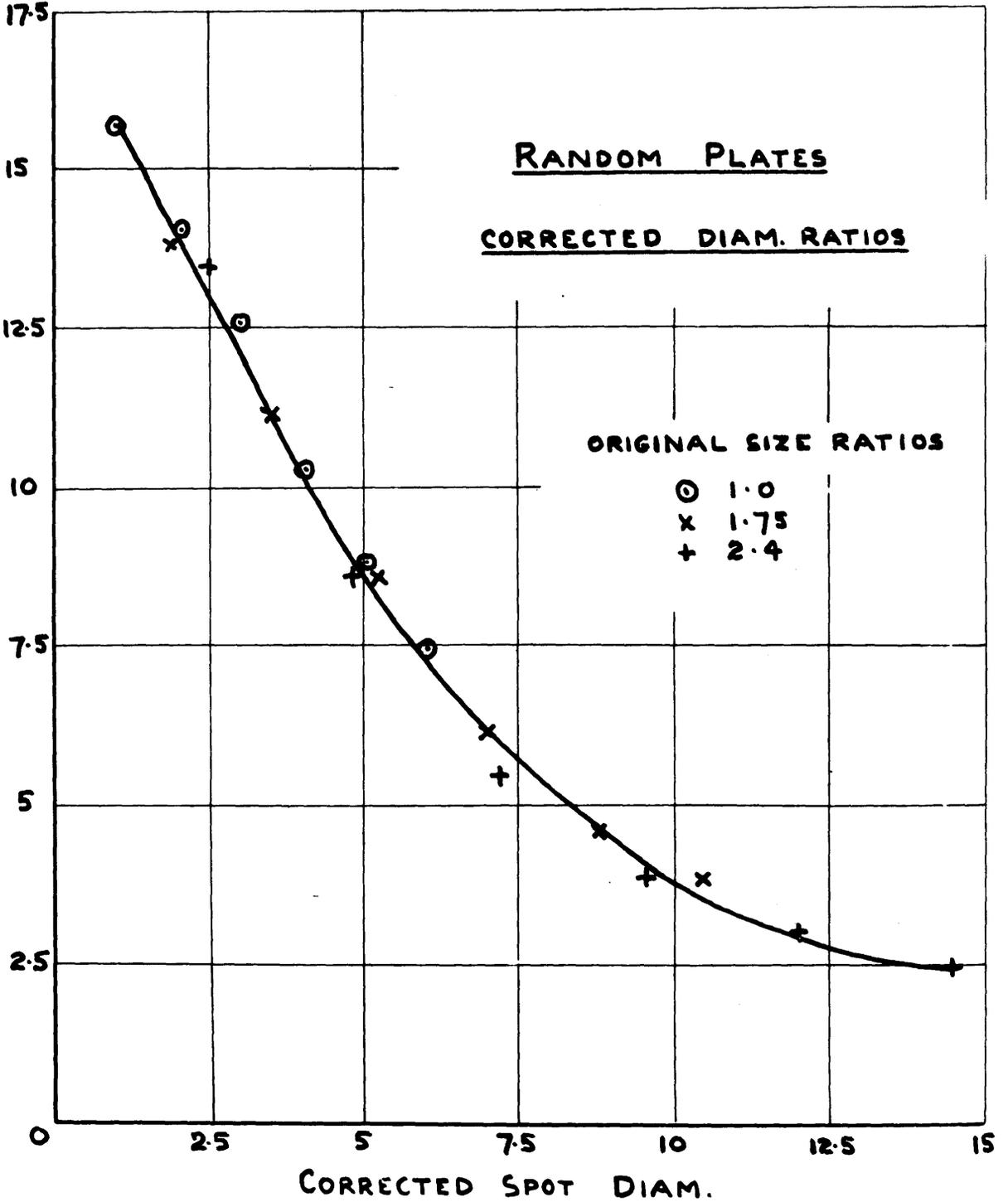
This could have been avoided by changing the scale photo-
graphically as in the next section.

4.512   Random Patterns.

A pattern containing an average of 20% black was
made up using a table of random numbers, the actual
procedure being detailed in Appendix III.   Perhaps the
pattern would have been more truly random had a further
orientation factor been introduced but since this does, to
some extent, arise from the sampling no extra term was
included.   A plot is given of m against Sample Diameter
(Fig. 12) for plates of three different scales.   The scale
was determined by the magnification used in the camera: three
plates in the arbitrary length ratios of 1 : 1.75 : 2.4 ,
were made up taken from different portions of the original
pattern.   These are also plotted with a horizontal scale
corrected for this ratio, and again one curve results (Fig. 13).
This seemed confirmation of the behaviour both of the apparatus
and the theory, and from this point the study of real mixtures
commenced.

4.52   Real Mixtures.

4.521   General.

The first interest was in the behaviour of m with
both sample size at a fixed stage of mixing, and with

FIG. 14

FIG. 15

EFFECT ON m OF SAMPLE SIZE.

+ GIVES MEAN m'

6 REVS.

12 REVS.

18 REVS.

24 REVS.

30 REVS.

36 REVS.

m (VOLTS)

SPOT DIAM. (IN.)
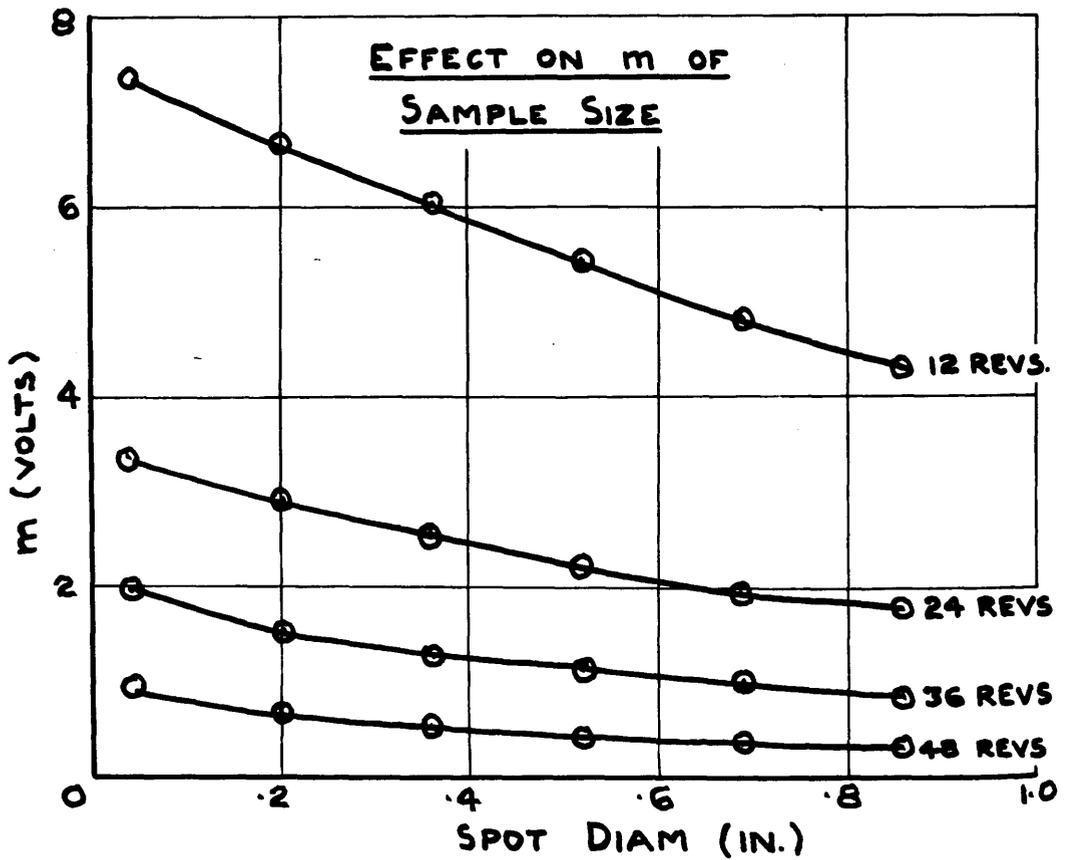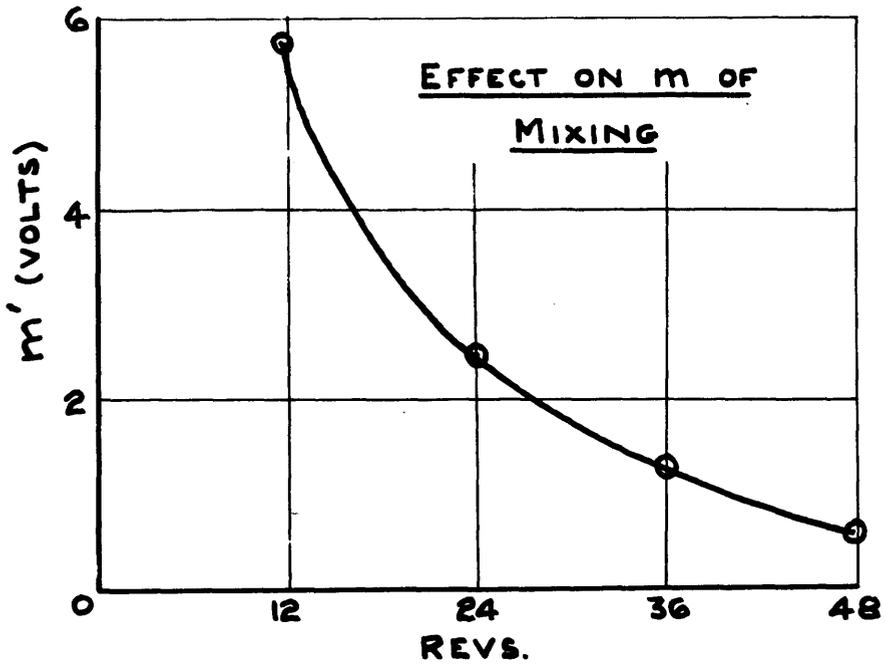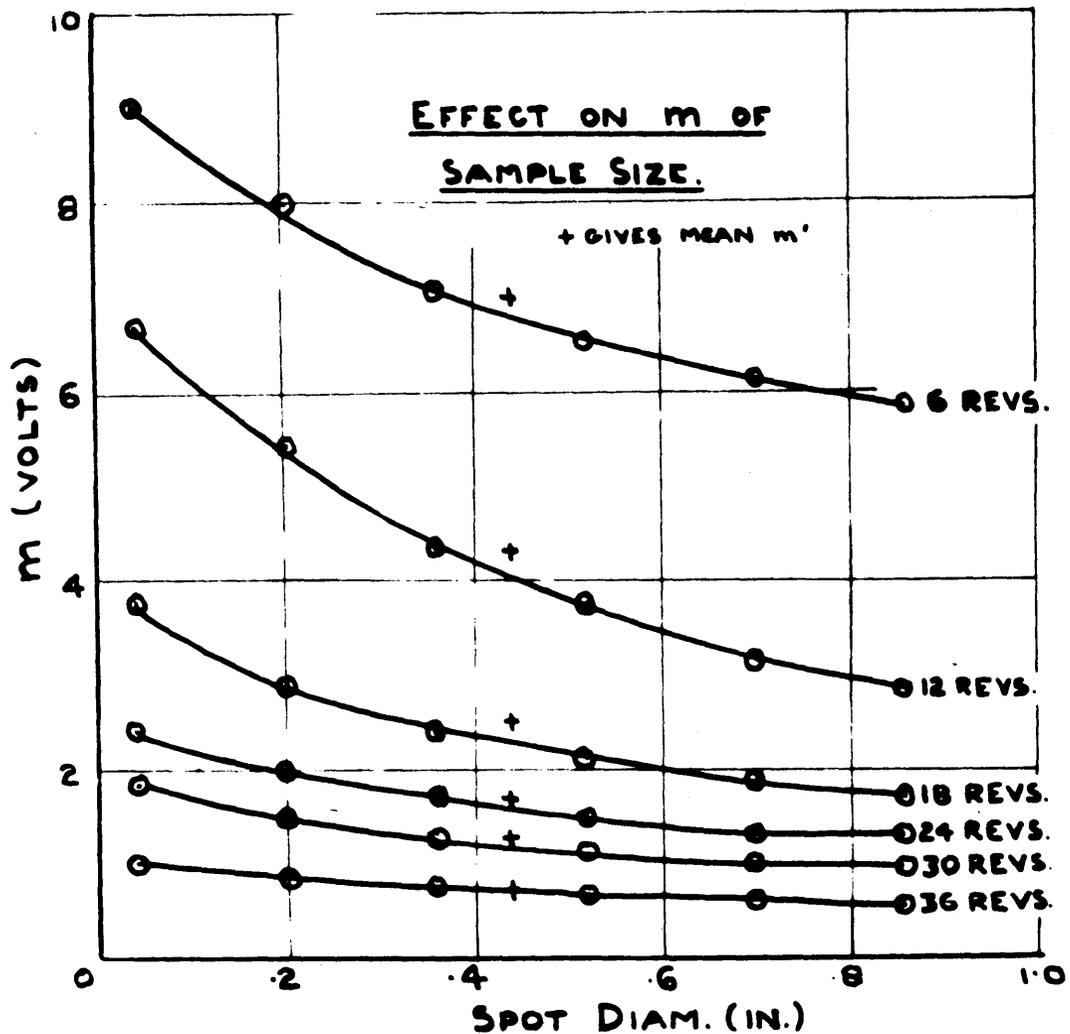
the converse problem, though in many respects similar as
shown in the theoretical section, of its variation with
mixing at fixed sample size.   A series of runs was carried
out using the Prong mixer, under various experimental condi-
tions which are not important in the present connection
which is concerned with patterns of behaviour.   The plots on
Figs. 14 and 15 are from one run and those on Figs. 15 ,
16 , and 19 from another, this latter being more complete
and so all of the effects are shown separately.   The actual
numerical figures used in plotting this set of graphs is
also given in Table I.   Figure 17 is included because it
is at a slower mixing rate to allow consideration over a
greater range of mixing revolutions.

4.522   Sample Size Effects.

        The effect of variations in sample size on m at a
        fixed degree of mixing, is shown on the various
curves of Figs. 14 and 15 .   Each curve on the graph
results from the mean value of the plate scans at a degree
of mixing indicated, in terms of revs. of the mixing arms, by
the numbers alongside.   They show the gradual decrease in
m with increasing sample size.   Since the larger sample
sizes are effectively averaging the values of the variation
to an increasing extent, this diminution in m is to be
expected.   It may be noticed that this variation is quite
considerable, and also that the rate at which it occurs alters

