MIXING OF SOLIDS

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I. Introduction

Solids mixing, although in wide use for a number of years, has received comparatively little rigorous treatment in the literature, compared to other widely used process operations. Quite recently, there has been a spurt of activity to remedy this situation.

Several studies have dealt with ways to evaluate the state of mixedness of a batch of solids. Also, some performance tests of various types of solids mixers have been published. Rate mechanisms have also been dealt with. In addition, there has been some literature concerning the analysis of particle motion during mixing. Each of these areas will be discussed.

The subject matter has been divided into four basic categories which deal with state of mixedness of a batch of solids, theoretical frequency distributions, rate equations, and equipment. Some papers will be discussed in more than one of these categories. Most of the literature deals with batch mixing, although some pertains to continuous mixing, but this method of categorizing has not been followed.

The material contained here, in addition to providing some useful techniques and facts for those who are interested in solids mixing work, can serve as a guide towards research on future problems. Criteria which are considered essential to the best interpretation of a study of mixing performance will be pointed out. Unfortunately, these are not always reported in published studies, and their continued omission can slow up the most fruitful use of such work as building blocks for the future. It is hoped that omissions of data in published literature concerning such things as size and operating variables for commercial equipment, or for that matter, any mixing equipment, will be diminished, and possibly eliminated. Drew (D5) pointed out that diffusivities, which were reported in the literature without frames of reference, imposed serious handicaps on those attempting to use these results for later correlations and to help explain diffusion phenomena.

From time to time questions pertinent to the topic under discussion will be asked, as a technique for stressing important considerations.

II. Related Process Steps

Wherever a solids mixer is necessary, thought must be given to the handling of the batch after mixing. The mixer may turn out an excellent product, but subsequent handling may render it unsatisfactory for the next step in the process. Dumping, shaking during transportation, vibrating, and flow through silos are some of the steps frequently following batch mixing. Each of these offers excellent chances for batch segregation. This phenomenon is probably a lot more widely known and thought about by those using solids mixing in a process, than the comparatively scarce literature on examples of it might indicate. However, batch segregation probably exists and is tolerated in many processes.

There are several reasons for this: (1) It is difficult to obtain an objective picture of the state of mixedness of a solids mixture (this will be discussed in a later section). (2) There are sometimes obstacles to finding out how much of the subsequent process troubles, limitations, and/or defective end products, can be traced to batch segregation in cases where further processing of the mixed batch is necessary. When these factors can be determined, they must be balanced against the cost of remedying the situation, if possible. Sometimes, no obvious solution is available, and it does not appear to be economically feasible to undertake a research and development program to find the solution. With the publication of more information on the mechanisms of batch segregation, this situation will be remedied. (3) It may sometimes be decided that more attention to the proper performance of the existing operations (i.e., better weighing of materials, less loss of dust, less contamination with impurities, etc.) is a more profitable way to reduce process costs and improve the product, with the limited amount of manpower and money for use in this area.

III. State of Mixedness of a Batch of Solids

A. CONCEPT OF DEGREE OF MIXING

One of the key questions that comes up whenever a mixture of solids is used, either to make a product directly or to be further processed, is: "Is this batch well enough mixed?" This question has many ramifications because "well enough mixed" may have a different meaning, depending on whether a commercial process or a research project is involved, and also on the particular purpose of the solids mixing operation. Some of the factors that may be considered before answering this question were mentioned in the preceding section. However, it is first necessary to answer the question: "How well mixed is this batch?"

A quantitative expression for the degree of mixing gives an unambiguous picture of the variation in batch composition. To be generally useful, it must be obtained from a study of batch samples, since only in special research projects will analysis of the entire batch be possible. The problem then resolves itself into a matter of how to best get the samples and what to do with them. Each of these subjects will be discussed separately.

B. SAMPLING CONSIDERATIONS

Several aspects of sampling will be discussed in this section, and related statistical methods will be covered later on. However, before getting into the details, it is well to stand back and first consider some general comments on the whole idea of sampling. Sometimes, obviously poor sampling practices are perpetuated primarily for lack of thoughtful care and attention (e.g., taking one 100-gm. sample from a 140,000-lb. shipment in a railroad car and deciding on this basis that an entire carload is satisfactory). Therefore, it is well as a starting point to ask whether the sampling is arbitrary or truly suitable to the problem to be studied. In reporting results, complete details of the sampling procedure should be given, including the method of taking spot samples; their location, size, and number; the method of analysis; and the fraction of the batch removed for sampling.

1. *Method and Location*

Because of the variety of situations possible, guiding principles rather than detailed rules for removing samples must be given. These are:

a. Removing the sample should cause as little disturbance of the mixture as possible.

b. It is desirable to sample within the mixer as well as after dumping the mixed batch. This will reveal gradients due to segregation and will also prevent confusing of mixer performance with the effects of dumping and "coning." Additional sampling during and after dumping can be carried out as desired to isolate any sources of segregation.

c. Samples should be taken throughout the entire batch volume, rather than from only one part of it.

d. If possible a sampling thief, especially adapted for the particular operation, should be made so that insertion into the batch is possible with a minimum of disturbance. The most desirable procedure is to insert the thief with the holes covered. When it is in position, uncover the sampler holes, trap the sample, cover the holes, and remove the thief.

e. If a sampling thief cannot be used, some special device will have to be made, bearing in mind the above rules. For very tiny spot samples, a special thief which was first used by Maitra and Coulson (M2), is described and shown in detail by Weidenbaum and Bonilla (W2). Larger scale devices, based on this principle, can also be used. For removing spot samples of approximately 0.8 gm. from their sand-salt mixture, a different type of sampling device was used. This sampler (Fig. 2) permitted the removal of a slug of mixture by the application of suction with a precautionary fine screen for preventing particle movement due to the

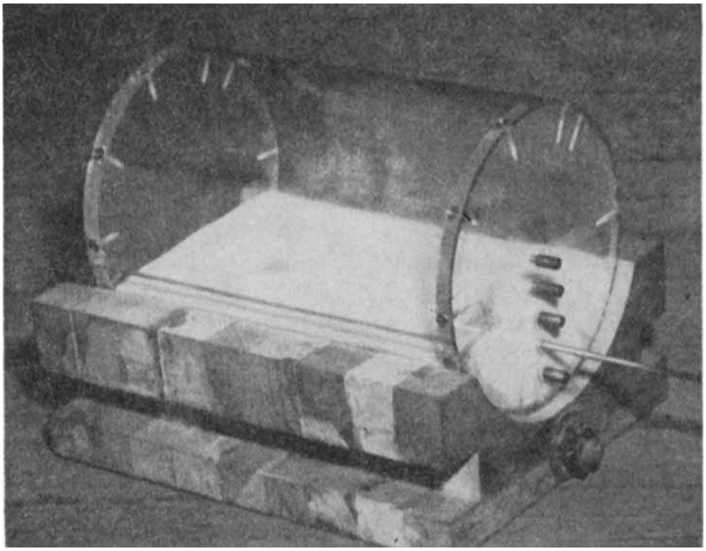

FIG. 1. Sampling thief for very small spot samples (W1).

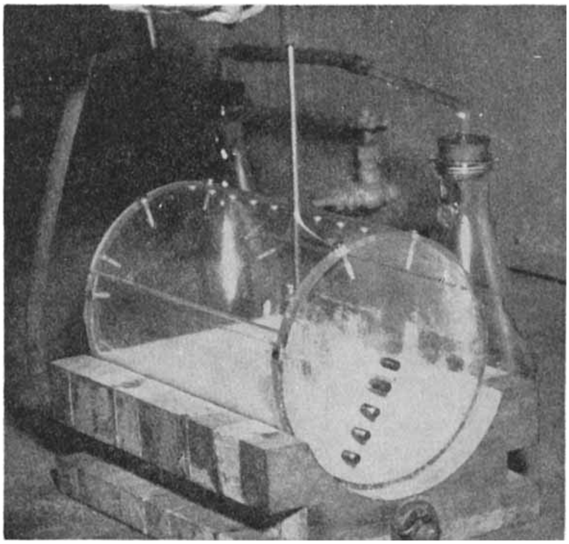

FIG. 2. Device for taking larger samples (W1).

suction. Pictures illustrating these two methods are shown in Figs. 1 and 2. Sometimes a thin-walled tube can be inserted into the batch, the open end closed off, and the sample thus removed. Upon removal of the tube, the closed-off end is opened and the sample will drop out. These are just a few examples of the improvisation which solids sampling may involve.

2. *Spot Sample Size*

The size of the spot sample will depend upon the use to be made of the mixture, in most cases. A convenient size where packaging or tableting of the mixture takes place is the actual package or tablet size. Where the mixture is to be used in bulk in a process, those familiar with the analyses to be performed on the spot samples and the significance of fluctuations in the mixture composition should be consulted before selecting the sample size. Not too much of the material should be removed during sampling, particularly if more than one set of spot samples is to be taken. A rough rule would be to remove not more than 5% of the mixture, if it is possible to do this while maintaining a meaningful spot sample size.

3. *Number of Spot Samples*

It is not possible to give a single arbitrary number of spot samples that will be optimum for evaluating any solids mixture. The purpose of the mixing operation, as well as the cost of sampling and analysis, must be considered. However, it is rather obvious that the larger the number of properly taken spot samples, the better and more clear-cut the picture of the solids mixture. Statistical methods for the quantitative use of this principle will be given in a later section.

4. *Analysis of Samples*

a. Quantitative. Solids mixing is used for many varied processes. The analytical procedure will depend on the purpose of mixing (which will decide what substances are to be determined, etc.), the facilities available, and economic factors. One of the pieces of information most often desired is the percentage of a certain substance in each spot sample. This determination represents an analytical problem which is outside the scope of this work. However, it is worth mentioning that recent advances in instrumental analysis have made it much easier to give rapid and numerous analyses, which are of great benefit in statistical work. Some of these methods are X-ray fluorescence, flame spectrometry, polarography, and emission spectroscopy. Some references dealing with methods of analysis are included in the bibliography (A2, H3, L5). Whatever method is chosen (gravimetric, volumetric, electrometric, particle counts, optical, etc.), the results of each spot sample analysis will be in numerical form, and can then be treated statistically. It is desirable that the analysis error be very small compared to the variation in the composition (or other property) between spot samples.

b. Qualitative. In some cases it may be possible by means of a non-quantitative test to determine whether any spot sample is satisfactory. For example, smearing a small sample with a spatula to determine if any streaks are visible may be all that is necessary to determine whether the product will be satisfactory. In such cases the desired result of mixing will be a percentage of "satisfactory" spot samples among the total number taken. The statistical treatment of this case differs from that where quantitative analyses are reported for each spot sample.

C. STATISTICAL TECHNIQUES

1. *General Comments*

As a result of the sampling and analyses, a group of numbers will have been obtained which show the compositions at several sampling spots in the mass of mixed batch. This situation is similar to a production line, where a certain amount of product has been made and samples have been taken to determine its quality level. There are well known statistical techniques for working up the data. These techniques have been used for years in fields such as production quality control, tests of significance in experimental work where materials or processes must be compared with one another, card playing and dice throwing, and even in the preparation of information on which insurance companies can base premium rates for different age groups. Among the well-known terms which are involved are the normal (or Gaussian) distribution, the binomial distribution, the Poisson distribution, chi-square, confidence intervals, quality control charts, and tests of significance. These well known and established techniques have a natural application in the quantitative determination of the state of mixedness of a batch of solids. Their use will be discussed here without repetitive derivations which are available elsewhere.

Certain basic statistical nomenclature is essential as a preliminary. The group of measurements is called a "sample" of n observations. (Note: The statistical term "sample" means the whole group of measurements. In order to distinguish between this and any particular measurement at a certain spot, the latter will be called "spot sample.") If a large enough "sample" is properly taken (which includes many "spot samples"), it will give a good picture of the batch (statistical term: population) from which it was drawn. Statistics helps in planning the size and number of spot samples and in working up the data so as to get a maximum of quantitative, objective information. Mathematical statistics and probability have been used to derive relationships for rate equations and other related applications. Familiarity with this aspect of statistics is not necessary for the engineer who merely wants to ascertain facts concerning the extent of mixedness of his batch.

There are many more terms used in statistical work which could be defined and discussed with varying degrees of complexity and mathematical expression. Naturally, it is desirable that further background material concerning these terms be studied wherever possible. It is not absolutely necessary, however, to go into all aspects of the meaning of these terms in order to be able to use them for practical problems in mixing. For example, random sampling is usually desired when taking spot samples.[1] The intuitive feeling, that this means choosing samples so as to avoid a bias in favor of any particular location or material, can serve in obtaining representative samples, even though the mathematical ideas concerning the independence of distribution functions and their relation to the population distribution function, are not used. Again, although discussions of the term "null hypothesis" could figure prominently in the section on statistical tests of significance, this concept has not been mentioned there. Instead, the general idea of a statistical test of significance has been pointed out, particularly as applied to problems of mixing.

This is not meant to imply that supplementary study of the meaning of these points is unimportant. On the contrary, it is definitely recommended where possible. However, use of those techniques that are available need not be delayed because of lack of familiarity with the theoretical background. Where the applicability of a statistical test may be questionable, it can be discussed with someone familiar with its background.

Some further general comments are essential before going into the details of the statistics. The methods that will be discussed should not be thought of as a final enumeration of all statistical methods that can be used to determine the state of mixedness of a batch. They are really just the beginning of an attempt to apply useful techniques in an area that is well suited for them. New statistical tools are constantly being developed. Old established methods are continually being streamlined, and easily usable graphs are continually appearing to replace more tedious analytical methods. The procedures shown below have been

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[1] In some special cases, however, special location sampling may be preferable when evidence of gradients in a certain direction is being sought.

presented in terms of solids mixing problems, in the hope that this will stimulate their use in that area. They are not meant to replace common sense, nor to substitute some magical mathematical manipulation for a sound intimate knowledge of the particular solids mixing operation and its purpose. They are merely additional tools to aid in utilizing this knowledge. In general, the most productive use of statistical methods in a solids mixing operation is obtained by cooperative work between someone who knows statistics well and someone who is familiar with the solids mixing operation and its purpose. If a single individual is competent in both these areas, the job is that much easier.

So much may be gained in increased efficiency and better product control where solids mixing is concerned, if the proper statistical methods are used, that it is worthwhile to point out some serious obstacles to the employment of statistics in this area. These are:

a. Immediate discouragement on the part of the "practical" man because the mathematical statistician may at first have suggested a procedure that is too impractical. (Such a procedure may involve too many costly analyses, perhaps the mathematical model suggested does not really simulate the actual situation, etc.) These difficulties can almost always be worked out to the mutual advantage of both parties, if the first pitfall due to differences in viewpoint can be overcome.

b. The too frequent tendency of authors, in articles on the use of statistical methods, to become elaborately involved in derivations (some of which have already been derived elsewhere), rather than concentrate on the application of known formulae and methods to mixing problems. To someone unfamiliar with statistics, this may give the impression that some new and untried mathematical ideas are involved, whereas the case may *simply illustrate the application of an old and generally accepted* statistical method.

c. The relatively few examples in the literature in which statistical methods are specifically applied to solids mixing problems. Although there are numerous cases dealing with statistical methods in mass production manufacturing, this is not as likely to be studied by someone who is groping for a better way to evaluate his solids mixing operation, as a problem dealing with solids mixing. More published examples of the use of statistical methods to evaluate or improve solids mixing operations specifically, would be a great help to their general acceptance and use throughout industry.

2. *Quantitative Measurements on Each Spot Sample*

a. The Relative Frequency Distribution. Returning now to the group of spot samples taken from the mixed batch, if enough spot samples were taken, then a fairly good graph could be drawn, showing "composition" (such as %A) on the abscissa, and "fraction of the spot samples" within a certain composition range on the ordinate, as indicated in Fig. 3. A truly representative graph of this type would give a good picture of the state of mixedness, since it would immediately show how the spot samples varied in composition. However, to get a representative graph, which is called a *relative frequency distribution* in statistical terminology, is a formidable task since a very large number of spot samples would be needed. Except for certain special cases, this is highly impractical. Statistics gives methods whereby objective estimates of the four characteristics, which are needed to completely describe such a distribution, can be made with a small number of spot samples. These characteristics, which are called "statistics" are: (1) Some measure of the number about which most of the values tend to cluster. Although many different measures exist (median, mode, geometric mean), the arithmetic mean is the most common. The statistical term for this is a "measure of central tendency." (2) Some measure which indicates the amount of variation among the values. Although the average deviation was formerly very popular, modern statistics has established the superiority of the variance as the most efficient means of extracting information concerning variation within a group of measurements. The standard deviation and range are other terms frequently used. The statistical term for this is "measure of spread" or "measure of variation." (3) Some measure indicating how symmetrical the distribution is with respect to a vertical axis through its mean. The statistical term for this is "measure of skewness." (4) Some measure which indicates how high or peaked the graph is in the neighborhood of the mean. The statistical term for this is "measure of peakedness" or "measure of kurtosis."