FIG. 16

EFFECT ON m OF
MIXING

FIG. 17

EFFECT ON m
OF MIXING

(WIDER RANGE)
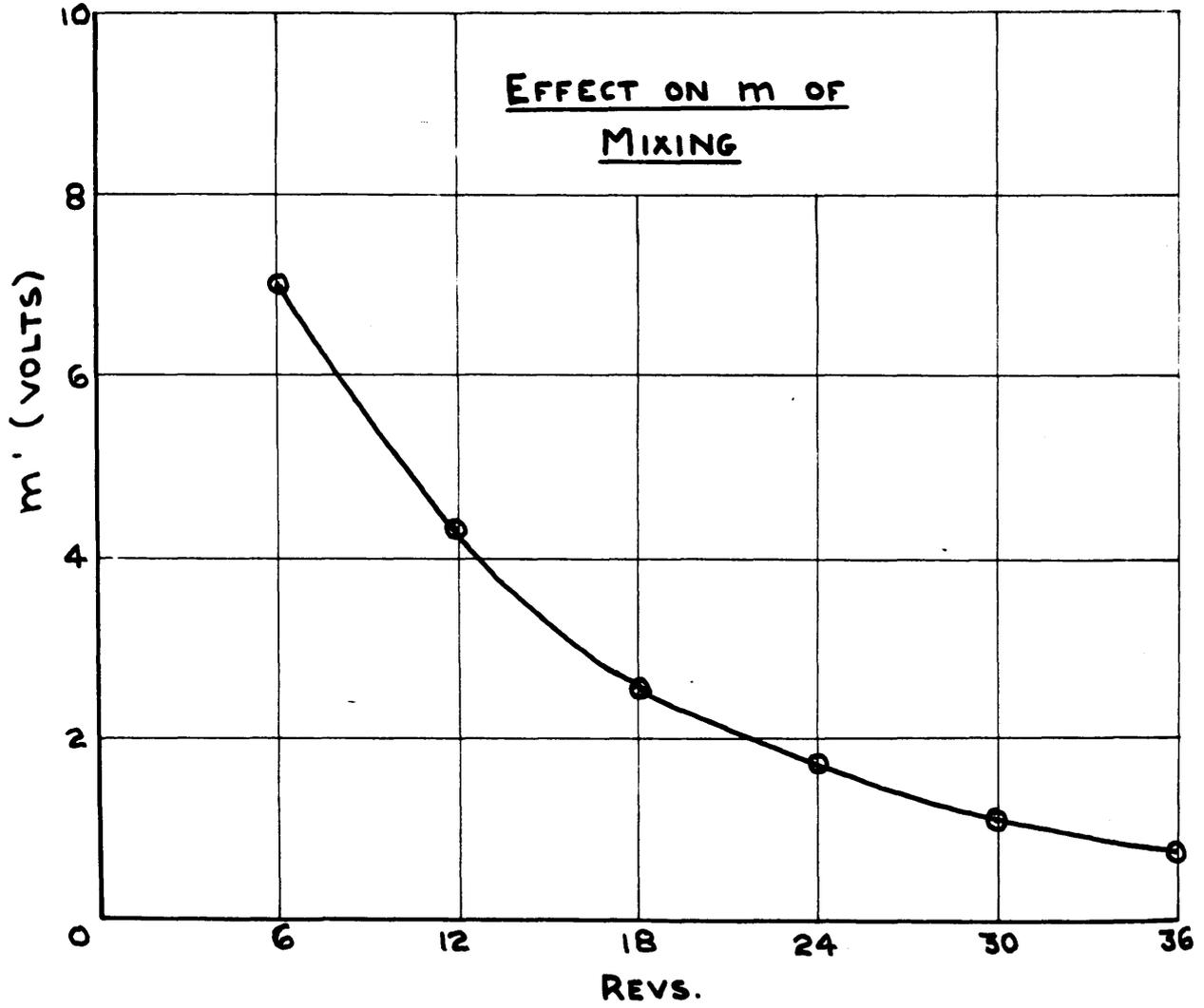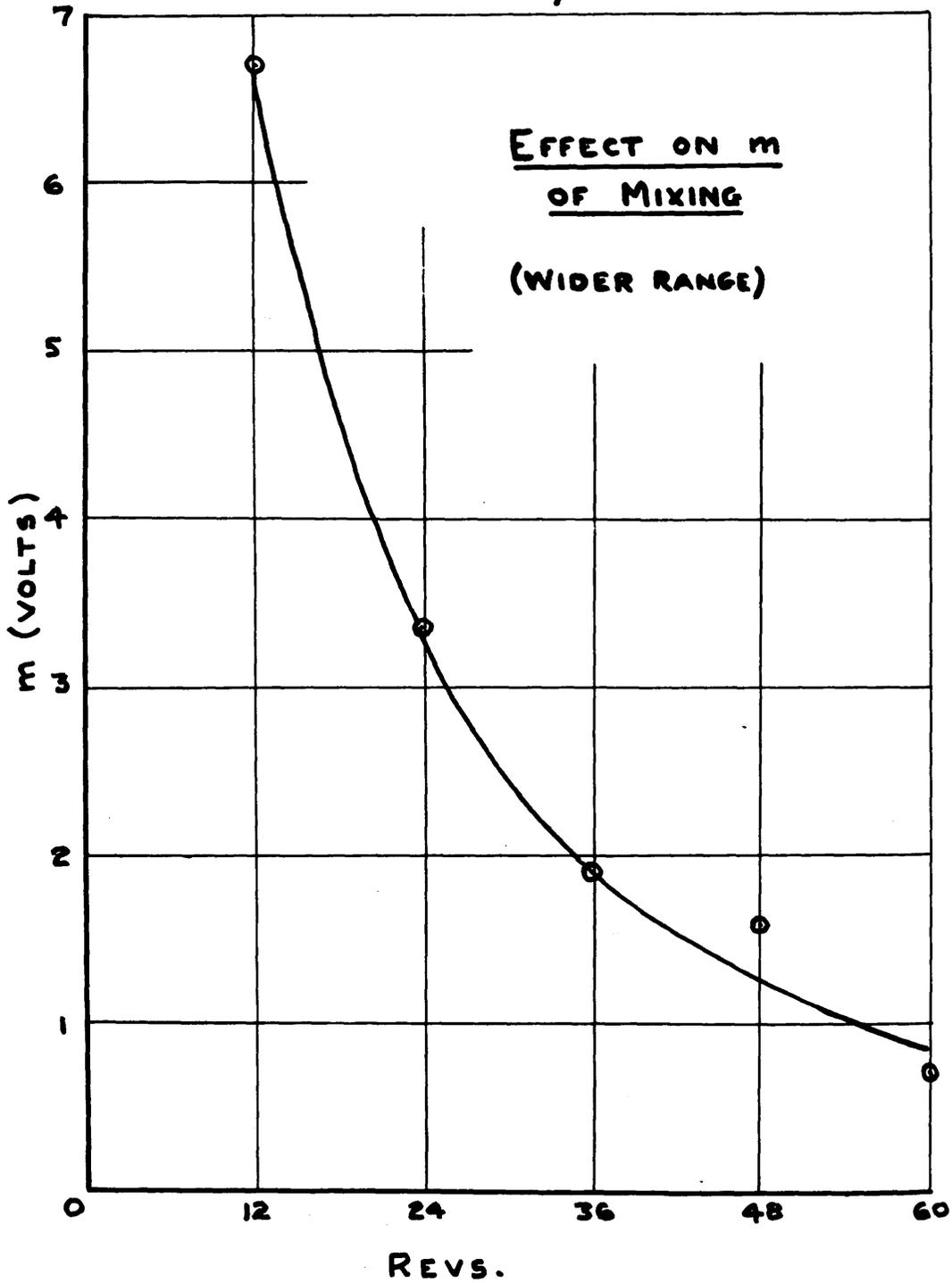
at the different stages of mixing.   Figure 15 shows this
effect particularly well, the curves at intermediate stages
being steeper in slope, and showing more pronounced variation,
than those at stages earlier or later.   Apart from this, the
shape of the curves is quite regular showing a smooth
monatonic decrease with sample size.

4.523   The Progress of Mixing.

From the same curves as were considered in the last
section it may be seen that, between the mixing intervals
considered, there is a very sharp drop in the m values at
any particular sample size.   For measuring rates of mixing
a single value has to be placed on the state of the mixture.
The obvious choice for this, in the experimental circum-
stances, seemed the mean value of m taken over the range
of sample sizes, giving equal weight to each.   These values,
m' , are plotted on Figs. 14 and 16 and show a smooth
downward progression with the revolutions of the mixer
blades.   Figure 17 gives the m' figures over a somewhat
wider range from another run.

The centrally placed curves on Figs. 18 and 19 show
the m' values for the first two runs, plotted logarithmi-
cally against revs.   There seems no reasonable doubt, from
the position of these points, that the curves are straight
lines.   Thus the measures used give, as predicted, a first

FIG. 18

MIXING RATES

SHOWING EFFECT OF THE
SAMPLE SIZE

X - ·04"D SPOT
O - MEAN
⊗ - ·86"D SPOT

m (VOLTS)

REVS.

FIG. 19

MIXING RATES

SHOWING EFECT OF THE
SAMPLE SIZE

X — ·04"D. SPOT
⊙ — MEAN
⊗ — ·86"D. SPOT

m′ (VOLTS)
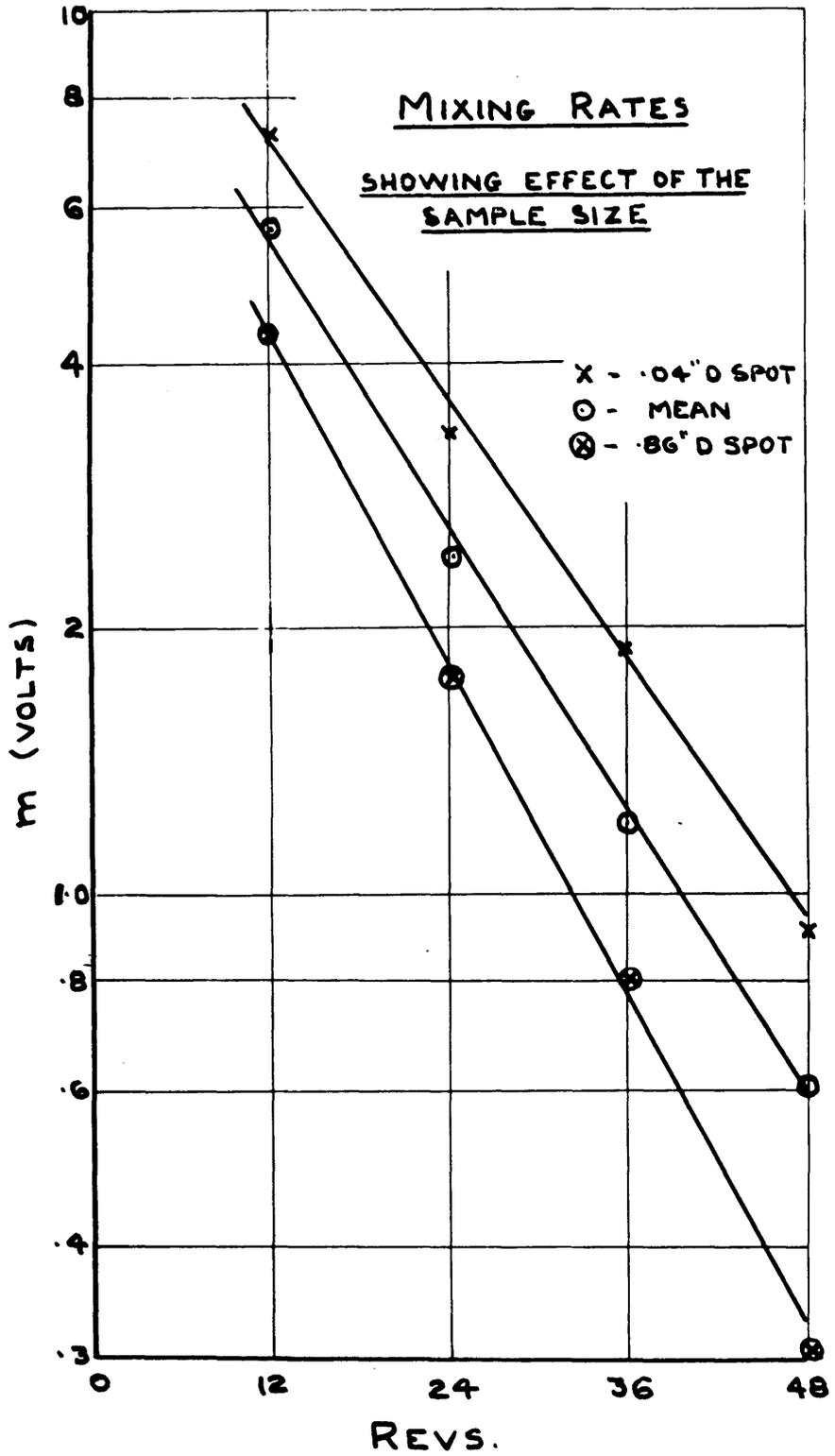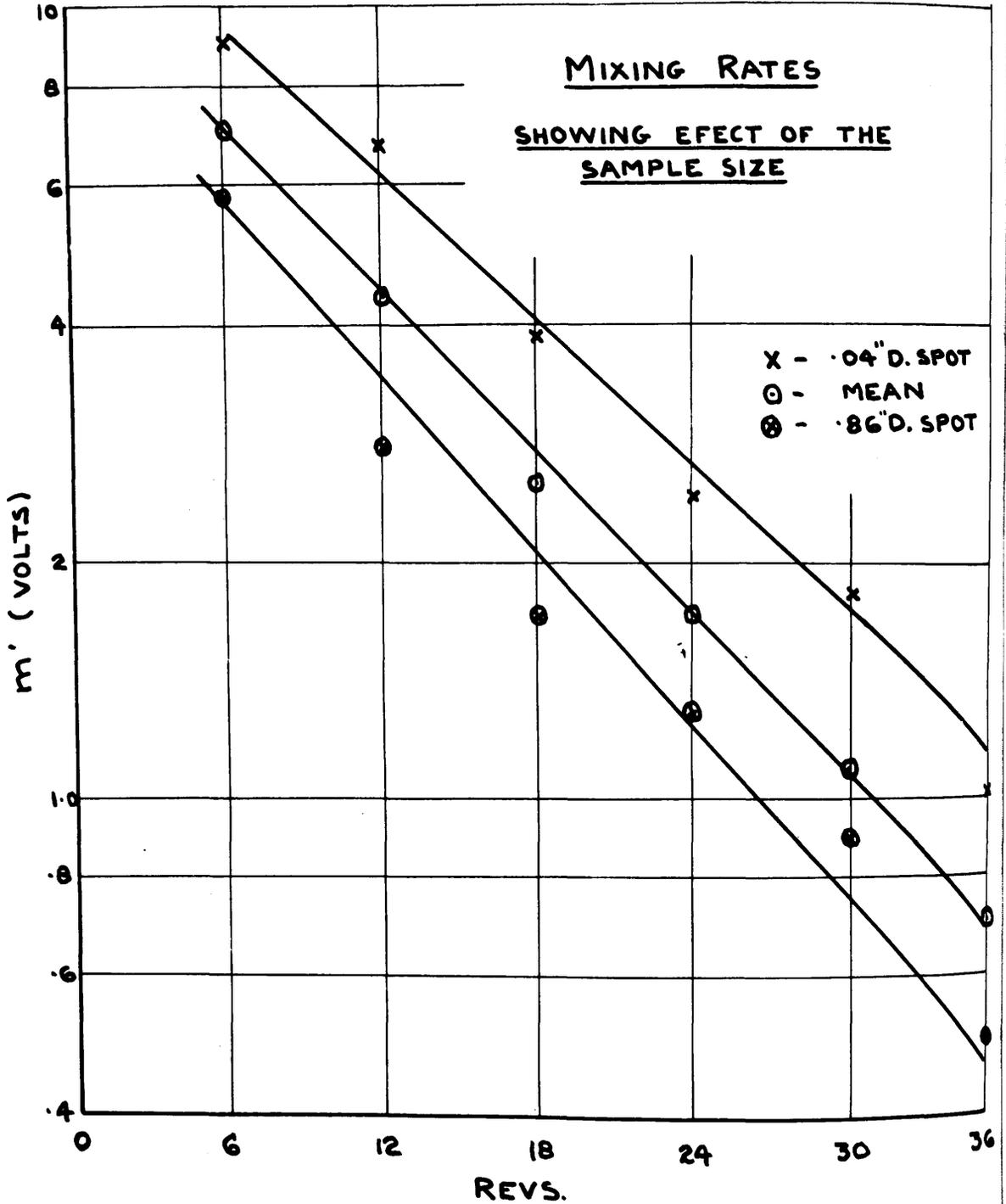
REVS.

order type of rate plot.

From these plots, though not given on them, it is easy to read off the number of revs. of the mixer necessary to diminish the value of m' by one half, and this can then be converted into a time of half-mixing using the speed of the mixer which is constant at 28 rpm. The linear nature of the plots, makes this time independent of the initial state chosen.

4.524   Reproducibility.

Having established in the previous section that the experimental values m and m' behave rationally and according to predictions within a mixing run, the next investigation was into the variation between runs under, so far as possible, identical conditions.

Figure 20 shows the results, taken at two stages of mixing from three similar runs. The band of variation, due to sensitivity to uncontrolled circumstances, is small. Since only two stages were taken, the rate plots also shown on Fig. 20 are scarcely significant, but they do indicate that, if the points lie in pairs on straight lines, then these lines are parallel and the rate values unaffected.