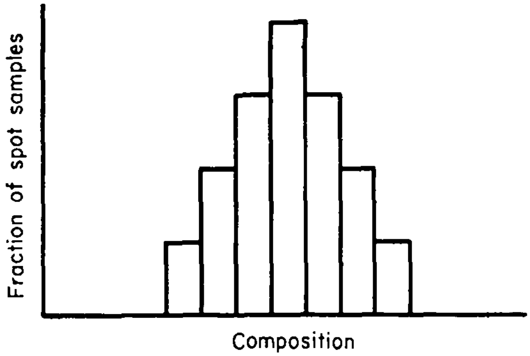


FIG. 3. Relative frequency histogram for spot sample compositions.

For most solids mixing problems, the measure of central tendency and measure of variation will be of greatest use. Therefore these will be defined and tests of significance given for them. Measures of skewness or peakedness can be found elsewhere (H5) if the occasion demands.

Other useful statistical tests, together with their background, will also be given later.

b. Definitions. i. Sample Arithmetic Mean. This well known and widely used term, which will be denoted by $\bar{x}$, is defined as:

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n} \tag{1}$$

where n = the number of spot samples (statistical term is "sample size")
x_i = the i-th value of x, which is a number representing composition or whatever else is being looked for in each spot sample.

The mean by itself should not be used as a degree of mixing, since, if the batch is properly sampled, the only variation between sample means should be the sampling variation, regardless of how well mixed the batch is. It is often desirable, however, to compute the sample mean in addition to whatever degree of mixing is used. Where the true mean is known (e.g., a known per cent of a certain material has been added in the mixer), this can be used to find out whether the sample mean is significantly different from the true mean. If this significant difference should occur, it would then be necessary to find out whether it were due to improper location and spacing of the spot samples, a bias during sampling (perhaps the sampling method was biased in favor of getting more of a certain material), or some peculiar segregating tendency which favored the concentration of one material in some small area.

ii. Sample Variance and Standard Deviation. The unbiased sample variance, denoted by $\hat{s}^2$, is defined as:

$$\hat{s}^2 = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n - 1} \tag{2}$$

[Note: The standard deviation $\hat{s}$ will be obtained by taking the square root of $\hat{s}^2$, although it happens that whereas $\hat{s}^2$ is an unbiased estimate of the population variance, $\hat{s}$ is not an unbiased estimate of the population standard deviation.] (The term unbiased indicates that $n - 1$ is used in the denominator instead of n, in defining variance. In order to avoid repetition from here on, the word unbiased will not be used although all variances and standard deviations will be of this type unless otherwise specified.) Both the standard deviation and variance have their own particular advantages and it is worthwhile to work with both of them. The standard deviation is handier for graphing and discussing mixing performance because it has the same units as the unit of measurement. However, the variance is more desirable for statistical tests of significance comparing variation, since it provides the most efficient means of extracting information concerning variation from a group of measurements, and **F** tables, which are used in statistical tests of significance involving variances, are easily available.

Either the variance or the standard deviation is usually a good first choice for degree of mixing. Sometimes expressions, involving these as well as other terms, are used for special applications, such as determination of the best plotting methods to reveal rate mechanisms.

A computing formula is available for ease in calculating the variance or standard deviation:

$$\hat{s}^2 = \frac{n \sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i \right)^2}{n(n-1)} \tag{2a}$$

c. Statistical Tests of Significance. i. Meaning of a Statistical Test of Significance. After the mean and variance have been computed, it is often desirable to compare them to some "reference" set. Statistical tests of significance give an objective means of doing this. Again, before the details are dealt with, it is essential that certain basic concepts be understood.

A *test of significance* prescribes a method for comparing a characteristic of the test samples with that of the reference samples by means of a term involving both. The probability that as large a numerical value of this term as computed would occur due to chance alone, is then looked up in the proper table. If it is improbable that this large a numerical value would have occurred due to chance alone, then it is concluded that there must be something else besides chance causing the difference between the test value and the reference value, and that therefore the two differ significantly. In the examples that follow, an improbable occurrence is defined as one that would happen by chance less than one time in twenty, in the long run. This means that the tests are run at the 5% level of significance. As is further mentioned under Section III, C, 7, other levels of significance could be chosen.

Choosing a "reference" by which the mean and variance can be compared, is not often an easy job. One possible way of doing this is by determining from a pilot plant run what mixture will be most satisfactory for further processing. A key characteristic of the mix can then be measured in many spot samples. The mean and variance obtained from these spot samples could then serve as "references" for comparison, when it is desired to go to large-scale production in a big mixer. The techniques to be shown can also be used to determine whether significant "unmixing" occurs after mixing, due to handling of the batch, as mentioned in the section on Related Process Steps (Section II).

ii. Test of Significance for Means (**t** *test*). If a known proportion of a certain component has been put into the mixture and the latter has been properly sampled, then the sample mean would not be expected to be significantly different from the known composition, which will be denoted by m. In this test, a method is given for determining objectively whether any observed difference is significant.

$x_1, x_2, x_3 \ldots x_n$ represents a group of measurements on n spot samples.

Step 1. Compute $\bar{x}$, the sample arithmetic mean and $\hat{s}$, the sample standard deviation, as shown previously.

Step 2. Compute

$$\mathrm{t} = \frac{\bar{x} - m}{\dfrac{\hat{s}}{\sqrt{n}}} \tag{3}$$

where n = the number of spot samples.

Step 3. From the **t** tables (H5, pp. 248, 249), determine whether this large a value of **t** would occur more than one time in twenty due to chance. (In statistical terminology: whether the value of **t** is greater than that given in the tables for the 5% level of significance in a two-tail test.) It is necessary to know the degrees of freedom ($= n - 1$) in order to use the tables.

Step 4. If the value of **t** is so large that it would occur by chance less than one time in twenty, conclude that $\bar{x}$ is significantly different from m.

Step 5. This is the most important part of the procedure, namely, the interpretation of the results of the test. If the means under comparison differed significantly, the sampling may have been biased due to location or method. If so, this bias should be corrected before further samples are taken. It should be stressed that statistics alone cannot generally point out exactly what is happening to cause the significant difference. This must come from a close knowledge of the operation.

iii. Test of Significance for Variances (**F** *test*). The need for this might arise as follows: A small-scale pilot plant experiment has shown that a satisfactory mixture can be produced for further processing. All of the work was done by a research group where considerable attention was given to preparing the mixture, since the primary purpose was to ascertain whether the entire process could be used. Time and manpower in preparing the mixture were not limited. Now the process is to be scaled up to production requirements, and it will be necessary to cut the cost per pound of product considerably.

A much larger mixer is needed than that used to mix the say 50-lb. lots for the pilot plant run. Mixing will have to be done in a much shorter time. However, since the mixture in the pilot run has been proven to process successfully, the large-scale, rapid mixing must also yield as good a mixture. The weight fraction of a key constituent in the mixture, which must be well distributed for successful later processing, is determined in a number of spot samples taken from the successful pilot mixture. The variation between spot sample compositions of the large-scale mix should not be significantly greater than the variation between spot sample compositions from the pilot mix. The following procedure indicates how to determine whether the variations are significantly different:

$x_1, x_2, x_3 \ldots x_n$ represent the pilot mixer measurements of which there are n_x.

$y_1, y_2, y_3 \ldots y_n$ represent the large mixer measurements of which there are n_y.

This test is to determine whether $\hat{s}_y^2$ is significantly greater than $\hat{s}_x^2$.

Step 1. Compute $\hat{s}_x^2$ and $\hat{s}_y^2$ as previously shown.

Step 2. If $\hat{s}_x^2$ is larger than $\hat{s}_y^2$, then the larger mixer is satisfactory, and no statistical tests are necessary. If $\hat{s}_y^2$ is larger than $\hat{s}_x^2$, form the ratio

$$\mathbf{F} = \frac{\hat{s}_y^2}{\hat{s}_x^2} \tag{4}$$

Step 3. From the **F** tables (H5, pp. 250–253), determine whether this large a value of **F** would occur due to chance alone more than one time in twenty. (In statistical terminology: whether the value of **F** is greater than that given in the table for the 5% point for the distribution of **F**.) $n_x - 1$ and $n_y - 1$ (denoted as degrees of freedom) are needed to use the tables.

Step 4. If the value of **F** is so large, that it would occur by chance less than one time in twenty, conclude that $\hat{s}_y^2$ is significantly greater than $\hat{s}_x^2$.

Step 5. The reasons for the greater variation must now be sought. Perhaps there is segregation in the mixer, or maybe a longer mixing time is necessary. (Note: It is desirable to make a similar comparison of variation after the mixer is dumped to see whether unmixing occurs.) This type of statistical test can be used to compare the variance among spot samples, taken at any point in the batch handling system, with the reference variance.

iv. Test of Significance for Distributions (**Chi-square** *test*). In Section III, C, 2a, the term *relative frequency distribution* was used to describe a graph showing "composition" on the abscissa and "proportion of spot samples within a certain composition range" on the ordinate. The ordinate values for any composition range are called relative frequencies, because they are expressed as fractions of the total number of spot samples. The mean and variance were mentioned as some of the characteristics needed to describe a frequency distribution, and previous tests dealt with ways to compare them quantitatively with reference values.

In some special cases, it may be desirable to determine whether a set of spot samples comes from a frequency distribution of a certain type, i.e., to compare the experimental frequency distribution with a theoretical one. An example would be the case of a mixture of nuts from which packages of nuts are to be made. If the nuts were mixed in a tumbling mixer then there would be an ideal limiting condition concerning the distribution of different kinds of nuts in the packages, assuming no segregation on packaging. Fifty per cent peanuts might be desired for each package, but the best that could be done by a random tumbling motion would be a certain distribution of "peanut fraction," with 0.50 as the mean. If a number of packages were made up from this mixture, the **chi-square** test would enable us to tell whether the distribution of "peanut fraction" came from a random mixture of peanuts with other nuts. This information would enable an objective decision to be made as to whether the variation in "peanut fraction" from package to package was as low as could be obtained by random tumbling—or whether it was much too large, indicating that some sort of segregation was taking place. The steps for the **chi-square** test are shown below:

Let $o_1, o_2, o_3 \ldots o_i \ldots o_n$ be a set of "observed frequencies" obtained by random sampling from the nut mixture, as previously described. Each of these frequencies is a number whose value shows how often a certain range of "peanut fraction" was obtained.

Let $e_1, e_2, e_3 \ldots e_i \ldots e_n$ be a set of "expected frequencies" obtained by theoretical calculation from the normal distribution. Each of these frequencies is a number showing how often a certain range of "peanut fraction" would be obtained with a certain spot sample size taken from a randomly mixed batch of nuts. The "peanut fraction" range should be chosen so that the expected frequencies are all greater than or equal to 5. The observed frequencies can then be compared with the expected frequencies for various "peanut fraction" ranges. Let k = the number of pairs of observed and expected frequencies to be compared.

Step 1. Compute χ^2 (called **chi-square**):

$$\chi^2 = \sum_{i=1}^{k} \frac{(o_i - e_i)^2}{e_i} \tag{5}$$

Step 2. From **chi-square** (χ^2) tables (H5, p. 246), determine whether this large a value of **chi-square** would occur due to chance more than one time in twenty. The number of degrees of freedom ($= k - 1$) is necessary in order to use the tables. The column heading labeled 0.05 would be used for the "one in twenty" test.

Step 3. If the value of **chi-square** is so large that, it would occur by chance less than one time in twenty, conclude that the observed frequencies represent a distribution which is significantly different from the expected (theoretical) distribution.

Step 4. Now again, the all important question of proper interpretation and use of the results must be considered. If the distributions were significantly different, why did this occur? Perhaps the curved cashew nuts tended to segregate in a certain area. Is there any gradient that can be found by plotting the location and order of the spot sample "peanut fractions"? Statistics does not answer these questions. It simply gives an objective way of pointing out, that there is significantly more variation in "peanut fraction" than there should be for a random mixture. If on the other hand, there is no significant difference, then the nuts have been mixed as thoroughly as possible in a random tumbling operation. There would be no point in looking around for any other type of tumbling mixer in the hope of getting less variation in "peanut fraction" from bag to bag. Instead, if the magnitude of random variation is unacceptable, some other method of nut packaging would have to be considered, such as, perhaps, hand distributing or automatic proportioning of the nuts to give a fixed number of each per package.

3. *Qualitative or Semi-quantitative Measurements on Each Spot Sample*

a. Smear Test. Sometimes, rather than use quantitative analyses for spot samples, a smear test is made. This consists of spreading a spot sample (or a portion from one such sample) in a thin layer on a flat surface by smearing with a spatula, and then visually examining it. Off-color streaks or spots which indicate a lack of complete homogeneity can thus be observed. Samples of a fixed size and a reproducible technique should be used when comparisons are to be made. As will be illustrated in the following two examples, either each spot sample can be judged satisfactory or unsatisfactory on the basis of the smear test (qualitative), or the average number of undesirable streaks per spot sample can be determined by adding up all of the streaks found and dividing by the number of spot samples (semi-quantitative). Where several differently colored streaks are present, the number of streaks of each color per spot sample could be determined, if this is desirable.

b. Test of Significance for Fraction Satisfactory. A case might arise where it is desired to mix differently colored fine materials. Because of the necessity for frequent changes in the materials used in the mixer, it might be desirable not to have any device for breaking up agglomerates in the mixer, even though this means that the final mixture might have a few agglomerates. In other words, in this particular case, the risk of ruining lots due to contamination from previous lots outweighs the advantage of achieving a better mixture by using a device for breaking down agglomerates. However, tests have been made which indicate that there is a limit to the number of agglomerates that can be tolerated, as measured by streaks visible from a smear test. Using a standard size of spot sample, 95% of the smear tests should show a maximum of one streak in order to be considered "satisfactory." The problem now is to determine whether a particular mixer, which is fine from a cleaning point of view, is good enough to meet the above smear test specifications, even though it was not designed for breaking down agglomerates.

In this case the aim of the statistical test is to objectively decide whether a desired "fraction satisfactory" of spot samples has been obtained after mixing.

If the experimentally determined "fraction satisfactory" is greater than or equal to the desired "fraction satisfactory," then there is no need for the statistical test. If it is less than the desired fraction satisfactory, then the following statistical test can be used to make a decision:

Let p = desired "fraction satisfactory" of spot samples, and ϕ = experimentally determined "fraction satisfactory" of spot samples.

Step 1. Compute $u = \dfrac{p - \phi}{\sqrt{\dfrac{p(1-p)}{n}}}$ (6)

where n = the number of experimental spot samples.

Step 2. Tables of the standard normal curve (H5, pp. 243–245. *Note:* Hoel uses t here for what is called u in Step 1) determine whether this large a value of u would occur due to chance more than one time in twenty. The value of n is not necessary for the use of these tables. The reason for this, very briefly, is that the standard deviation

$$(= \sqrt{p(1-p)/n})$$

used in computing u, is not an estimate but an exact value, based on a "fraction satisfactory" level equal to p.

Step 3. If the value of u is so large, that it would occur by chance less than one time in twenty, conclude that the desired "fraction satisfactory" is significantly greater than that obtained by sampling the mixer.

Step 4. An unsatisfactory mixture may require longer mixing, or it may be that a more intense type of mixing cannot be avoided if the desired agglomerate breakdown is to be achieved.

c. Test of Significance for Streaks per Spot Sample. In this case two mixers are to be compared to see which will give a product with the fewest streaks per spot sample for a particular mixture. The time necessary to reach the best mixture is not a major factor, so that only the "equilibrium" mixtures for the two mixers are to be compared as to the number of streaks per spot sample. There is no stated lower limit for this number, but these two mixers have been found equally desirable from the cleaning standpoint, and whichever gives the lower number of streaks per spot sample will be chosen.

The significance test for this situation is somewhat similar to the one employed in comparing the sample mean with a known mean, except that in this case two sample means are being compared. First their variances must be compared to see whether they are significantly different. Then, depending upon whether or not the variances are significantly different, one of two alternate tests of significance on the means can be performed. These tests are outlined below:

Let $\bar{\alpha}$ and $\bar{\beta}$ be the "equilibrium" values of streaks per spot sample for mixers A and B respectively. (A statistical test given in Section III, C, 4 shows how the equilibrium values can be objectively obtained.) Let $\hat{s}_\alpha^2$ and $\hat{s}_\beta^2$ be the variances for the spot samples used to compute $\bar{\alpha}$ and $\bar{\beta}$, respectively. First perform an **F** test as previously shown to determine whether $\hat{s}_\alpha^2$ and $\hat{s}_\beta^2$ differ significantly. (Note: This test is not identical with that of the previous example, which was designed to find out whether one variance was significantly *larger* than a given variance; in this case the purpose of the test is to ascertain whether two variances *differ* significantly.)

The remainder of the test will depend on whether or not the variances were found to differ significantly.

CASE I—*Variances do not differ significantly*

Step 1. Compute

$$\mathbf{t} = \frac{\bar{\alpha} - \bar{\beta}}{\sqrt{\dfrac{\Sigma(\alpha_i - \bar{\alpha})^2 + \Sigma(\beta_i - \bar{\beta})^2}{n_\alpha + n_\beta - 2}}} \tag{7}$$

Step 2. From **t** tables determine whether this large a value of **t** would occur by chance more than one time in twenty. The number of degrees of freedom ($= n_\alpha - n_\beta - 2$) is necessary in order to use the tables.