On Fig. 21 are plotted results of a more extensive series of runs. In these some further possible sources of variation are introduced which will be discussed in the next

FIG. 20

REPRODUCIBILITY

RESULT FROM THREE

SIMILAR RUNS.
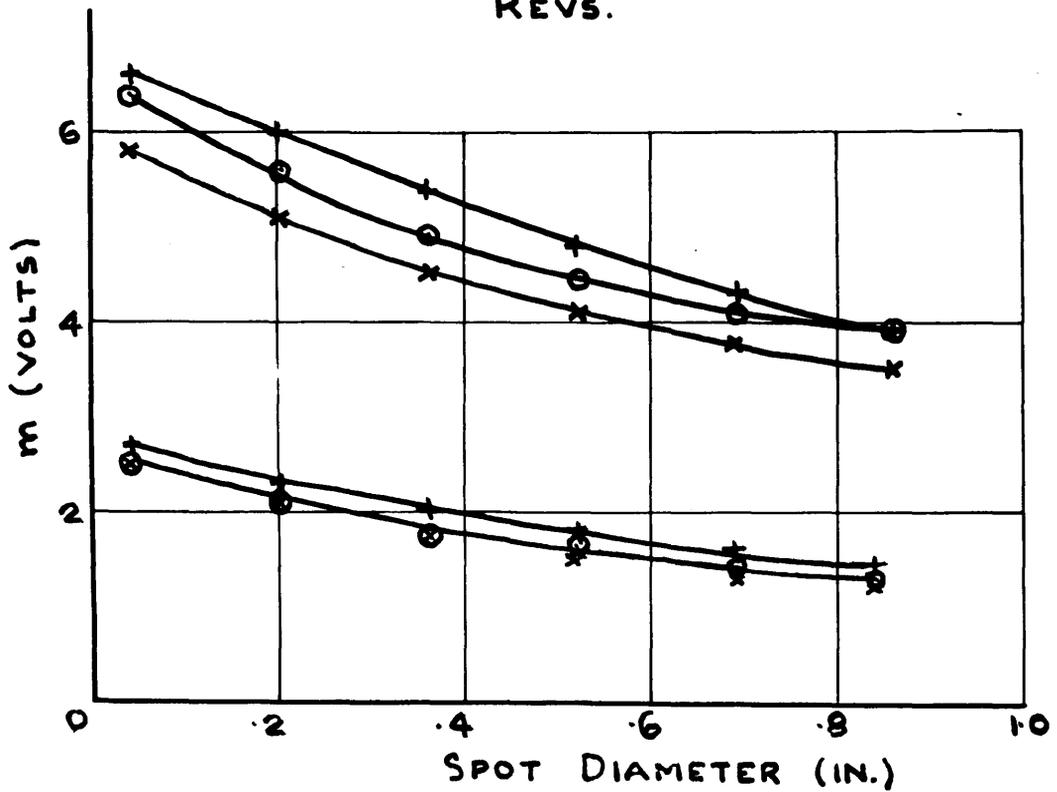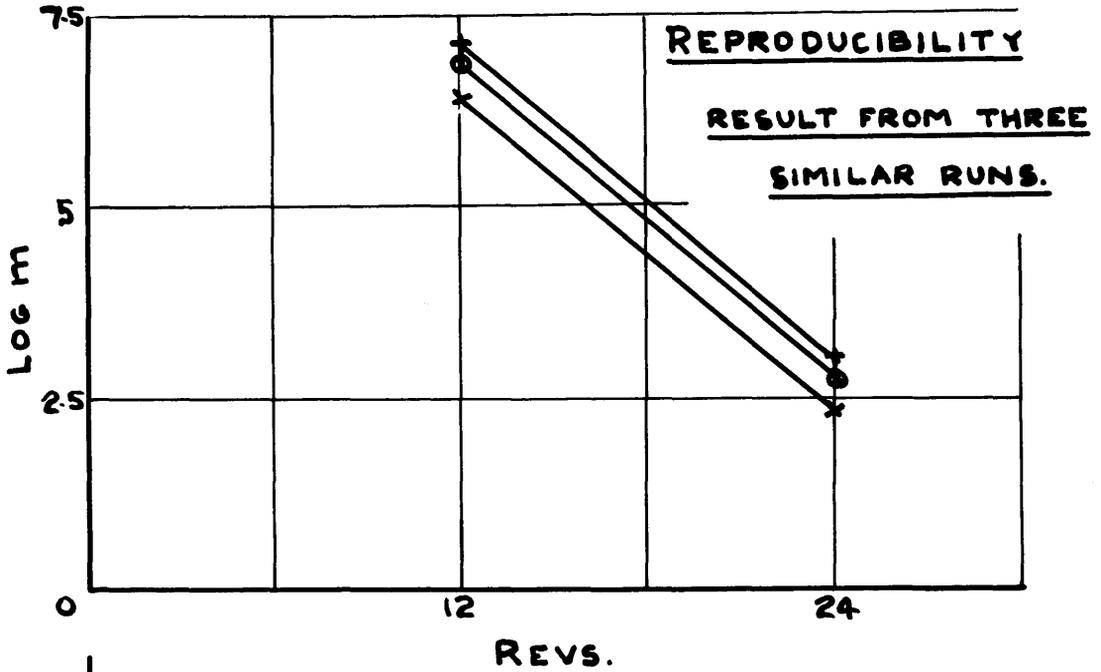
section, but these seem to have no effect thus again demonstrating the extent of uncontrolled variation. It is satisfactorily small.

4.525   Effect of the Sampling Process on Mixing.

The real purpose of the runs giving the results of Fig. 21 , was to show the effect of the sampling process.   It could be argued that the operation of taking the mass from the mixer, and then cutting and squeezing it, was actually further mixing, and furthermore mixing of an uncontrolled and arbitrary nature quite independent of the machine which the methods were designed to assess.   This is quite true: the experiments illustrated were designed to estimate the magnitude of this effect, and to see whether allowance would have to be made for it when considering the results.

The method was to consider the values of m taken from mixes prepared identically except for variations in the sampling procedure.   One mixture was sampled at 12 , 24 , and 36 revs., the curves for 12 and 36 being shown. Three mixes were sampled at 12 and 36 revs. only, both curves being shown for each, while finally two runs were. taken without prior sampling directly to 36 revs., and the results of these are also plotted.

The results show that the variation due to mixing or

FIG. 21

REPRODUCIBILITY.

RESULT OF RUNS UNDER
VARIOUS SAMPLING
CONDITIONS.
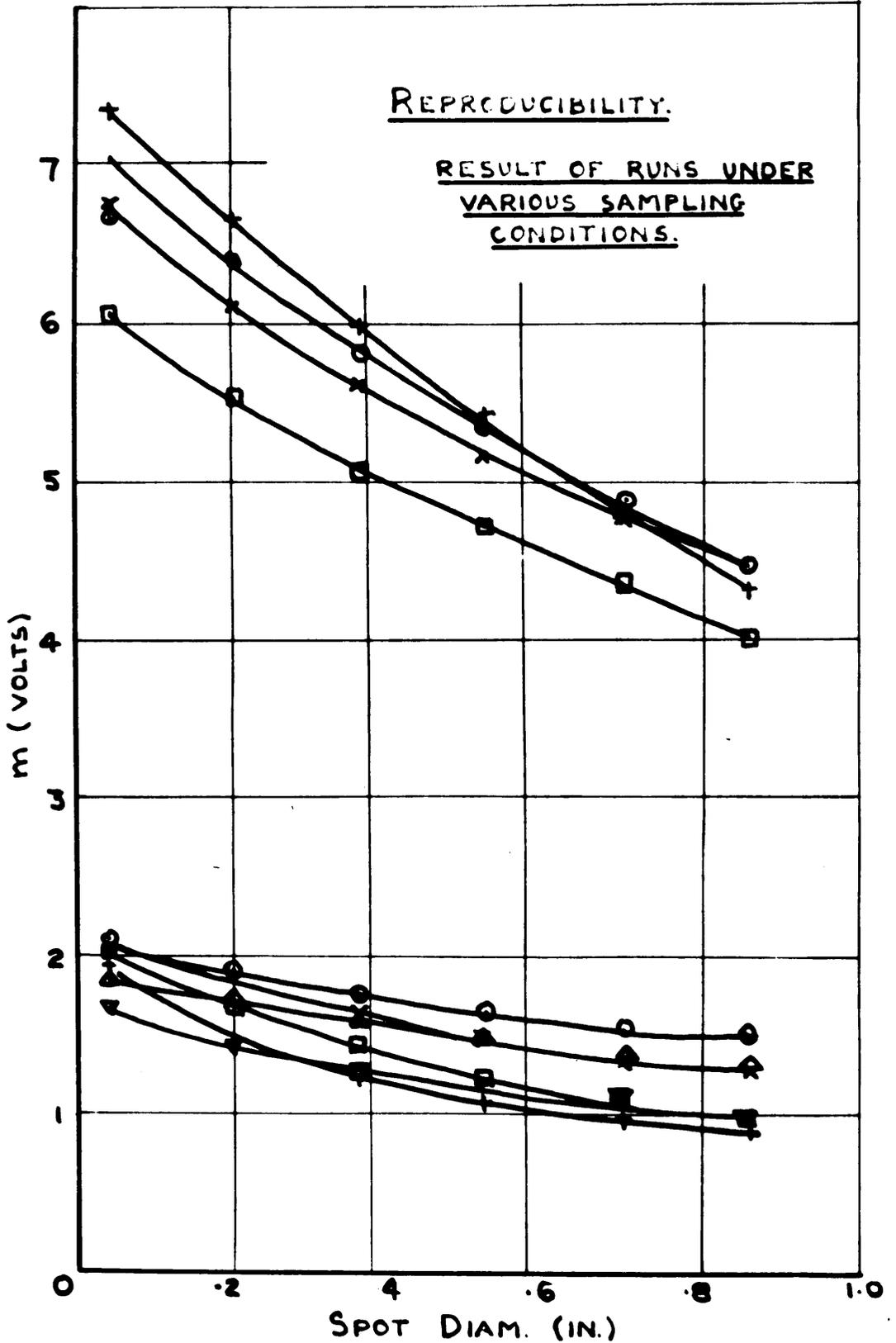
other effects arising from the sampling procedure, is small compared with that due to mixing in the machine.   Also, it is apparently arbitrary.   Consequently the band width, indicated by these curves at the same mixing stage, may be taken as representing the variation from all sources outside the experimental control.

4.53   The Effect of Sample Size on Rates.

It was wished to form some idea of the influence of sample size selection on measured rates of mixing. Using the same experimental runs as are plotted on Fig. 14 , and on Figs. 15 , and 16 , the values of m at the largest and smallest sample sizes available over the various mixing stages are plotted on to Figs. 18 and 19. This gives curves above and below those of m' which are already plotted. At the smaller sample sizes the variation will always be higher than at the mean: the plotted points, however, lie on a straight line which is approximately parallel to that for the mean values. The larger sample sizes give a similar plot but below the main curve.   There is a definite tendency towards convergence at the zero-mixing end which is to be expected, but despite this the lines are very nearly parallel over the range considered, so it appears that the choice of arbitrary sample size will affect the absolute values of   m , but will have little influence on the rate figures which are

FIG. 22
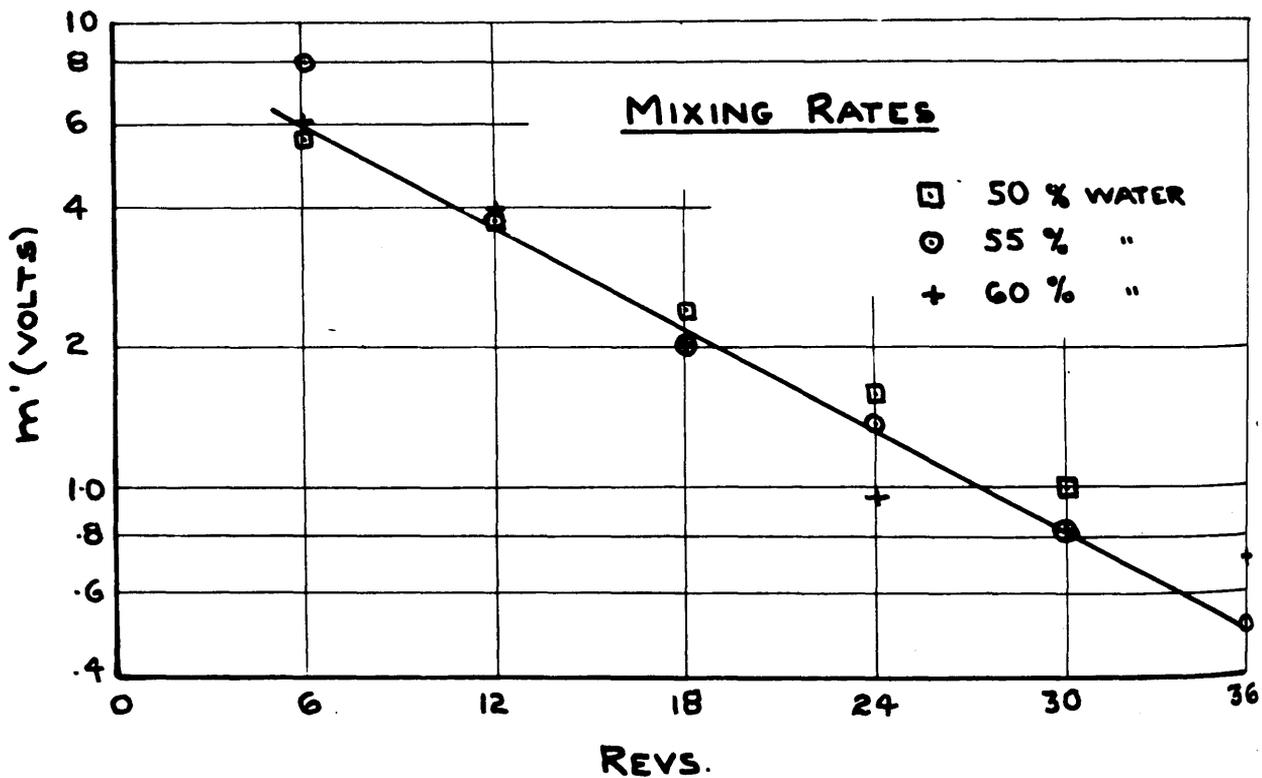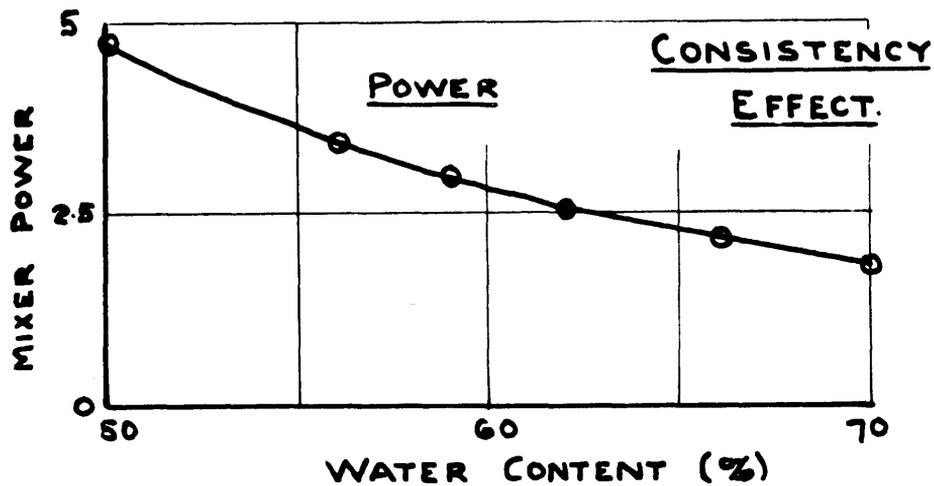
represented by the slopes of the lines.

4.54   The Effect of Consistency.

As mentioned elsewhere, particularly in Appendix II,
it is not possible to characterise, adequately, the
physical properties of doughs.   These do, however, alter
to a very marked extent according to the amount of water
that is added to the flour.   This effect may be termed the
consistency of the dough, and Fig. 22 gives the extent of
this variation, plotting the power necessary for mixing a
fixed quantity of dough in the Brabender mixer against the
quantity of water present.   To investigate the effect of
this consistency on mixing rates three runs were carried
out, using 50% , 55% , and 60% of water (on a dry basis),
the same total quantity of dough being used in each case.
Rate plots for these runs are shown on Fig. 22.   A line is
drawn on this, more to indicate the trend than precise rates.
There is some scatter of the points, but there does not
appear to be any substantial alteration in rates despite the
large changes in consistency.

4.6   The Effects of Dough Quantity.

It was expected that mixing rates would vary with the
quantity of material in the mixer, and an extensive
series of runs was undertaken to investigate this.

FIG. 23

FIG. 24

BRABENDER MIXER

RATE PLOT

QUANTITY
×   225
▯   300
▽   400
◇   500
+   600
△   700 GM.

m' (VOLTS)

REVS.