Step 3. If the value of t is so large that it would occur by chance less than one time in twenty, conclude that there is a significant difference in smears per spot sample between mixers A and B.

Step 4. Whichever mixer gives the fewer number of smears per spot sample would be better for the job.

CASE II—*Variances differ significantly*

Step 1. Compute $$\nu = \frac{\bar{\alpha} - \bar{\beta}}{\sqrt{\frac{1}{n_\alpha} \hat{s}_\alpha^2 + \frac{1}{n_\beta} \hat{s}_\beta^2}} \qquad (8)$$

Step 2. From special tables (A3), determine whether this large a value of ν would occur by chance more than one time in twenty. The ratio

$$\frac{\hat{s}_\alpha^2/n_\alpha}{\hat{s}_\alpha^2/n_\alpha + \hat{s}_\beta^2/n_\beta}$$

must be calculated in order to use the tables. Because the tables are set up for a one-sided test, what is really being tested here is whether $\bar{\alpha}$ is greater than $\bar{\beta}$, rather than whether $\bar{\alpha}$ is different from $\bar{\beta}$.

Step 3. If the value of ν is so large, that it would occur by chance less than one time in twenty, conclude that $\bar{\alpha}$ is significantly larger than $\bar{\beta}$.

Step 4. Assuming the latter conclusion, mixer B should be chosen since it has been able to produce a mixture with significantly fewer streaks per spot sample than the one produced by mixer A.

4. *Test of Significance for Determining When Equilibrium Is Reached*

In the test of significance for comparing streaks per spot sample between two mixers, the "equilibrium" value was referred to. By this is meant the value which does not change significantly with further mixing. The method described below is an objective way of determining whether or not there still is a trend in the value of streaks per spot sample, after a certain period of mixing.

Let $\alpha_1, \alpha_2, \alpha_3 \ldots \alpha_i \ldots \alpha_n$ represent values of streaks per spot sample determined at times $t_1, t_2, t_3 \ldots t_i \ldots t_n$ after it appears that equilibrium has been reached.

Step 1. Compute $$q^2 = \frac{\sum_{i=1}^{n-1} (\alpha_{i+1} - \alpha_i)^2}{2(n-1)} \qquad (9)$$

Step 2. Compute $\hat{s}_\alpha^2$

Step 3. Compute $$r = \frac{q^2}{\hat{s}_\alpha^2} \qquad (10)$$

Step 4. From r tables (H1, p. 359) determine whether this large a value of r would occur by chance more than one time in twenty.

Step 5. If this large a value of r would occur by chance more than one time in twenty, conclude that there is still a trend, i.e., equilibrium has not been reached. Briefly, the reason for this is that q^2, which is a measure of variation taking into account the order of obtaining α, is significantly different from $\hat{s}_\alpha{}^2$, which is a measure of variation in which the order of obtaining α is not taken into account.

Step 6. If there is still a trend, get another α for t_{n+1}, and repeat the test with α_2 to α_{n+1}. Continue this procedure until equilibrium is reached. (Note: Calculations can be kept to a minimum by leaving room on the computation sheet for several extra points after equilibrium is suspected.)

Step 7. When equilibrium has been reached, the α's finally used in the test, which indicated that there was no longer a trend, should be averaged to give $\bar{\alpha}_e$, which is an estimate of the equilibrium value of smears per spot sample for the mixer. (Note: The example given above involved computing the equilibrium value of smears per spot sample. The test for determining whether equilibrium has been reached for any other measure of mixing, such as the standard deviation, would be similar.)

5. *Confidence Limits*

a. Meaning of Confidence Limits. In the above example for determining the equilibrium value of α, it was stated that $\bar{\alpha}_e$ was an estimate of this value. The term *estimate* was used because there is variation among the α's used in computing $\bar{\alpha}_e$. It might intuitively be felt that it should be possible to state the limits of a range of values within which one can be confident, that the true but unknown value of streaks per spot sample lies. The term "one can be confident" can be expressed quantitatively by a percentage of the time that the given limits will fulfill their function in the long run. These are known as *confidence limits.* Although the above illustration deals with confidence limits for a mean, they can also be computed for a standard deviation or a variance. The statistical term for the true but unknown value, of which the sample value is an estimate, is *population parameter.* Confidence limits for a sample estimate of a population parameter are limits which will include the true but unknown value of the population parameter a certain specified proportion of the time, in the long run. In the examples that follow 95% confidence limits have been used for illustrative purposes. These will include the true but unknown value of the quantity being estimated nineteen times out of twenty, in the long run. As is further mentioned in Section III, C, 7, other % confidence limits could be chosen.

It sometimes helps to graph the confidence limits along with the measure of mixing when plotting the latter versus time. This will give a band, rather than a single line for the rate curve, and is a way of showing graphically how sampling variation places limitations on exact statements such as "at 2 minutes the measure of mixing is exactly 1.20." This will be covered in greater detail when Stange's paper (S4) is discussed in paragraph C, 5d of this section. Methods for computing confidence limits are shown below.

b. Confidence Limits for the Mean. The confidence limits for $\bar{\alpha}_e$ are:

$$\bar{\alpha}_e \pm \mathbf{t}\frac{\hat{s}_\alpha}{\sqrt{n}} \tag{11}$$

where the value of **t** is taken from the same **t** table previously mentioned under Tests of Significance for Means (**t** test). As stated there, the number of degrees of freedom ($= n - 1$) is necessary for the use of the tables. For 95% confidence limits, the value of **t** is chosen from the 0.05 probability column when using a two-tail test table and from the 0.025 column when using a one-tail test table. In this case n is equal to the number of α's used to determine $\bar{\alpha}_e$. In the case where confidence limits are to be obtained for a mean $\bar{x}$, n will be the number of values of x taken at one specific time. The confidence limits will be:

$$\bar{x} \pm \frac{\mathbf{t}\hat{s}_x}{\sqrt{n}} \tag{12}$$

c. Confidence Limits for the Variance. Confidence limits for the variance $\hat{s}^2$, require use of *chi-square* tables. These confidence limits are not symmetrical around the variance; instead the 95% confidence limits would be computed as shown below:

Step 1. Using $n - 1$ as the number of degrees of freedom, look up, in the chi-square (χ^2) tables, that chi-square value which is (1) so small that anything less than it would occur by chance less than 2.5% of the time (χ_1^2), or (2) so large that anything greater than it would occur by chance less than 2.5% of the time (χ_2^2). These would be values for $P = 0.025$ and $P = 0.975$, respectively. The values of chi-square between these two limits would occur by chance 95% of the time. (Note: Since in the chi-square tables the nearest columns to the desired $P = 0.975$ and $P = 0.025$ may be $P = 0.98$ and $P = 0.02$, it may be more convenient to use 96% confidence limits to avoid the necessity for extrapolation.)

Step 2. The upper confidence limit of $\hat{s}^2$ is $\frac{n\hat{s}^2}{\chi_1^2}$.

Step 3. The lower confidence limit of $\hat{s}^2$ is $\frac{n\hat{s}^2}{\chi_2^2}$.

Step 4. If σ^2 is the true but unknown value of the variance which is being estimated by $\hat{s}^2$, then the above discussion concerning its confidence limits can be summarized as:

$$\frac{n\hat{s}^2}{\chi_2^2} < \sigma^2 < \frac{n\hat{s}^2}{\chi_1^2} \tag{13}$$

d. Confidence Limits for the Standard Deviation and Their Use in Planning Proper Sample Size for a Prescribed Confidence Range. i. Confidence Limits. If σ is the true but unknown value of the standard deviation which is being estimated by $\hat{s}$, then it follows from Eq. (13) that the confidence limits of σ are:

$$\sqrt{\frac{n\hat{s}^2}{\chi_2^2}} < \sigma < \sqrt{\frac{n\hat{s}^2}{\chi_1^2}} \tag{14}$$

Ordinarily, chi-square tables would be necessary to determine the confidence limits in a manner analogous to that for the variance. However, a recent paper by Stange (S4) has shown a graphical method for computing 90%, 95%, and 99% confidence limits. Stange plots σ/s on the ordinate and the number of degrees of freedom, $\mathcal{H}$, on the abscissa as shown in Fig. 4. (Note: Although Stange refers to $\mathcal{H}$ as number of samples in his first paper (S4), the manner in which he uses the graph in connection with a discussion of degrees of freedom in his other paper (S5) shows $\mathcal{H}$ to actually be degrees of freedom. [When variance is calculated as in equation (2), degrees of freedom $= n - 1$.]) An upper and lower graph is given for each value of confidence limits. What this amounts to, is plotting $\sqrt{n/\chi_2^2}$ *vs.* $\mathcal{H}$ (lower curve), and $\sqrt{n/\chi_1^2}$ *vs.* $\mathcal{H}$ (upper curve) to graphically express the inequality:

$$\sqrt{\frac{n}{\chi_2^2}} < \frac{\sigma}{\hat{s}} < \sqrt{\frac{n}{\chi_1^2}} \tag{15}$$

which is simply Eq. (14) divided through by $\sqrt{\hat{s}^2}$. In Fig. 4, Stange's graph is shown with different nomenclature, which, it is hoped, will make it clearer and immediately usable to those unable to read the original German article. Stange shows how the confidence limits, obtained from a preliminary experiment with an arbitrary number of spot samples, can be used to plan the number of samples for the next experiment so as to give a prescribed confidence range.

These ideas are illustrated with various examples by Stange. In discussing them, standard deviation will be denoted by s, rather than $\hat{s}$, for consistency with Stange's work. Figure 5 simply shows what a rate plot with upper and lower confidence limits looks like. Figure 4 can supply the factors to enable quick computation of confidence limits needed for such a plot.

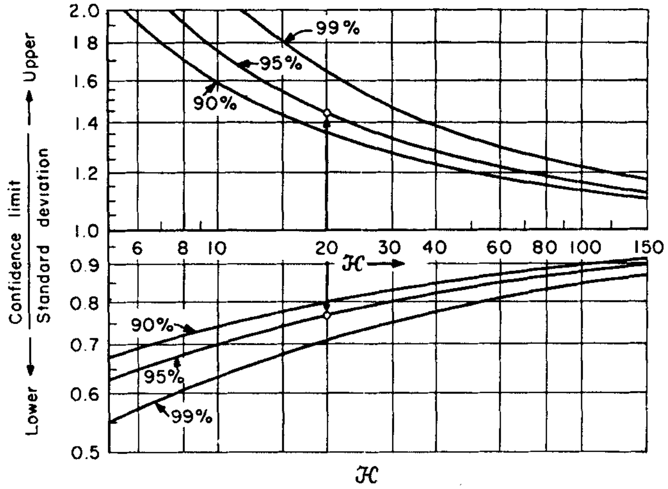


FIG. 4. Confidence limits for the standard deviation as a function of degrees of freedom. This is taken from Stange (S4), with nomenclature changed. The upper graphs are s_u/s *vs.* $\mathcal{H}$ and the lower graphs s_l/s *vs.* $\mathcal{H}$, where s_u is the upper confidence limit, s_l is the lower confidence limit, s is the experimental standard deviation, and $\mathcal{H}$ is the number of degrees of freedom. σ, the true but unknown standard deviation, which is being estimated by s, will fall between s_u and s_l nineteen times out of twenty in the long run, for 95% confidence limits.

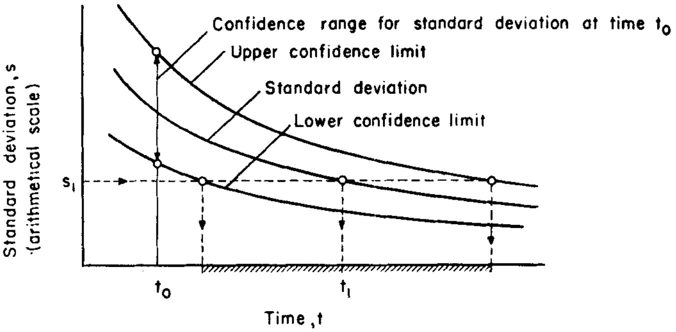


FIG. 5. Illustrative numerical plot of standard deviation *vs.* time with 95% upper and lower confidence limits. From Stange (S4) with different nomenclature. Cross-hatched area indicates Stange's estimate of confidence range for time, t_1, which corresponds to standard deviation s_1.

Figure 6 illustrates a method given by Stange for estimating confidence limits on the mixing time necessary to achieve a certain specified standard deviation. Lowry's data (L4) for the mixing of 80% ammonium nitrate and 20% TNT by weight to form the explosive *Amatol* is used. (Note: Herdan (H2) contains a discussion of Lowry's report.) Figure 6 indicates how Stange obtains lower (3.8 minutes) and upper (6.0 minutes) confidence limits on the time necessary to achieve the desired value of standard deviation, $s = 1.0\%$. (Note: although the confidence limits for s are based on $\mathcal{H} = 6$, and are, respectively, $2.21s$ (upper—off scale on Fig. 4) and $.645s$ (lower), it would seem that $\mathcal{H} = 5$ should have been used, since six spot samples were taken at each time and $\mathcal{H}$ is the number of degrees of freedom.) Although not stated by Stange, the per cent error involved in this graphical method for estimating confidence limits on the time would be worth knowing.

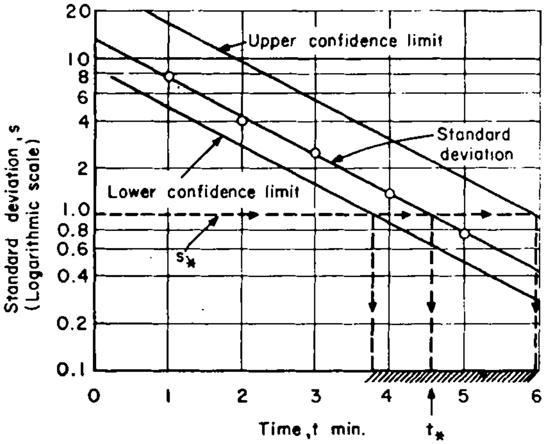


FIG. 6. Logarithmic plot of standard deviation *vs.* time with 95% upper and lower confidence limits. From (S4) with different nomenclature, but data are originally from (L4). Six spot samples taken at each time, t; t_* = time to achieve desired value of standard deviation, s_*. Crosshatched area indicates estimate of confidence range for t_*.

ii. Sample Size for a Prescribed Confidence Range. If a pilot experiment has shown that a certain sample size (= n spot samples) gives a certain mixing curve of s *vs.* time (= t), then it is possible to use this information in planning the next experiment to give a prescribed confidence range for s, by taking the proper number of spot samples. Stange has shown a graphical method for this operation, which is based on the approximative procedure mentioned previously for getting confidence limits for the mixing time. The limitations mentioned there should be borne in mind when using the following procedure:

Step 1. At the desired time in the pilot curve, compute the slope

$$\frac{A - B}{C + D} = |\dot{s}_*| \tag{16}$$

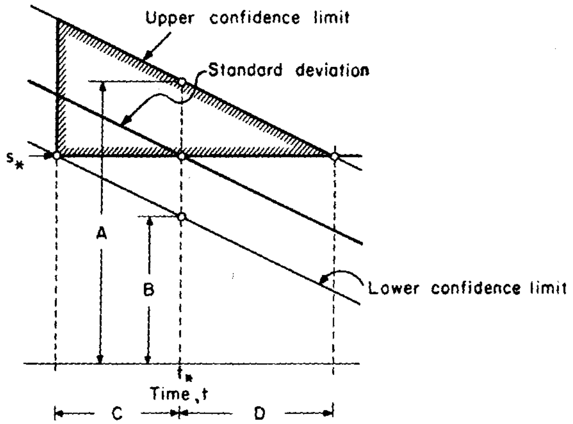


FIG. 7. First part of a graphical method for using a pilot run, in which an arbitrary number of spot samples are taken at each time, to estimate the number of spot samples needed to obtain a confidence interval, the latter being a specified fraction of the desired mixing time, t_*. From Stange (S4) with different nomenclature.

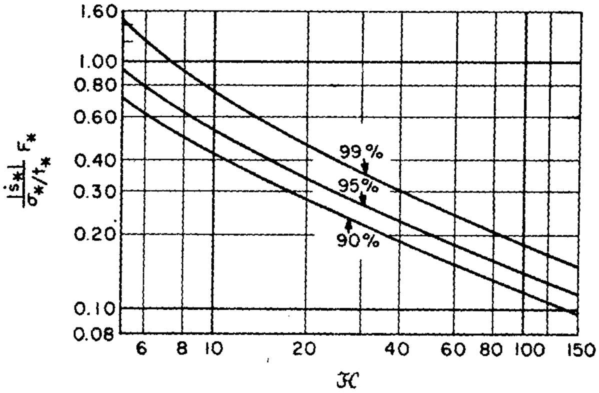


FIG. 8. Second part of graphical method mentioned under Fig. 7 (S4). See Section III, C, 5d.

The nomenclature is shown in Fig. 7. Graphs are assumed to be straight lines in this region.