FIG. 25

FIG 26

FIG. 27

PRONG MIXER
RATE PLOT

QUANTITY
⊙ 450
△ 525
✕ 600
+ 750
▣ 900 GM.

m' (VOLTS)

REVS.
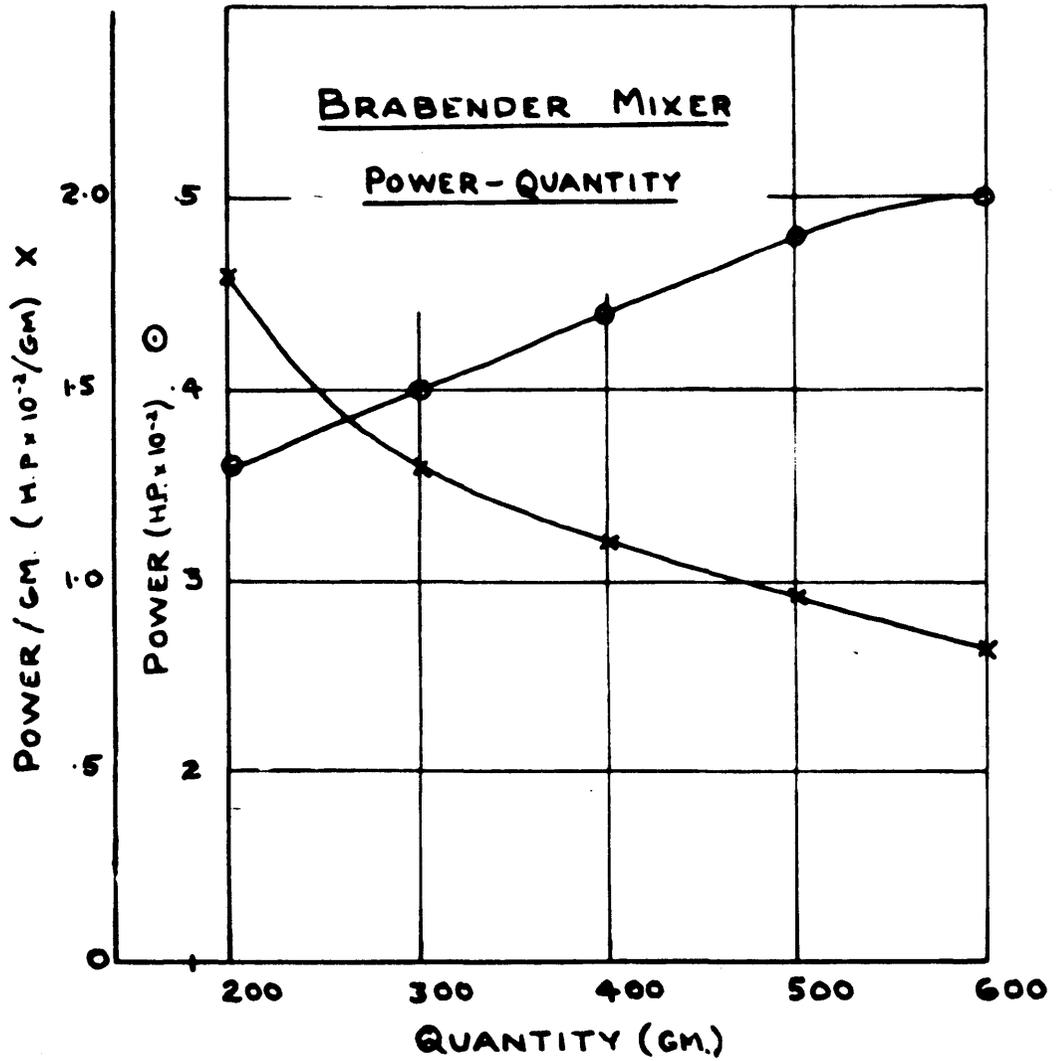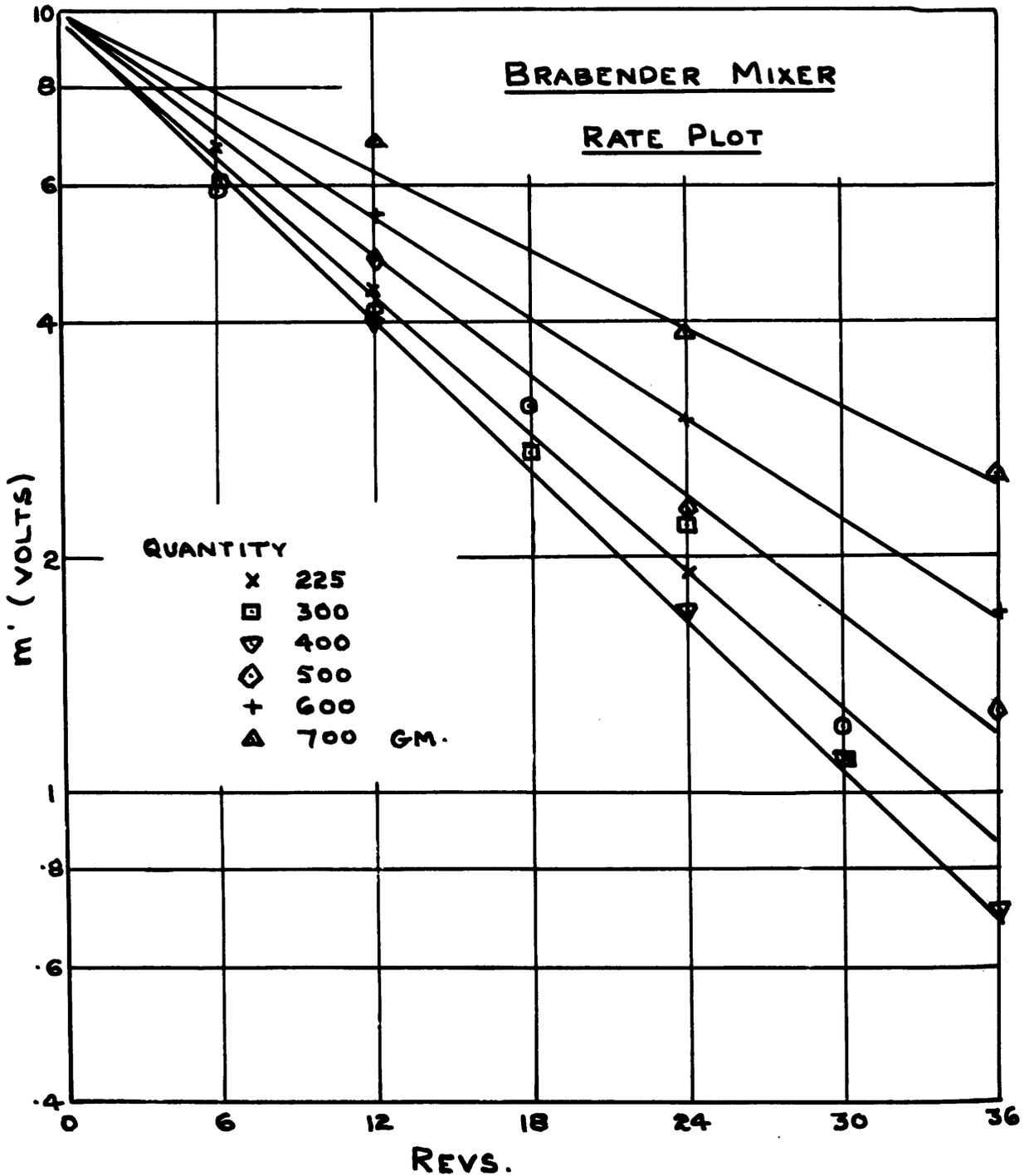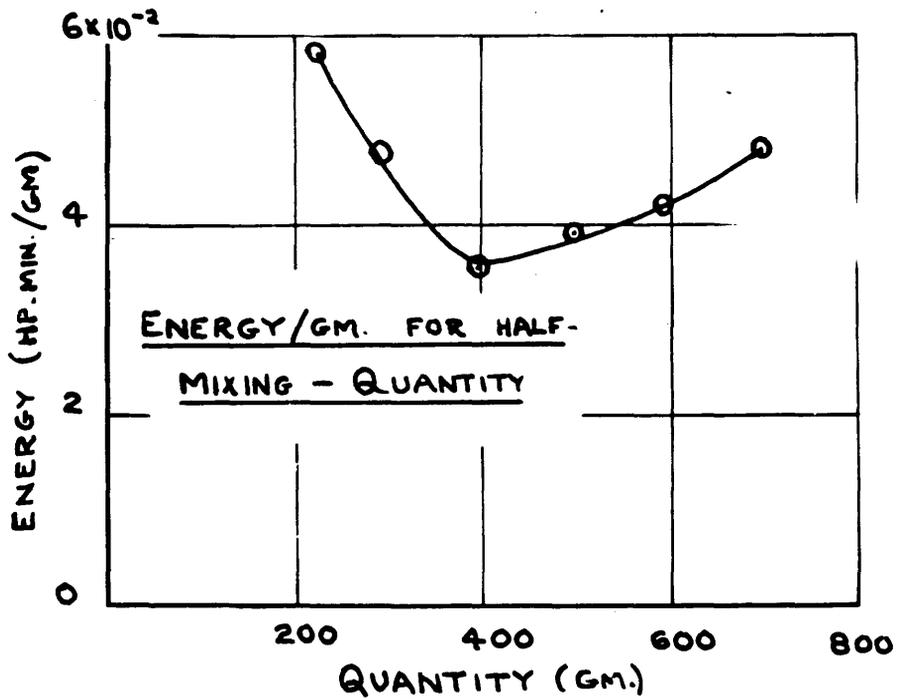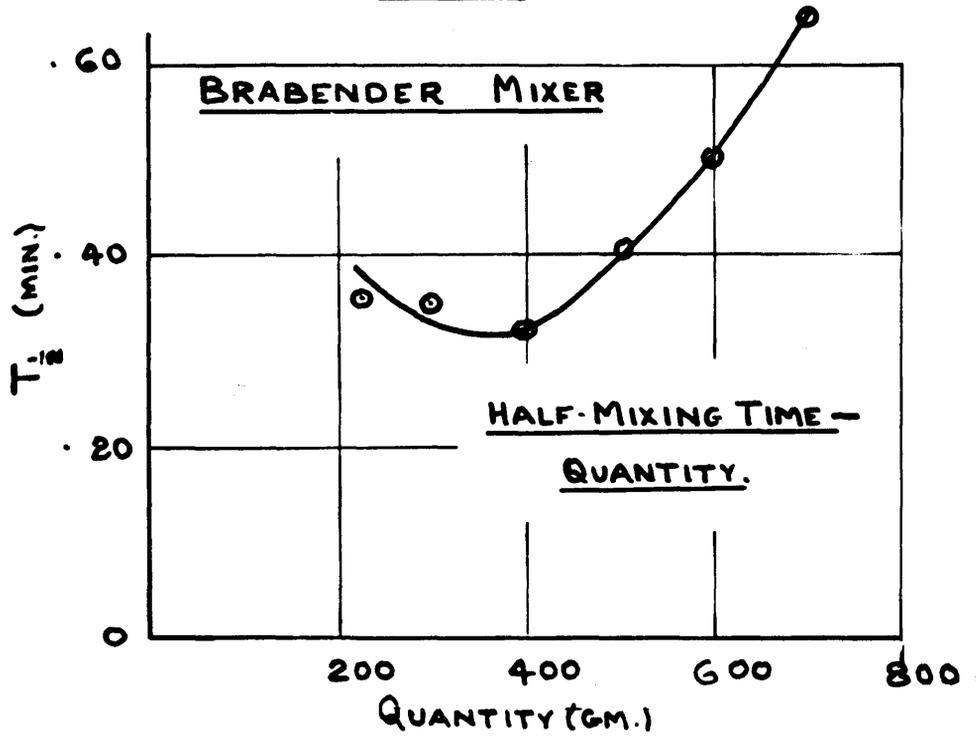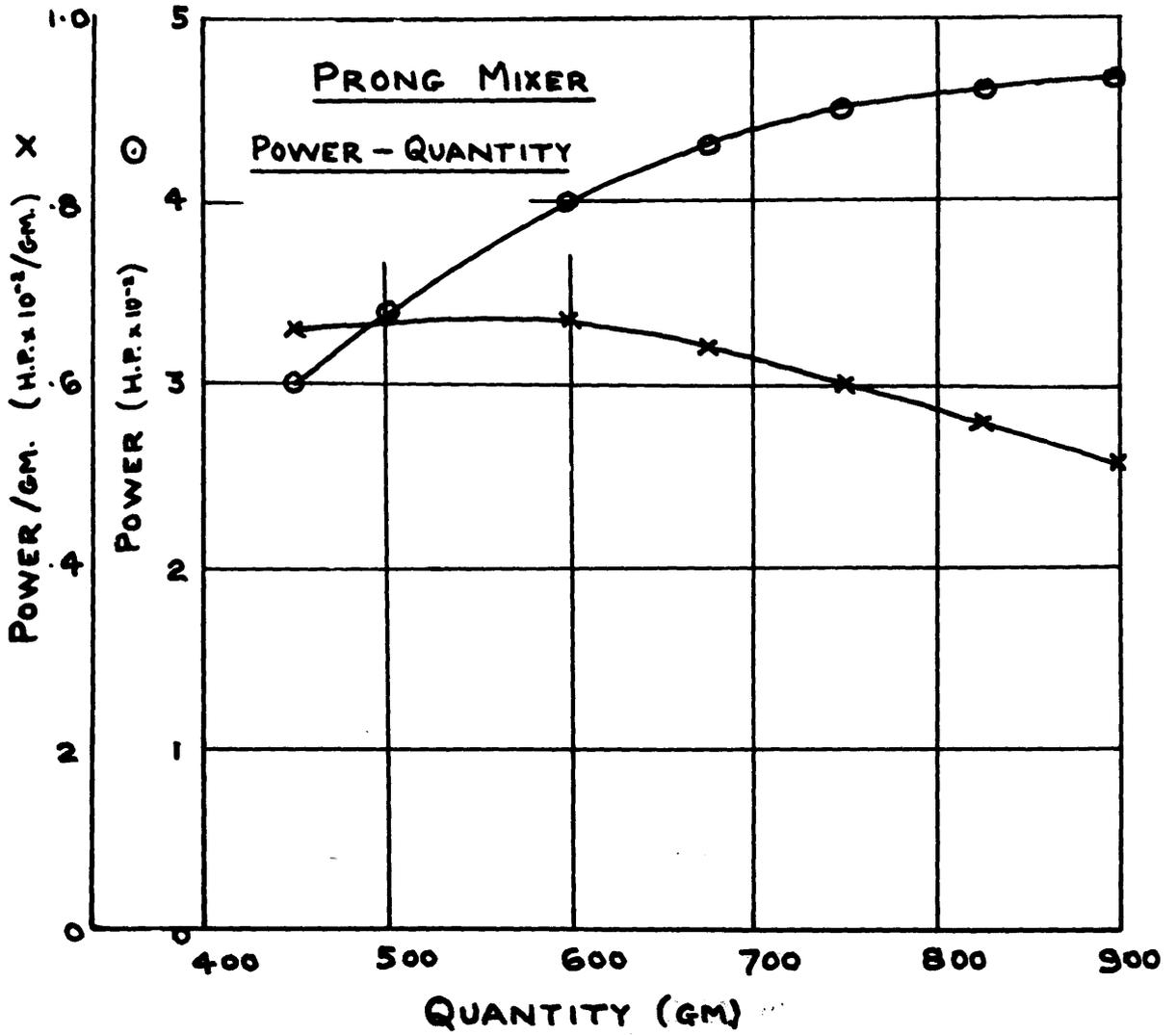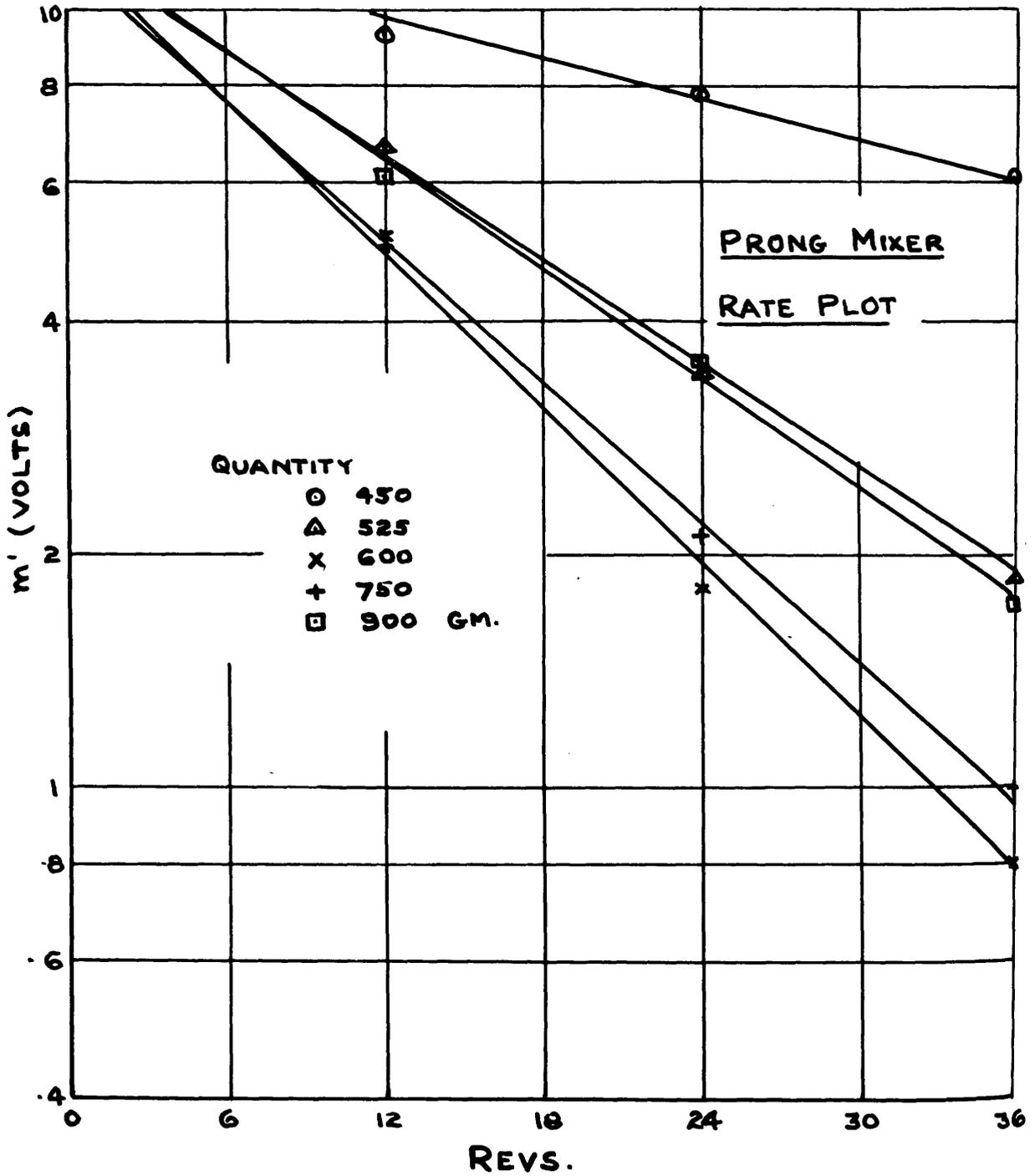
FIG. 28
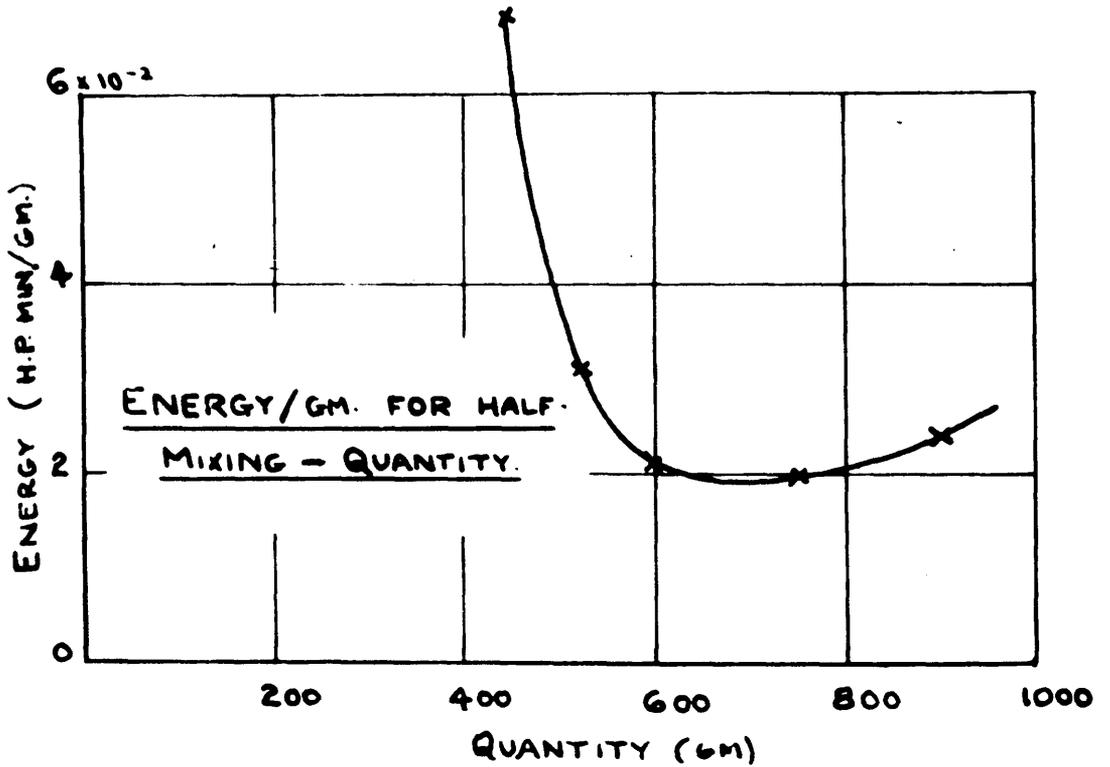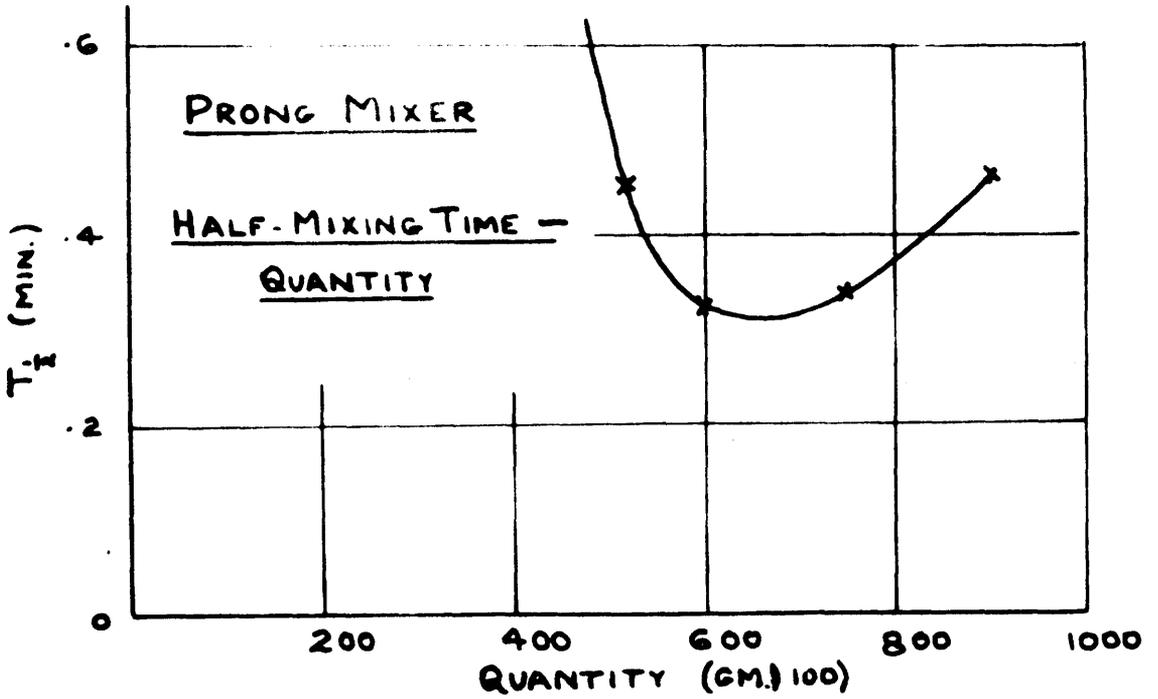
Firstly, using the Brabender mixer, runs over a considerable range of quantities were carried out. The first interest was in the power consumption of the mixer at the various stages of loading. Figure 23 shows the results obtained, both the measured power, and the power per unit weight of dough, are plotted against the quantity of dough in the mixer.

Also the mixing rates were measured, and Fig. 24 shows the values obtained for these, plotted logarithmically against revs., for the different quantities of dough used. From these rate plots values for the time of half-mixing can be taken, and these then give the time necessary for the machine, under the loading conditions stated, to perform a standard mixing task. On Fig. 25 , a plot of this time against quantity is shown. Also shown on Fig. 25 is the energy required per unit weight for half-mixing. This is derived from the power and the time for half-mixing values, and is again plotted against the quantity of material in the mixer.

This same series of investigations was then repeated using the Prong mixer, and the results, plotted in the same way and in the same order, are shown on Figs. 26 , 27 , and 28.

4.7   Extension of the Method to a Plant Mixing Machine.

To determine whether the method could be applied

Fig. 29.
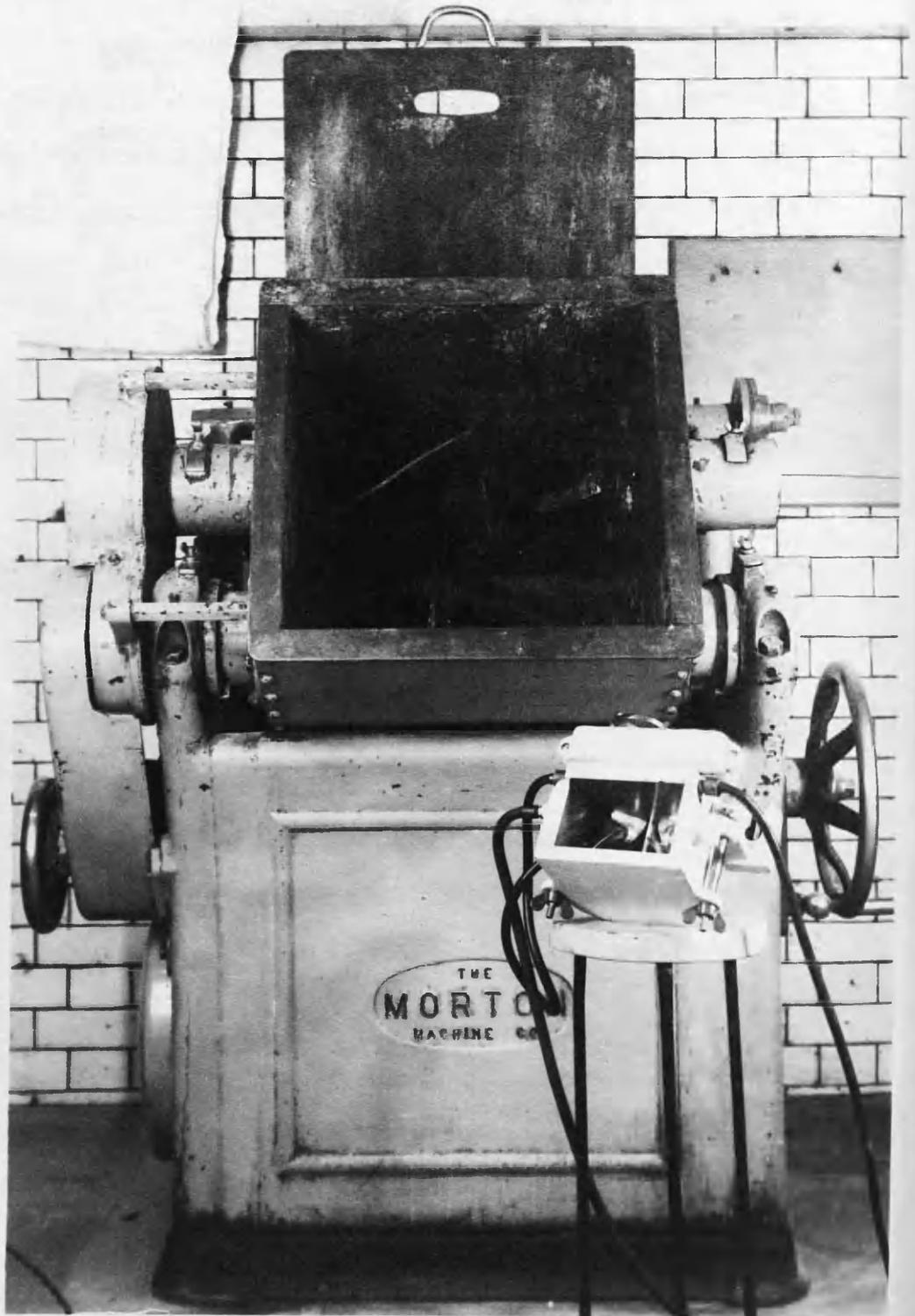
MORTON DUPLEX MIXER

without modification to a commercial size of mixing machine,
a run was carried out on a "Morton Duplex" dough mixer.
This machine,which is designed apparently to take up to 70 lb.
of flour,is shown on Fig. 29 . It uses the "sigmoid arm"
blades the slower of these rotating at 45 rpm. and the
other at 73 rpm. The dimensions of the mixing bowl are
18" x 18" x 16" deep. The quantity used for the run was
30 lb. of flour in all and 55% of its weight of water was
added, the higher quantity of water in the mixture being
necessary because the machine would not handle the 50%
doughs these being too stiff. The doughs were made up in
the usual 4 : 1 colour proportions. Experimental
procedure was as for the smaller runs, but using a set
geometrical selection for the samples themselves. Four
plates were taken at each stage of mixing. The resulting
rate plot is shown on Fig. 30 . Again it corresponds very
closely to a straight line over the whole of its length.

FIG. 30

MORTON DUPLEX MIXER

RATE PLOT

m' (VOLTS)

REVS.

The Physical Values of the Constants

For practical computation purposes, ...

S E C T I O N   5.

DISCUSSION AND CONCLUSIONS

...

...

The errors introduced by the various ...

5.   DISCUSSION   AND   CONCLUSIONS

5.1   The Numerical Values of the Results.
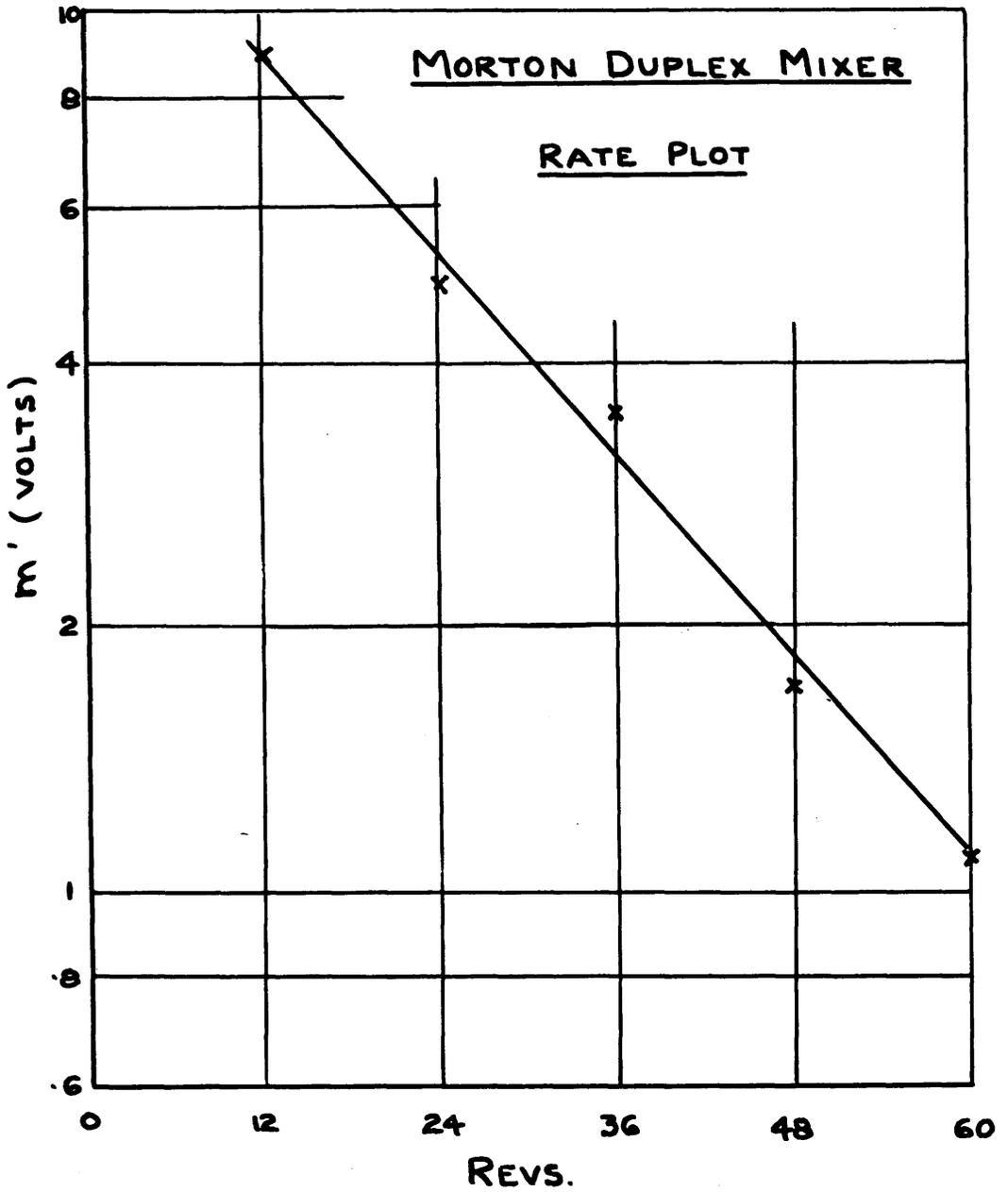
5.11   For practical comparative purposes, the most impor-
         tant features of an experimental method of following
mixing are its consistency and reliability.   The following
sections discuss these under various aspects.   In any
statistical investigation absolute reproducibility cannot be
expected, but it is shown that in this work the margins are
small, allowance being made for the difficult nature of the
questions asked.   The measure of mixing which is used, m ,
has not been transformed to behave in standard fashion e.g.
to have a maximum value of one at no-mixing.   Such trans-
formation is unnecessary so long as the measure used is
clearly explained; it would merely alter numerical values
and not conclusions from them, and might conceal some of the
variation.