Step 2. Compute the ratio:

$$\frac{|\dot{s}_*|}{\sigma_*/t_*} F_* \tag{17}$$

where, using Stange's nomenclature (except that time T_*, is changed to t_*),

$F_* = \Delta t_*/t_*$ = desired relative precision of time to achieve desired quality of mixing (95% confidence limits mean $F_* = 0.05$)
σ_* = desired quality of mixing
t_* = mixing time to achieve σ_*

Step 3. From Fig. 8, determine the number of spot samples required. It should be remembered that because of approximations inherent in the above methods this is not a rigorously exact figure.

e. Confidence Limits for Fraction Satisfactory. Confidence limits for "fraction satisfactory" (= ϕ) may also be computed. These are:

$$\phi \pm u\sqrt{\frac{\phi(1-\phi)}{n}} \tag{18}$$

The normal tables mentioned in Section III, C, 3b are also used here to find the value of u for 95% confidence limits. This is equal to 1.96.

6. *The Quality Control Chart*

In addition to the analytical techniques previously described, which permit an objective decision as to whether a solids mixture is satisfactorily mixed, there are other techniques which have long been used in manufacturing processes and are applicable to solids mixing studies. The quality control chart is a well known graphical method for this purpose. Some recent papers on solids mixing which make use of quality control methods are Herdan's discussion of industrial mixing (H2), and the paper of Adams and Baker (A1). Before going into these, some general comments on quality control may serve as an introduction.

The quality control chart for the sample mean is a graph showing a center line which is a grand average mean, and upper and lower lines which are control limits. These control limits can be calculated in a manner similar to that employed to determine confidence limits on the mean. There are tabulated shortcuts available for their computation. These shortcuts involve the use of the range, rather than the standard deviation, and make use of the fact that the standard deviation is a known function of the range under certain conditions. The range is denoted by R—the difference between the highest and lowest values of a spot sample property in a group of spot samples.

Control charts can also be made for the range itself. Since the range is an easily computed measure of variation among a group of spot samples, this kind of control chart would be applicable to mixing work, where it is desired to find out how the variation among spot samples decreases with mixing. A book relating to statistical quality control can be read for further background information (G1). However, for the purposes of illustrating how the techniques can be applied to a solids mixing problem, examples which have appeared in solids mixing literature will be used here without delving into the theoretical background. The American Society for Testing Materials, *Manual on Quality Control of Materials* (A4), goes into considerable detail on the control chart method of analysis and presentation of data.

Herdan (H2), using data from Lowry's report (L4) on the incorporation of *Amatol*, illustrates a method for following mixing via a control chart. He has rearranged the original data so as to get 15 groups of four spot samples each, at each time of mixing. (Note: The statistical term for each group of four spot samples is a "rational subgroup.") For each spot sample, the per cent ammonium nitrate has been determined. Actually, Lowry took six samples at each time of mixing, and these were combined in 15 different ways by Herdan to give 15 groups of four, but this rearrangement is not involved in the idea of a quality control chart; it was made only to obtain numbers with which to illustrate the method.

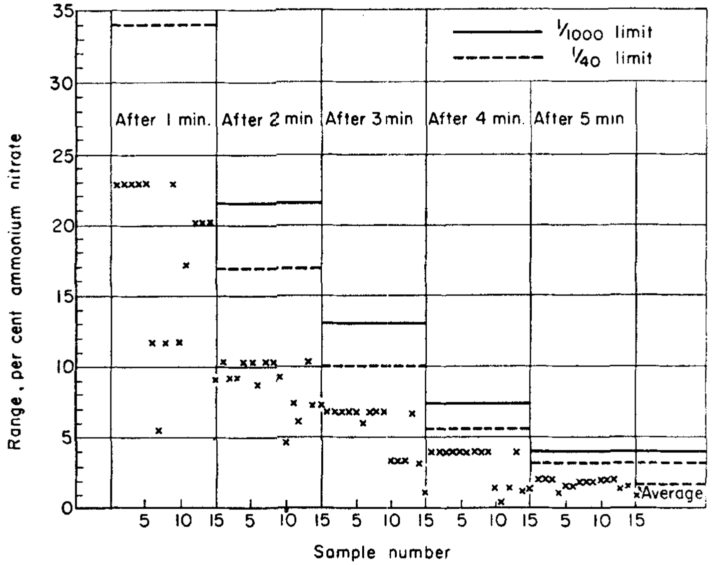


FIG. 9. Quality control chart for range (H2). (Courtesy Elsevier Publishing Co., Amsterdam.)

Mixing is considered complete when the standard deviation among rational subgroups, of size $n = 4$, reaches a certain specified value. Because of the functional relationship between standard deviation and range, an equivalent criterion would require that the range reach a certain value. Since sampling variation is present, instead of a single value of the range, control limits, based on an average of range values for the 15 groups of four, are given. If all the values of range based on groups of four fall within these control limits, then mixing has been completed.

Figure 9 illustrates the use of the quality control chart for the range in connection with the previously mentioned problem on the incorporation of Amatol. The $\frac{1}{1000}$ and $\frac{1}{40}$ control limits are shown, and ranges outside of these limits would occur by chance one time in a thousand and one time in 40, respectively.

As an example of how such control limits may be calculated consider the 15 groups of four spot samples, each taken after 5 minutes of mixing. The average range is denoted by $\bar{w} = 1.64$. Table I, from the Herdan book, gives factors used in the quality control chart technique. Of these d_n, $D_{0.025}$, and $D_{0.001}$ are not directly involved in this example, since they are concerned with cases where control limits for the standard deviation are to be computed. By multiplying the average range ($\bar{w} = 1.64$) by the factors $D'_{0.025}$ and $D'_{0.001}$ the respective upper $\frac{1}{40}$ and $\frac{1}{1000}$ control limits can be obtained. These are 3.17 and 4.22. The lower control limits will be zero in both cases. As can be seen in the column headed "After 5 min.," all of the ranges fall within these limits. Thus, the quality control chart has shown that the present mixture is "in control" within the prescribed limits.

TABLE I

Factors Used in the Quality Control Chart Technique[a]

Numbers in sample (n)	d_n	$D_{0.025}$	$D_{0.001}$	$D'_{0.025}$	$D'_{0.001}$
2	1.128	5.62	8.24	2.81	4.12
3	1.693	5.09	6.99	2.17	2.99
4	2.059	4.99	6.65	1.93	2.57
5	2.326	5.00	6.52	1.81	2.36
6	2.534	5.02	6.47	1.72	2.22
7	2.704	5.06	6.45	1.66	2.12
8	2.847	5.11	6.45	1.62	2.04
9	2.970	5.14	6.46	1.58	1.99
10	3.078	5.19	6.47	1.56	1.94

[a] From Herdan (H2). (Courtesy Elsevier Publishing Co., Amsterdam.)

Adams and Baker (A1) have illustrated how other kinds of quality control charts were used to evaluate dry blending equipment. Since these charts were based on the Poisson distribution, a discussion of them will be postponed until theoretical distributions have been covered.

7. *Remarks on Statistical Techniques*

It should be stressed that the above discussion is merely an introduction to some of the many available statistical techniques. To cover them thoroughly would require considerable additional background material and many more examples. It is hoped, however, that the simple examples given will stimulate both investigation of the possibilities of this field by those interested in solids mixing, and particularly, discussions of its applications between the mixing engineers and statisticians. Some comments concerning cooperative work between the engineer and the statistician appear in a recent article (M3).

The choice of "5%" level of significance or of "95%" confidence limits is an arbitrary one used for illustrative purposes. Although these criteria are frequently employed, other values can also be used and may be more suitable for specific applications. The Discussion of the paper by Adams and Baker (A1) includes some material on this topic.

8. *Choosing a Degree of Mixing*

The many varied approaches in different kinds of mixing studies preclude giving one single measure of mixing which will be ideal for all cases. Weidenbaum and Bonilla (W2) have mentioned several considerations which will affect the degree of mixing.

These include (1) unit size of the end product; (2) whether a little too much of one component in the end product would be undesirable, even if over-all variation between samples were low; (3) whether a random mixture of several solids or a coating of one solid with another is to be achieved; and (4) whether composition gradients within the mixer due to segregation are to be determined. As these authors have indicated, each investigator must ask whether the degree of mixing for a particular case is arbitrary, whether it is truly suitable for the problem at hand, and also whether the most efficient use is being made of the information contained in the spot samples. They further state (p. 31J of reference W2): "When any degree of mixing is used, complete details of sampling procedure should be reported, including size, number, and location of samples, method of their removal, fraction of mixer contents removed, and method of expressing compositions."