5.12   Instrumental Readings.

         The errors introduced by the various electrical
instruments, the calculations exposure of the film develop-
ment etc., can be computed in some cases and summed.
However, much the better estimate of the total error from
these sources is implicit in the figures in Table III.   This
shows the m values obtained from the scanning of two plates

which were taken of the same dough sample, and put independently through the whole of the processing. The greatest variation is $2\frac{1}{2}\%$ and the mean variation much less. It is not unreasonable to place a figure of 2% on the variation from all of these sources, though it may be higher than this at low numerical values and smaller at higher ones.

5.13   Mixing Techniques.

It was difficult to standardise, completely, the procedure for loading and unloading the mixers and for cutting and preparing the samples. The extent of the error introduced by these is obtained from the band over which the results of replicate experiments range. Figure 20 shows such results, and the band width is of the order of 20% of the mean values.

In Fig. 21 a definite possible source of variation, that of the disturbance or mixing effected by the actual sampling procedure, is introduced. This seems to produce no definite trend, and the band width is still of the order of 20% , though rather greater in the more mixed stage. It is concluded that, if a new source of variation has been brought in, then it is of the same order as those present from uncontrolled sources, and that the error from all of these is of the order of 20% .

5.14   Sampling Within Runs.

Table I gives the numerical results of one run,
that plotted on Figs. 15, 16, and 19.   The variances
of all the m values for this have been computed, and are
given, at the various sample sizes and mixing states, in
Table II .   This represents the standard deviation of the
individual numerical values, expressed as a percentage of
their mean.   The means of the m values taken over all of
the eight values, will have a smaller expected error than
the individual values, the standard error of the mean being
$\frac{1}{\sqrt{8}}$ times the standard deviation of the individual results.
Thus from the table it appears, taking pessimistic
views:-

1.   The standard deviation of individual results is $\doteqdot$ 25%
2.   The standard error of their means is $\doteqdot$ $\frac{25}{\sqrt{8}}$ % $\doteqdot$ 10% .

It is not permissible to continue this process and
divide by a further factor taking into account the averaging
process over the various sample sizes, because these values
are not estimates of the same thing, but this does give an
added factor of confidence.   Thus it appears that the
overall sampling spread of the mean values is of the order
of 10% , and quite likely to be substantially less than
this figure.

In connection with the table of standard deviations,

it is interesting to notice that these increase substantially as the sample size increases. The only explanation of this would seem to be in large scale 'clumping' of material that is already partially mixed. The large scale of the clumps would make the plates rather a crude sample and so give a large variation in the m values, but the values themselves would be small, because of the partial mixing, giving much lower concentration differences.

5.15   The Photographic Process.

The source of error considered under this heading, is that arising from the non-linearity of emulsion sensitivity with concentration. There is a departure at both ends of the scale tending to decrease the total fluctuation. It is impossible to calculate the effect of this since it will depend on the actual pattern being scanned and then in a very complex manner, but it should be greatest in the earlier stages when the concentrations are at their maxima.

5.16   Sample Means.

The theoretical $\bar{s}$ is derived from a calculation of the root-mean-square of the deviations from the overall mean. However the scanning process, by reason of the condenser eliminating the D.C., measures only the A.C. fluctuation about its own mean, that is the mean over the annulus swept

out by the scanning spot.   This will not in general be the
same as the overall mean, so that the value of m as calcul-
ated will not be exactly proportional to the theoretical $\bar{s}$
because of this factor.

All measurements being relative there is no provision
for standard intensities, and so it is not possible to know
what this true mean is in terms of the electrical readings.
Estimates can be made, but they are subject to the same
sampling errors as any other estimates made from the plates.
An attempt was made, on the basis of such estimates, to
correct the readings using the standard process for trans-
ferring second moments, but the effect on this of the uncer-
tainty of the true mean was so large as to make the procedure
very dubious.   Thus, since the labour of the calculations
which cannot be put into convenient computational form was
considerable, and the results probably subject to an error
at least as large without the correction, (and they certainly
did not appear any more consistent), the scheme was abandoned.

Actually, not only are the sample means not the same as
the true mean, but they may vary with the sample size, but
at no time did any inconsistency arise from this so its
effect was apparently quite small.

5.17   Overall Errors.

Although all sources of error cannot be fully computed,

the total is probably not more than 20-25% for a single result. For comparative tests, e.g. the progress of a mixing run, the error would appear from the consistency of the results to be substantially smaller, of the order of 10% or less. Mixing rates, being effectively the mean of an even larger number of results, would be expected to be more reliable still, though no figure can be given for this.

5.2 The Application of Theory to Results.

5.21 State of Mixtures.

The two major theoretical aspects of this presented are the distribution spectrum as characterising component distribution, and the sample size effects.

5.211 The Distribution Spectrum.

To consider firstly the spectrum conception. This was introduced to clarify the background to practical measures, rather than to supplant them; consequently the fact that the results cannot be used to calculate distribution spectra is not necessarily disastrous, either to the idea or the results. The reasons for this are principally in the laborious nature of the work to obtain even the results given, much of the experimental process being inevitably slow. For normal measuring purposes mean values of the results can be employed, which adds very largely to

their reliability when such large variations as are found in them, occur. The individual results which would be required for calculating the spectrum are too uncertain, especially in view of the comparatively low sensitivity of the distribution spectrum to them. Incidentally the extent of this variation could most clearly be seen, not from the numerical values, but from the monitoring cathode ray oscilloscope, though necessarily in qualitative form, where the fluctuation patterns were set out in striking fashion. These at once suggested the basis of a distribution spectrum measure, and the difficulty of its numerical attainment.

5.212   Sample Size.

The sample size effect work was more obviously successful. There was no experimental published work on this at all and, except for desultory mention in theoretical papers as a problem, the matter seems to have been ignored so the results, which are quite extensive, should be of interest.

The shape of the plotted variation of $\bar{s}$ (actually m which is proportional to $\bar{s}$) against sample size is as the theory predicts. In the earlier stages of mixing, that is when the "clump" size is large, the slope of the curves is comparatively slight, indicating that the ratio of sample size to "clump" size is only changing slowly and that over the portion of the curve where this ratio tends to be less

than one. In the intermediate stages the slopes are steeper and the numerical magnitude of the m values less, which shows that the "clump" sizes are decreasing though the ratios, changing more rapidly and so altering the horizontal scale, minimise this effect. The later stages show gradual sloping, coming into the region of reciprocal relations for the larger spot sizes, with the "clump" size roughly comparable with the smallest scanning spot. Figure 15 shows these effects most clearly.

In the cases of the artificial random patterns where the ratios are known, the effect can be shown quantitatively by plotting length ratios, and this clearly demonstrates that the mixing stage curves are really portions of the same curve, but to a different scale. Since the spectrum and from it some notion of "clump" size, cannot be calculated, this merging cannot be done for the real mixtures, but the curve shapes show the possibility of it. This shows that the curve of standard deviations against sample size is a key to the whole mixing process because of the two effects it demonstrates. These are, the changes with sample size of the mixing measures at a fixed mixing degree, and the changes of mixing measure with degree of mixing for a constant sample size, assuming that spectrum shape remains effectively constant over the mixing.

5.22   Rates of Mixing.

5.221   The Kinetic Law.

The results from all the runs quite definitely
support a first order kinetic law for mixing systems,
if the degree of mixing is measured by changes in the sample
composition standard deviation.   There is no apparent sign
of the rate falling away from this as the mixing progresses,
but the range was not wide enough to cover extended mixing,
so that there may be deviations outside the region considered.

These straight line plots, on logarithmic paper, give
considerable confidence to the measuring of mixing machine
rates of performance by either the slopes of the lines, which
are the rate constants, or by the half-life times which per-
haps give more readily appreciated figures.   Even if the
rates do subsequently fall off from this there is nothing to
suggest that the different machines will perform differently
at different mixing stages, so the half-mixing times give
useful comparative figures, independent of whether or not
rates are first order over considerable ranges.

5.222   The Effect of Sample Size.

The other important rate effect which was investigated
was the influence of sample size on rate measurements.
From the plotted curves it may be seen that this effect is
quite small.   This was a point which seemed a possible

weakness in published rate figures where sample size differences had not been considered. If these lead to different rates, then the choice would be critical if the results were to have any meaning beyond the special circumstances under which they were taken, and scale effects might be very large. However the results show that using either different fixed sample sizes, or the mean value over a range, does not lead to markedly different rate constants though the individual mixing degree measurements at the various stages will vary considerably. Thus the results from taking what are proportionately large samples from laboratory size mixers, can give useful information as to the behaviour of the similarly sized samples from much larger mixers, which will be the expected experimental arrangement since the sample sizes have apparently been most frequently determined by convenience.

Two further effects which can be predicted from the theory on sample sizes are shown by the curves on Figs. 18 , 19 . Using again the scale ratio concepts, the curves at large and small sample sizes may be thought of as being instead at the same sample size, but from different sized but geometrically similar mixers. This means that on the generalised $\overline{X}_r^2$ - r plot with the larger mixer, i.e. corresponding to the smaller sample size curve, the initial value of r will be smaller, and since the curve is steeper in

this range the rates measured will be higher than for the case of the smaller mixer, which corresponds to the larger sample size.   This is shown by the curves being slightly steeper at the smaller sample sizes.

Also the intercepts at no-mixing on Figs. 18-19 will not be the same, because of this ratio effect.   In a given mixer the initial clump size is fixed; on scanning this with a sample comparable in size to the clumps, there will be a proportionately larger number of mixed samples, than if the scanning sample size is much smaller than the clumps. Using a mean value, e.g. m' , the intercept should be inter- mediate between these, and this can be seen from the graphs by producing the lines to the axis.   Only when the sample size is very small indeed, will the calculated value of m at no mixing, evaluated on the basis of all samples being either pure A or non-A , be realised.

5.23   Efficiency and Power.

The efficiency criteria employed were, theoretically, perhaps crude, but they show pronounced trends and for all their crudity demonstrate an experimental technique for comparing the performances of mixing machines.   A basis for this has been established to consider either the speed of accomplishment of a standard mixing task $(T_{\frac{1}{2}})$, or the amount of energy required for this, irrespective of the time taken.

Which of these is used as determining will depend on the
point of view, and economics will come into the practical
considerations.

Few details are given of the power measurement procedure
because these seem to be entirely conventional, the mean
values of the torque-time curves being used in a straight-
forward calculation.   In practical mixing cases this will be
more difficult because reaction torque measurement requires
somewhat elaborate apparatus, and probably some electrical
power records, with their no-load and other disadvantage
will have to be used.   This however is a problem in mechanics,
not mixing.

5.3   Mixing Performance Results.

5.31   Most of the earlier experiments reported in this
        study were designed to establish the method, and the
results of these have already been dealt with under the
appropriate headings.   Having verified the method, runs
could be made to investigate the mixing process itself.

5.32   Sample Size.

        Some practical effects arising from the rate plots
        on Figs. 18-19 should be mentioned.   The variation
in rates, that is the slopes of the curves, is approximately
20% over a sample size range of 20 : 1 .   This may then

be taken as a general guide to the magnitude of this effect.
It is most marked when sample and clump sizes are comparable
and should always be considered in connection with rate
measurements.   Its magnitude is not so great, however, as to
raise difficulties in most practical work.

5.33   The Effect of Consistency.

Figure 22 shows the results of three runs carried
out in the Brabender Mixer with doughs of markedly
different consistencies.   With flour doughs there is no way
of measuring this so called consistency, except in empirical
terms.   However Fig. 22 shows its effect on the power
required for the mixing, and this indicates the considerable
range over which the properties of the three doughs lay.

Although the spread of the individual results is
substantial there is no evidence of substantial differences
in trend, the effect being more a scatter.   Experimentally
the doughs of lower consistency were difficult to handle
and this may account for some of the variation, but the
conclusion may be drawn that consistency had no marked effect.
This is to be expected, since none of these doughs flows
easily under its own weight and consequently all mixing has
to be accomplished by the purely geometrical re-shuffling,
accomplished each revolution by the mixing arms.   Plasticity,
over a wide range, has no effect on this, though the power

required to move the arms varies very considerably.

5.34   The Effects of Quantity.

The double arm type of mixer investigated is sensitive to the quantity in the bowl.   When this is small, the whole of the material can be gathered up by the arms and carried round with no consequent mixing.   With large amounts the material cannot all fit into the mixing space over the central saddle, so it lies above this and takes little part in the mixing only feeding in very slowly. Between the extremes it was assumed that there would be some optimum loading, and the problem was to determine this for both the Brabender 'sigmoid arm' mixer, and for the Prong mixer made up for the trials.   At the very low loadings it is difficult to obtain reliable results because the mixing was often intermittent, sampling removed the material from the blades and consequently it mixed for some time before accumulating on them again.   Power measurements were taken throughout the range of loading also, and were again difficult with small quantities.

The mixing rate curves for both mixers are shown on Figs.24,27. The results are much as might be anticipated, the prong mixer having a slightly higher rate and a sharper maximum.

From the power readings and the time of half mixing, it

was possible to calculate energy per unit weight of material
to perform the operation of half mixing in the different
machines over the range of loading.   The results of this
are shown on Figs. 25 , 28 .   It is quite interesting that
the optimum conditions occur in very much the same positions
as the optimum rates, and further that there is quite a
considerable difference in the 'efficiencies' in this sense
over the loading ranges.   Also the conclusion can be drawn
that the Prong mixer is appreciably more efficient than the
'sigmoid arm' type.   This is interesting because the latter
type is very popular for work of this nature, and presumably
ought to have been designed, at least on empirical grounds,
whereas the Prong mixer had no rationalised design whatever
because there was nothing available on which to base it.

This is the type of investigation which it is envisaged
could be carried out on an existing mixer with a view to
determining its optimum loading, and,as it can be seen from
these results,the effect of this loading can be very
considerable.

5.35   The Plant Mixer Run.

The rate plot for the run using fifty pounds of dough
in a plant scale mixer is shown on Fig. 30 .   The intention
of this run was to establish that the method would continue
to give consistent results on a larger scale machine, and this
it does.   To investigate this mixer in the same way as

for the smaller ones described above would be a very laborious
procedure, and furthermore would need some adequate power
measuring equipment, but there is no doubt that it could be
done.

It is difficult to compare the results on this with those
on the smaller mixer of the same type, the Brabender.   The
loading for the larger mixer was probably well below optimum ,
and to complicate matters further the differential speed ratios
of the arms were not the same   (2 : 3 for the Brabender
compared with 1.8 : 3 for the Morton).   Blade geometry of
the machines also differed.   The highest measured rate for the
smaller machine gave a figure of just over 9 revs. for half
mixing, contrasted with that of 17 for the larger.

The direct comparison cannot be made without knowing the
variation in rates for the large mixer with changes in loading,
but these results, and qualitative impressions gained during
the runs, indicate that the scale effects are not very large.

5.4   Appraisal of the Method.

Assuming a given mixture, the experimental method
consists of two stages;   the first, is the trans-
ference of the sample concentration distribution pattern to
a similar pattern of the densities on a photographic plate,
and the second, the analysis of this pattern in numerical
terms.   It is probably best to consider these separately,

as they need not necessarily be used in conjunction.

5.41   The Use of Photography for Sampling.

5.411   Advantages.

i)   It permits the sampling of systems such as the flour
        dough one considered, for which normal chemical or
        physical methods could not be employed.

ii)   The camera can sample large or small portions of the
        material, depending on the magnification used.

iii)   The demands made on the material to furnish colour
        differences are slight, and leave the other proper-
        ties relatively undisturbed.   Thus practical, and
        not merely artificial mixtures, can be studied.

iv)   Subsequent analysis can quite easily be performed,
        and over large numbers of samples.

v)   It is comparatively quick, and convenient to operate.

vi)   The sample plates once taken are permanent, and any
        number of measurements, of any sort, can be made on
        them.

vii)   The sampling procedure leaves the mixture largely
        unaffected, and it can then be returned for further
        mixing.   The volume of the mixture is unchanged by
        the sampling.

viii) Sampling of the plate can readily be to any size
scale, so that the measurement can take varying
sample size into account.

5.412   Disadvantages.

i)   The difficulty of selecting colours and initial
concentrations of them to give linear concentration-
silver density relationships.

ii)   The comparative expense of the plates.

iii)   The samples are two, and not three dimensional.

iv)   The method is restricted to systems in which the
components do not interdiffuse, or at least do so
slowly.

v)   The glass and interfacial surface optical properties
affect the plates to an extent which limits the use
of the method when the variation becomes comparable
to this.   This occurs approximately at the level
where the mixture becomes homogeneous to the eye.

5.42   The Analysis of the Plates.

5.421   Advantages.

i)   It is convenient.   The analysis of one plate, taking
two annuli and five sample sizes on each, takes
roughly a quarter of an hour.

ii) The sample size can readily be altered.

iii) Electrical instruments are convenient to operate and read, and are relatively stable and consistent.

5.422 Disadvantages.

i) The expense and cumbersome nature of the equipment.

ii) The relatively restricted path available for convenient scanning.

iii) The fact that the measured variation is about the sample mean, and not the overall one.

TABLES

TABLES

PLATE

931 A

IRIS

LIGHT
SOURCE

DIAM.

A

V₁
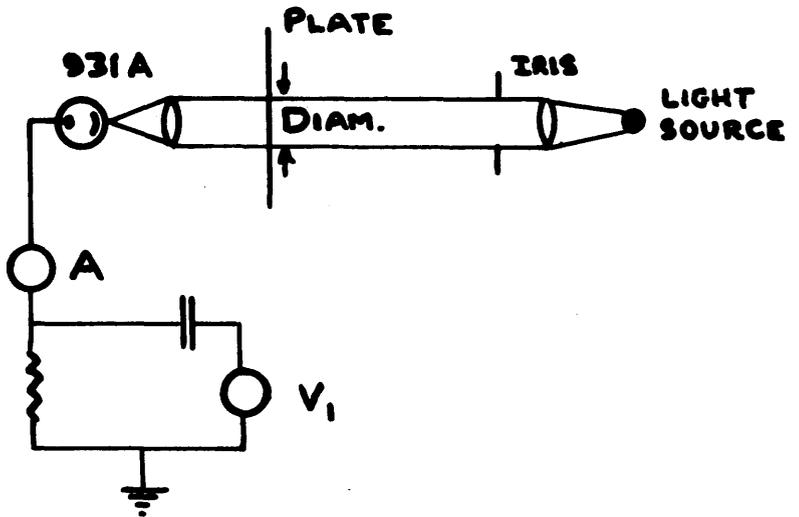
SCHEMATIC DIAGRAM FOR

TABLE I

TABLE I

TYPICAL SET OF READINGS FOR ONE RUN

Table I(a)

Diam.	.86	.69	.52	.36	.20	.04
1.(a)						
A	24.5	23	22.8	23.3	22.2	22.2
V_1	58	49	40.7	40.4	34	31.4
V_2	2.38	2.16	1.97	1.96	1.8	1.72
m	9.73	9.39	8.64	8.4	8.1	7.75
(b)						
A	22.3	20.9	23.9	23.9	24.7	22.8
V_1	54	43	49.5	45.5	45.5	37.2
V_2	2.29	2.03	2.18	2.08	2.08	1.89
m	10.05	9.71	9.14	8.7	8.42	8.28
2.(a)						
A	23	22.8	22.9	23.9	22.9	21.7
V_1	46.5	35	27.5	26	21.5	18.2
V_2	2.1	1.83	1.59	1.55	1.39	1.27
m	9.41	8.03	6.95	6.49	6.06	5.85
(b)						
A	23	24.2	23.5	23.6	23.5	22.3
V_1	52.5	47.5	38.5	35.4	33	28.5
V_2	2.25	2.13	1.92	1.84	1.76	1.63
m	9.79	8.8	8.07	7.8	7.49	7.31
3.(a)						
A	23	23	23.7	22.2	22.5	22.3
V_1	20	18.1	17.2	14	13.2	12.7
V_2	1.34	1.27	1.23	1.1	1.07	1.04
m	5.83	5.53	5.19	4.95	4.75	4.66
(b)						
A	23.5	22.5	23.7	24	23.3	22.4
V_1	37.8	31.2	29.5	26	20	16
V_2	1.89	1.72	1.66	1.55	1.34	1.18
m	8.05	7.64	7.01	6.45	5.75	5.27
4.(a)						
A	23.6	23.5	24	23.9	23	23.8
V_1	31	22	14.5	9.4	6.1	4.9
V_2	1.71	1.41	1.13	0.85	0.71	0.61
m	7.25	6.0	4.71	3.35	3.1	2.68
(b)						
A	23.3	24.3	23.9	23.7	24.2	23
V_1	53	45.5	31	20.5	16.4	12.5
V_2	2.26	2.09	1.70	1.36	1.19	1.04
m	9.7	8.61	7.11	5.73	4.92	4.52

Diam.	.86	.69	.52	.36	.20	.04
From this point m values, only, are given						
5. (a)	6.06	4.21	3.13	3.05	2.47	2.05
(b)	6.79	5.57	4.36	3.37	2.54	2.13
6. (a)	8.06	6.7	5.64	5.02	4.42	4.2
(b)	7.2	5.95	5.0	4.58	4.14	3.86
7. (a)	6.11	4.67	3.76	3.25	2.78	2.39
(b)	7.18	6.0	5.18	4.56	3.83	3.15
8. (a)	5.9	4.53	3.51	2.89	2.44	2.18
(b)	6.47	5.27	3.97	3.07	2.57	2.28
9. (a)	2.59	1.84	1.59	1.47	1.36	1.23
(b)	3.93	3.1	2.62	2.34	2.04	1.66
10(a)	3.59	2.61	1.81	1.43	1.17	.97
(b)	3.91	2.72	1.79	1.44	1.2	1.09
11(a)	4.31	3.26	2.62	2.36	2.26	2.0
(b)	4.26	3.86	3.42	3.08	2.8	2.55
12(a)	3.65	2.61	2.02	1.75	1.5	1.33
(b)	4.04	3.52	3.29	2.98	2.66	2.37
13(a)	2.11	1.77	1.43	1.3	1.23	1.19
(b)	2.38	1.97	1.65	1.45	1.27	1.24
14(a)	2.44	2.03	1.71	1.37	1.2	1.14
(b)	3.16	2.78	2.49	2.3	2.03	1.75

	Diam.	.86	.69	.52	.36	.20	.04
15(a)		2.15	1.51	1.37	1.25	1.11	1.0
(b)		2.28	1.99	1.79	1.65	1.51	1.39
16(a)		2.49	2.07	1.71	1.44	1.29	1.15
(b)		2.48	2.01	1.7	1.43	1.27	1.13
17(a)		1.42	1.04	.87	.70	.6	.53
(b)		1.71	1.34	1.05	.76	.6	.56
18(a)		1.55	1.23	.95	.82	.74	.66
(b)		1.79	1.53	1.31	1.14	1.0	.83
19(a)		1.88	1.4	1.13	.99	.91	.85
(b)		1.83	1.41	1.08	1.04	.98	.88
20(a)		1.83	1.64	1.5	1.4	1.38	1.38
(b)		2.61	2.47	2.29	2.21	2.15	2.07
21(a)		.78	.58	.46	.4	.33	.29
(b)		.99	.74	.63	.58	.57	.38
22(a)		1.11	.95	.86	.78	.71	.58
(b)		1.19	1.04	.9	.84	.8	.7
23(a)		.88	.6	.48	.44	.38	.36
(b)		.99	.82	.73	.64	.57	.55
24(a)		.99	.86	.77	.69	.63	.58
(b)		.88	.77	.73	.68	.66	.62

Table I(b)

Mean values from the above table taken over the eight
estimates of m at a fixed sample size and state of mixing.

Diam. Revs.	.86	.69	.52	.36	.20	.04
6	8.85	7.46	7.12	6.57	6.07	5.66
12	6.72	5.36	4.32	3.72	3.15	2.78
18	3.79	2.94	2.4	2.11	1.87	1.65
24	2.4	2.02	1.73	1.52	1.36	1.25
30	1.77	1.51	1.27	1.13	1.05	.97
36	.98	.8	.7	.63	.57	.51

Table I(c)

Mean values of m' from above at a fixed state of mixing.

Revs.	6	12	18	24	30	36
m'	6.95	4.34	2.46	1.71	1.28	.70

Notes: 1. The rows A are the reading on the D.C. microammeter
$1 = .425 \ \mu a.$

The rows V_1 are scale readings on the A.C.
galvanometer.

The rows V_2 are the r.m.s. volts across the
931 A load resistor, and are obtained from V_1 using
the calibration chart (Fig. 10 illustrates the
relationship).

The rows m are $\dfrac{V_2}{A}$ x 100

2.   Although three figures are given only the first two are
     significant.   Since working was done with a slide rule
     the third figure was retained: it preserved trends to
     some extent but, particularly in the individual readings,
     no reliance whatever should be placed on it.

3.   The arrangement is such that the numbers (1 - 24)
     represent plates and these are grouped in fours, each
     four being samples at one stage of mixing.   The letters
     (a) and (b) represent the two scans taken on each plate.

4.   Only the set at 6 revs. Nos. 1 - 4 is given complete.
     This shows the scheme of the readings, and for the subse-
     quent sets m-values only are given.

TABLE II

STANDARD DEVIATIONS OF m VALUES IN TABLE I.

Figures giving the standard deviation,expressed as a
percentage of the mean,for each set of 8 estimates of m
at sample size (diam.) and mixing stage (revs.) as given.

Diam.	.86	.69	.52	.32	.2	.04
No. of Revs.						
6	13	24	24	25	28	38
12	11	15	19	22	24	27
18	13	20	26	29	33	34
24	14	15	19	22	19	15
30	20	26	33	40	45	50
	12	18	16	22	27	33
36	9	15	18	21	22	25

The arithmetic means of these at the various
stages of mixing are

No. of Revs.	6	12	18	24	30	36
% S.D.	25	20	26	17	36,21	18

Notes: 1. The figures from which this table was computed
are given in Table I; the individual figures
are in the first section of this table and the
means, at fixed mixing stage and sample size,
are in the second section.

2. Two figures are given in each place in the row corresponding to 30 revs., and in the corresponding mean values. Referring to Table I it may be seen that the values, 20(b), are different to a marked degree from the other estimates of the same thing. These seem freak values and so standard deviation figures are quoted including and excluding this particular set. With the set excluded the remaining figures conform to the general trend: the odd members could be rejected on statistical grounds.

TABLE III

PROCESSING AND SCANNING VARIATION

Results from two plates taken of the same dough sample but put independently through further processing.

Diam.		.86	.69	.52	.36	.20	.04
1.(a)	A	40.2	40.1	39.8	39.8	40	41
	V_1	55.5	47	38	31	25.5	22
	V_2	2.32	2.12	1.9	1.71	1.53	1.41
	m	5.8	5.3	4.8	4.3	3.8	3.4
(b)	A	41.7	39.6	40.5	41	40	39
	V_1	66	50.5	45.5	39.5	31	24.5
	V_2	2.56	2.2	2.08	1.93	1.71	1.5
	m	6.1	5.6	5.1	4.7	4.3	3.8
2.(a)	A	39.5	40.5	41	40	39	42
	V_1	54.5	49	41.5	32	25	23.5
	V_2	2.3	2.16	1.99	1.74	1.52	1.46
	m	5.8	5.3	4.9	4.4	3.9	3.5
(b)	A	41.8	39.5	40.5	39	41.5	41.5
	V_1	65.5	50	44.5	36.5	33	28
	V_2	2.55	2.19	2.06	1.84	1.77	1.61
	m	6.1	5.5	5.1	4.7	4.3	3.9

Notes: 1. The symbols have the same significance as for Table I.

2. Sets 1.(a) and 2.(a) represent scans on the same track on the different plates, similarly with 1.(b) and 2.(b).

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A P P E N D I C E S

APPENDIX I

The Background to the Investigation.

Interest in the mixing of flour doughs arose in
connection with the problem of chemical improvers in
flour, and their relation to health.   Oxidising agents,
such as bromates and nitrogen trichloride ("Agene"), have
for many years now been used with flour for baking: they
improve the protein quality giving, a better sized loaf,
and the colour of the bread.   Then a controversy arose
from a publication by Mellanby[*] in which he showed that
"Agene" had reacted with some of the flour proteins, giving
a toxic product which could induce hysteria in dogs, and he
suggested that it might also be harmful to human beings.

Investigation into this commenced, and efforts were
made to find harmless alternatives to chemical improvers
since the baking industry was loath to abandon the advantages
these provided.   Work by Hay[**] and others, showed that
much increased mixing gave the desired effect.   Almost
certainly the beneficial effects of this mixing came from
increased exposure to atmospheric oxygen, and this was suppor-
ted by experiments carried out at the Royal Technical
College[***] , in which the mixing was conducted in an

[*] Mellanby,E. Brit.med.J., 1946, (ii), 885.
[**] Rank,J. and Hay,J.G., B.P.646, 311, (1950).
[***]Hawthorn,J. and Todd,J.P. J.Sci.Food Agric., 1955, 6, 501.

atmosphere of oxygen, and the desired improvement occurred
under normal mixing conditions.   From this work consider-
able interest in the mixing of flour doughs was aroused,
and one of the problems associated with this was the quanti-
tative measurement of dough mixing.

APPENDIX II

Dough as a Material.

A crude picture of flour dough may be given as a mass
of starch particles, held together by an interlacing
network of protein fibres.   In any question of physical
properties it is these proteins which matter: the starch
merely, from this viewpoint, forms the bulk.   The proteins
are long chain molecules, with an elaborate system of active
groups.   It is this which prevents any simple chemical
substance being added to one component of a dough mixture
and subsequent analysis of samples for this, as the additive
is adsorbed at these active centres and cannot, by ordinary
means, be removed.

Furthermore the elastic properties of these chains are
altered, markedly, by both oxidation and mechanical working.
Oxidation may be effected either by chemical oxidising
agents, which must be weak or the molecules will be disrup-
ted, or atmospheric oxygen which acts more slowly, and this
reaction is catalysed by water.   The mechanism of this
action is not understood, but it may be by attack on the
sulphydryl groups removing the hydrogen and thus giving
rise to additional chain linkages, strengthening the struc-
ture to give it a higher elastic modulus and reducing its
extensibility.

Working the dough gives the reverse effect, apparently breaking down cross links, and lowering the elastic modulus and viscosity. After leaving the dough for some time after working it relaxes and apparently its original properties return. It is this change with time effect which makes its properties difficult to characterise. Many papers have been written on the subject, the earliest being those by Schofield and Scott Blair[*] in which they picture dough as being analogous to a system of springs and dashpots together with an elastic after effect. Later investigations have added only to the complexity of the situation, and it still remains for any adequate treatment to be put forward.

The time dependence makes any measurement of absolute fundamental properties very difficult, and for practical purposes almost meaningless. Consequently no such attempt has been made for it is a study in itself.

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[*] Schofield, R.K., and Scott Blair, G.W., Proc.roy.Soc., 1933, A 139, 571; A 141, 72.

APPENDIX   III

Mathematical Derivations.

A. Limiting Cases of $\bar{s}$ § 3.122 (iv)

The initial state.   In this case all samples contain either pure A or non-A.   The assumption is that mixed samples are very rare in comparison.

$$\text{Thus} \quad \bar{s}_o^2 = \bar{a}(1 - \bar{a}) + (1 - \bar{a})(0 - \bar{a})$$
$$= \bar{a}(1 - \bar{a})$$

The random state.   The assumption is made in this state that the chance of drawing a particle of A is $\bar{a}$, a constant and independent of any previous sampling. From this it follows that the chance that n_a particles, of a sample of n particles, will be A is given by

$$P(n_a) = \binom{n}{n_a} (\bar{a})^{n_a}(1 - \bar{a})^{n - n_a} \quad \dots 3.$$

This gives what is known as the Bernouilli, or Binomial, distribution.

Now a can take values 1 or 0 with probabilities $\bar{a}$ and $(1 - \bar{a})$ thus the expected value of a^2 in one trial is

$$E(a^2) = \bar{a} \cdot 1^2 + (1-\bar{a})0^2 = \bar{a}$$

and similarly the expected value of a is

$$E(a) = \bar{a} \cdot 1 + (1-\bar{a})0 = \bar{a}$$

Thus the variance per trial is $E(a^2) - \left[E(a)\right]^2$

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

But the sample is made up of n independent trials, so the variance for the sample is $n\bar{a}(1 - \bar{a})$. This is the variance of the number of successes; the variance of the proportion of successes will therefore be $\dfrac{n\bar{a}(1 - \bar{a})}{n.n}$

$$= \frac{\bar{a}(1 - \bar{a})}{n} \qquad \dots\text{. 4.}$$

B. <u>Relationship Between the Spectral Function and the</u>
<u>Autocorrelation Function.</u>   § 3.146

The equation $\omega(f) = 4 \displaystyle\int_0^\infty R_r \cos \omega r \, dr$ $\dots$12.

is a standard result known as the Wiener-Khintchine Theorem, and a proof can be found in the mathematical texts e.g. Wiener[*].   The result may also be expressed by the pair of Fourier Transforms

$$\omega(f) = 4 \int_0^\infty R_r e^{-i\omega r} \, dr$$

$$R_r = \int_0^\infty \omega(f) e^{-i\omega f} \, df$$

The result $\dfrac{d}{dr}\left(r^2 \overline{X}_r^2\right) = 2 \displaystyle\int_0^\infty \frac{\omega(f)}{f} \sin fr \, df \, \cdots \, 14$

is due to MacDonald[**]

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[*]   Wiener, N. Interpolation Extrapolation and Smoothing of Time Series, John Wiley and Sons, New York, 1949.
[**] MacDonald, D.K.C. Phil. Mag., 1949, 40, 561.

C. Effect of Variance on Sample Size (Discrete Values) §3.1491.

Consider the series $x_1, x_2, x_3, \ldots x_n$ $n \gg 1$

let the mean value $\bar{x} = 0$ $\therefore \bar{x}^2 = \overline{(x-\bar{x})^2} = \frac{1}{x}\sum_{s=1}^{n} x_s^2$

put $R(r) = \dfrac{\overline{x_s\, x_{s+r}}}{\bar{x}^2}$ $\therefore \overline{x_s x_{s+r}} = R(r)\,\bar{x}^2$

The problem is to find $\overline{X}_r^2$

Putting

$$\frac{1}{r}\left(x_1 + x_2 + \cdots\cdots + x_r\right) = S_1$$

$$\frac{1}{r}\left(x_2 + x_3 + \cdots\cdots + x_{r+1}\right) = S_2$$

$$\vdots \qquad\qquad \vdots$$

$$\frac{1}{r}\left(x_{n-r+1} + \cdots\cdots + x_n\right) = S_{n-r+1}$$

$$\overline{X}_r^2 = \frac{1}{n-r+1} \sum_{s=1}^{n-r+1} S_s^2$$

$$= \frac{1}{r^2(n-r+1)}\left\{\left[(x_1^2 + x_2^2 + \cdots + x_r^2) + (x_2^2 + x_3^2 + \cdots + x_{r+1}^2) + \cdots \right.\right.$$
$$\left.\left. + 2(n-r+1)\bar{x}^2\Big[(r-1)R(1) + (r-2)R(2) + \cdots + (r-s)R(s) + \cdots + R(r-1)\Big]\right]\right\}$$

$$= \frac{1}{r^2(n-r+1)}\left\{(n-r+1)(r)\bar{x}^2 + 2(n-r+1)\bar{x}^2\left[r\sum_{s=1}^{r-1}R(s) - \Big[R(1) + 2R(2) + \cdots + (r-1)R(r-1)\Big]\right]\right\}$$

$$= \bar{x}^2\left\{\frac{1}{r} + \frac{2}{r^2}\left[r\sum_{s=1}^{r-1}R(s) - \sum_{s=1}^{r-1}s\,R(s)\right]\right\}$$

$$= \bar{x}^2\left\{\frac{1}{r}\left[1 + 2\sum_{1}^{r-1}R(s)\right] - \frac{2}{r^2}\sum_{1}^{r-1}s\,R(s)\right\} \quad\cdots\cdots\ 17$$

Extending this to the continuous case such that the interval

between the x values tends to zero gives the result

$$\overline{X_r^2} = \frac{2\overline{x}^2}{r} \int_0^\infty R(r)\, dr - \frac{2\overline{x}^2}{r^2} \int_0^\infty r\, R(r)\, dr$$

$$= \frac{2}{r} \int_0^\infty R_r\, dr - \frac{2}{r^2} \int_0^\infty r\, R_r\, dr \qquad \ldots 20.$$

D. The Relationship Between $\overline{X_r^2}$ and R_r .

Let r_1 be some particular value of r

$$\text{Then} \quad X_{r_1} = \frac{1}{r_1} \int_x^{x+r_1} C(x)\, dx$$

$$\overline{X_{r_1}^2} = \frac{1}{r_1^2} \left[\int_x^{x+r} C(x)\, dx \right]^2$$

$$= \frac{2}{r_1^2} \int_0^{r_1} \int_0^{r_1-r} \overline{C(x) C(x+r)} \, dx\, dr \qquad \ldots\ldots 15$$

$$= \frac{2}{r_1^2} \int_0^{r_1} (r_1-r)\, R_r\, dr \qquad \text{Since } \overline{C(x) C(x+r)} \text{ is}$$

$$\text{independent of } x$$

$$= \frac{2}{r_1} \int_0^{r_1} R_r\, dr - \frac{2}{r_1^2} \int_0^{r_1} r\, R_r\, dr$$

$$\doteq \frac{2}{r_1} \int_0^\infty R_r\, dr \qquad \text{if } r_1 \gg r_0 \text{ where for } r > r_0,$$

$$\text{all } R_r = 0$$

E. Fourier Analysis of Regular Systems   § 3.1493

i) If

$$C(x) = \sum_{n=1}^\infty a_n \cos nx + \sum_{n=1}^\infty b_n \sin nx$$

$$X_r = \frac{1}{r} \sum_{n=1}^\infty \int_x^{x+r} a_n \cos nx\, dx + \frac{1}{r} \sum_{n=1}^\infty \int_x^{x+r} b_n \sin nx\, dx$$

$$= \frac{2}{r} \sum_{n=1}^{\infty} - \frac{a_n}{n} \cos n \left(x+\frac{r}{2}\right) \sin nr + \frac{2}{\pi} \sum_{n=1}^{\infty} - \frac{b_n}{n} \sin n\left(x+\frac{r}{2}\right) \sin nr$$

Taking the mean value of the square of this all terms vanish except those in $\sin^2 n\left(x+\frac{r}{2}\right)$ and $\cos^2 n\left(x+\frac{r}{2}\right)$ the mean value of these is $\frac{1}{2}$.

$$\therefore \overline{X_r^2} = \frac{1}{2} \frac{4}{r^2} \sum_{1}^{\infty} \left(\frac{a_n}{n}\right)^2 \sin^2 nr + \frac{1}{2} \frac{4}{r^2} \sum_{1}^{\infty} \left(\frac{b_n}{n}\right)^2 \sin^2 nr$$

$$= \sum_{n=1}^{\infty} K_n^2 \frac{\sin^2 nr}{n^2 r^2} \qquad \text{where } K_n^2 = 2\left(a_n^2 + b_n^2\right) \qquad \ldots 21.$$

ii) The chessboard pattern is evaluated by the same method.   § 3.1494

$$C(x,y) = X(x)\, Y(y)$$

Using double Fourier series for a chessboard of side

$$C(x,y) = \frac{4}{\pi^2} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{1-\cos m\pi}{m} \frac{1-\cos n\pi}{n} \sin \frac{m\pi x}{a} \cos \frac{n\pi y}{a}$$

Integrating this over a sampling square of side r leads to

$$\overline{X_r^2} = \frac{16 a^2}{\pi^4} \sum \sum \left(\frac{1-\cos m\pi}{m^2}\right)\left(\frac{1-\cos n\pi}{n^2}\right) \sin \frac{m\pi}{a}\left(x+\frac{r}{2}\right) \sin \frac{m\pi r}{2a}$$

$$\sin \frac{n\pi}{a}\left(y+\frac{r}{2}\right) \sin \frac{n\pi r}{2a}$$

$$\ldots 22.$$

Again taking the mean square value of this only the
coefficients of

$$\sin^2 \frac{m\pi}{a}\left(x+\frac{r}{2}\right) \text{ and } \sin^2 \frac{n\pi}{a}\left(y+\frac{r}{2}\right) \quad \text{survive leading to}$$

$$\overline{X_r^2} = \frac{64 a^4}{\pi^8 r^4} \sum_{m=1}^{\infty} \frac{(1-\cos m\pi)^2}{m^4} \sin^2 \frac{m\pi r}{2a} \sum_{n=1}^{\infty} \frac{(1-\cos n\pi)^2}{n^4} \sin^2 \frac{n\pi r}{2a}$$

$$= \sum_{m=1}^{\infty} K_m^2 \frac{\sin^2 \frac{m\pi r}{2a}}{\left(\frac{m\pi r}{2a}\right)^2} + \sum_{n=1}^{\infty} K_n^2 \frac{\sin^2 \frac{n\pi r}{2a}}{\left(\frac{n\pi r}{2a}\right)^2} \qquad \dots 23.$$

F. The Relationship Between d and $\bar{s}$ if the Variables
are Normally Distributed. § 3.241

If $\phi(x)$ is the distribution function σ its standard
deviation and O the mean,

Then for a normal distribution

$$\phi(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{x^2}{2\sigma^2}}$$

$$d = \int_0^{\infty} |x| \, \phi(x) \, dx$$

$$= 2\int_0^{\infty} x \, \phi(x) \, dx \qquad \text{(symmetrical)}$$

$$= \frac{\sqrt{2}}{\sigma\sqrt{\pi}} \int_0^{\infty} x e^{-\frac{x^2}{2\sigma^2}} \, dx$$

Whence $d = \left. \dfrac{\sigma\sqrt{2}}{\sqrt{\pi}}\, e^{-\frac{x^2}{2\sigma^2}} \right]_0^\infty$

$= \sigma\sqrt{\dfrac{2}{\pi}}$

whence $d(d) = k\, d\sigma$

APPENDIX   IV A

Calculation of Iris Diaphragm Ratios.

The arrangement of the optical system is shown in Fig. 5 .   From the dimensions of this and the focal length of the lenses that ratio of the iris aperture to the image of this thrown on the plate, and hence the sample size, can be calculated.

The standard lens formula

$$\frac{1}{v} + \frac{1}{u} = -\frac{1}{f}$$

by putting $R = \frac{u}{v}$ and $K = u + v$

gives the form $\frac{R+1}{K} + \frac{R+1}{RK} = -\frac{1}{f}$

i.e. $R^2 f + R(2f+K) + f = 0$

From the actual measurements

$$f = -8" \qquad K = 33"$$

whence, since the image is diminished,

$$R = 1.42$$

hence

$$\frac{\text{iris diameter}}{\text{scanning spot diameter}} = \frac{1.42}{1}$$

APPENDIX IV B

The Preparation of Random Patterns.

This was done using decimal graph paper.   Spots were blackened on this according to the following plan:-

1. The large squares (1cm.side) were numbered across the page and then down (i.e. in the sequence of the words on a printed page).   To each of these, in order, a random number in the same order was taken from a table of four digit random numbers in "Statistical Tables for Research Workers" by Fisher and Yates.

2. Within the 1cm. squares, the small squares (1mm.side) were numbered in the same fashion as above, 1 - 100.

3. The first digit in the random number gave the size of spot in terms of small squares, to be inserted into each large square according to the scheme:

No.	0	1	2	3	4	5	6	7	8	9
Spot Size	7x7	7x7	7x5	7x3	7x1	5x5	5x3	5x1	3x3	3x1

This distribution of sizes was arbitrary and gives the average spot size as 21.8 squares.

4. The second number gave an orientation factor to the asymmetric spots, if it was 0 - 4 the long axis was horizontal, if 5 - 9 this was vertical.   With symmetric

spots this number had no significance.

5. The remaining two numbers gave the position of the small square whose centre corresponded to the centre of the spot.   The choice of odd numbers for square sizes simplified this.

   e.g. If the eighth number in the random table were 4673 this would imply that a spot would be drawn, 7 x 1 small squares in size, situated so that the seven squares would lie vertically, and that the fourth of these would occupy small square number 73 within the eighth large one.

   Any overlapping, quite rare owing to the comparatively small amount blacked in, was ignored.

APPENDIX IV C

Estimation of the Initial Values of "m".

It is possible, knowing the maximum and minimum light

transmitted through the plate by the "pure white" and

"pure black", to calculate the initial value of m i.e. the

value at no-mixing.   Owing to sampling errors this will

probably not correspond exactly with the experimental values,

but it affords a check on these.

Let the mean light transmitted be L_m the maximum

L_{max} and the minimum L_{min} .   The proportions of black to

white are known as 1:4 .

Then

the r.m.s. fluctuation $= D \sqrt{\dfrac{4 \times 1 + 1 \times 16}{5}} = 2D$

where $D = L_m - L_{min}$

In the practical case this is as read in terms of the current

in the 931 A load resistor, in scale units of the D.C.

microammeter.   The calibration of this meter is

1 division $= .445$ μa and the load resistor is .25 megohms.

Hence $\bar{S}_o = \dfrac{D}{m} \dfrac{2.5}{23.5}$ volts

From measurements on a number of plates the mean values are

$L_{min} = 8$, $L_{max} = 79$, $L_m = 22$

whence $\bar{S} = \dfrac{28}{22} \dfrac{2.5}{23.5} = \underline{13.5}$ volts

GENERAL NOTATION

A , B	Components
$a(a_1, a_2 \ldots), b$	Component concentration (proportions)
$\bar{s}$, $\bar{s}^2$	Standard deviation and variance of a
d	Mean absolute deviation of a
n	No. of particles in sample and general no.
L , r , x	Length measures
$C(x)$	Concentration of a at point x
X_r	Mean concentration of a over a length r
X_r^2	Variance of
R_r	Autocorrelation function
$R(r)$	Coefficient of correlation $R(r) = R_r / \bar{a}$
$a_m, a_n, x_n, K_n,$	Fourier coefficients
$\omega(f)$	Spectral function
f , ω .	Length frequencies
m, n, u, s	General numbers
M , M_m	Generalised mixing measure, final state M
k	Mixing rate constant
t , $T_{\frac{1}{2}}$	Time, time for half mixing
m	Mixing measure in experimental work
m'	Mean value of m over sample size range

NOTATION QUOTED FROM REFERENCES

M_i	Mixing index	(7)
χ^2	Chi squared (statistical measure)	(2)
$Z = 2 \sin^{-1} \sqrt{a}$	Variable transformation	(2)
S	Linear scale of segregation ...	(6)
V	Volume scale of segregation ...	(6)
I	Intensity of segregation ...	(6)
$[a_i^o]$	Initial position matrix	(11)
$[a_i^m]$	Final position matrix	(11)
$[D_{ij}]$	Distribution matrix	(11)
S	General interfacial surface ...	(3,5)
S_m , S_o	Maximum interfacial surface ...	(3,5)
X	Percentage mixed	(5)

Numbers in brackets give the reference containing the
symbol.