Although the above comments may seem obvious, some examples from the literature will indicate the value of emphasizing them. Weidenbaum (W1) has discussed a statement made by Coulson and Maitra (C3)—comparing their method of computing degree of mixing with that used by Hixson and Tenney (H4)—and has pointed out the dangers inherent in comparing degrees of mixing which were meant for entirely different purposes. Coulson and Maitra estimated the per cent mixed by withdrawing approximately thirty samples of about 150 particles each from different positions in the mixing drum, examining the samples with an eye lens, and so determining how many of them had "approximately the same composition as in the whole system." Call this number n. The mixture was then defined as $n/30 \times 100$ per cent mixed. The authors gave no further details on what was meant by "approximately the same composition as in the whole system." Concerning their method of sampling, they stated (M2): "Since the theory relies on a statistical examination of the mixture, 30 samples are insufficient to give adequate accuracy. In general, three tests were carried out under as far as possible identical conditions and in this way the mean of 90 readings could be obtained for the extent of mixing at any time." Coulson and Maitra then stated that their method of expressing degree of mixing is to be preferred "to the mixing index of Hixson and Tenney (H4) where only a small number of comparatively large samples are taken."

Coulson and Maitra's degree of mixing was intended to measure extent of mixing in a batch of solids which were sampled at intervals, starting with the partially mixed loaded state. The Hixson and Tenney mixing index was used to give a measure of the degree of uniformity of a mixture of solids and liquids which were in a state of dynamic equilibrium due to agitation. For the case where liquid is present in excess, their degree of mixing is defined as per cent mixed $= S/S_0 \times 100$, where S and S_0 represent the per cent by weight of a solid in a sample and in the total mixture, respectively. The average of the percentages mixed, of a number of samples taken from the vessel, was considered the measure of the degree of uniformity of mixture.

Further discussion of these two cases indicates the danger of overall comparison of degrees of mixing when such indices are used for different purposes. In Hixson and Tenney's studies, assumptions made as to system symmetry, due to use of a centered, top-entering agitator in a flat-bottomed cylinder, led to taking all of the samples on one side of the agitator shaft. Solids might be expected to concentrate near the bottom when the agitator did not keep them uniformly dispersed. Segregation would occur if the agitator were stopped. The mechanics of taking a sample without too much disturbance of the "suspension regime," and the method of analysis, presented problems peculiar to this type of system. In Coulson and Maitra's work, a sloping, particulate solids mixture in a drum was being studied. System symmetry with respect to mixing patterns of the different components was not obvious nor were the concentration gradients known, should segregation occur. The materials being mixed would not tend to rapidly segregate when the mixer was stopped.

The removal of small samples without too much disturbance of the mixture was possible, via the very useful sampling thief which Coulson and Maitra devised.

The ambiguity of the term "approximately" in Coulson and Maitra's definition was pointed out above. The Hixson and Tenney mixing index uses an average of the per cent mixed, based on samples at definite locations. Thus the value of this measure of mixing will be heavily dependent upon the location of the samples. A very pertinent comment made by Chilton (C1) in the discussion of the Hixson and Tenney paper (H4) states: "In regard to the 'mixing index' used by the author, would not this figure come to 100% if enough samples were taken? Would not a factor which would represent the deviation of the samples from the average be a better measure of the uniformity of the suspension produced by the agitator?"

Another example illustrating the need for clarity is a discrepancy in an illustrative problem given by Brothman *et al.* (B5). After deriving a rate equation theoretically, they illustrated its use by means of a blending problem, which was stated as follows: "Consider a conical tumbler blender in which it is proposed to blend 5 cu. ft. of carbon black with 3 cu. ft. of calcium carbonate. A fair sampling of the contents at the end of ten spins of the mixer device indicates that where one-cubic-inch samples are withdrawn, 0.2 of the samples contain a minimum of 1 mg. of calcium carbonate." Without considering the rest of the problem, reflection on this statement will show, that if originally three-eighths of the mixture (by volume) were calcium carbonate, a fair sampling after ten spins would be expected to reveal that more than 0.2 of the one-cubic-inch samples withdrawn would contain a minimum of 1 mg. of calcium carbonate.

9. *Starting a Quantitative Study*

It is extremely difficult, as has been pointed out previously, to suggest a single ideal criterion for a degree of mixing. However, should someone be groping for a place to start a study of solids mixing involving quantitative measurements on spot samples, either the standard deviation or the variance is suggested for simplicity, efficiency in utilizing data, unambiguousness, and adaptability, if desired, to later mathematical manipulations. The sample mean should also be computed, and information on sampling and analysis should be clearly stated.

D. Literature Summary: Degrees of Mixing

A variety of methods have been used to determine and express the degree of mixing of a solids mixture. These are summarized below together with short resumés of the papers from which they were taken. In order to facilitate reference to the original papers, each method for expressing degree of mixing is given in the original author's own terminology, which is defined when it is introduced. The general format to be followed is: author, description of contents of paper, and method used to determine and express degree of mixing or term for evaluating uniformity of mixture. In cases where the definition of degree of mixing has not been separately published by the original author but is mentioned in someone else's published paper, it will be listed after the latter although the original author will be given.

1. *Oyama*

(Note: Because much of this work is in Japanese, it will be given a more detailed discussion than some of the other papers, which are more easily accessible to those who only read English. Some of the material is taken from the thesis of Weidenbaum (W1) which includes a translation by Chai Sung Lee of Oyama's photometric method for measuring degree of mixing.)

a. In a series of papers dealing with "the motion of granular or pulverous materials in a horizontal rotating cylinder," Oyama covered the following subjects:

1. Relations between rpm of the cylinder and the state of motion of the materials (O1)
2. The types of mixing and the determination of mixing velocity (O2)
3. The effect of the cylinder diameter on the state of the motion of materials (O3)
4. The effect of a flight [baffle] on the state of the motion of materials (O4)
5. Packing and mixing of binary system (O5)—(Note: previous work had been done with particles of uniform size and shape.)
6. Theoretical study of motion of granular materials (O6)
7. Study of power consumption (O7)

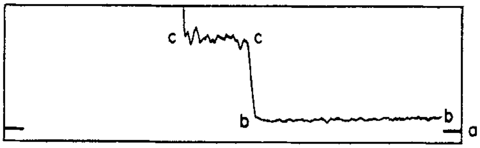
A paper entitled "Studies on Mixing of Solids: Mixing [in a] . . . Binary System of Two [Particle] Sizes by Ball Mill Motion" (O8) is available in English and covers some material from (5) above as well as fragments from some of the other works.

b. For Mixing Particles of Uniform Size and Shape but Differently Colored. In work with particles of uniform size and shape, Oyama used photographic methods to determine what he called the mixing grade or "mixing effect." In his procedure, light was passed through a film obtained by photographing the end of the cylinder as mixing proceeded (O2). The light went through a properly sized slit to a photoelectric bulb which generated a current. This current actuated the fiber of a fiber-potentiometer and the motion of the fiber was recorded on a moving-picture camera. Thus it was possible to record a curve which was related, as explained above, to the changes in what Oyama called the "photographic density," as mixing proceeded. A formula is given for the intensity of light (i) received by the film from a group of particles:

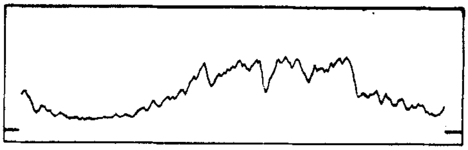
$$i = \frac{1}{t}\left(\frac{o}{o'}\right)^{\frac{1}{\gamma}} \tag{19}$$

where t = time of exposure
o = degree of obscureness (or absorbity)
o' = degree of obscureness (or absorbity) of the original fog on the negative
γ = a constant depending on the film and developing conditions (given as 1.53 by Oyama).

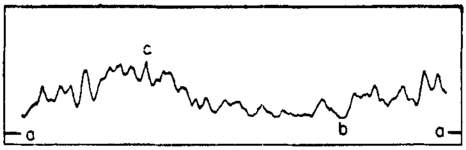
Thus, i can be measured and, as will be shown, is used to obtain a number which, in turn, can be utilized in an expression for the degree of mixing. The graph of i *vs.* different portions of the negative (gotten by photographing the cylinder end) has two main parts before mixing: one due to the black particles which have been loaded on the bottom, and one due to the white layer on top; a sharp jump occurs in the graph as the light passes through the borderline between the two layers. This is



Start of mixing



3.8 revolutions



4.9 revolutions

FIG. 10. Tracings of photographs from Oyamo (O2), showing change in pattern of

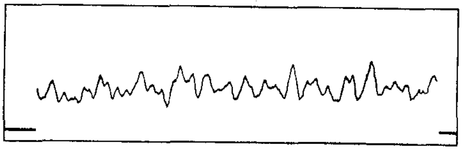
shown in Fig. 10. As mixing proceeds, the difference between the two extremes will become smaller while the frequency of small peaks and depressions will increase (Fig. 10). Note that in the picture corresponding to 4.9 revolutions, the difference between *b* and *c* is less than that for the initial state. Also, the large number of small peaks and valleys as compared to the initial state indicates that alternate layers of the differently colored particles are beginning to form.

Oyama defined his degree of mixing as follows:

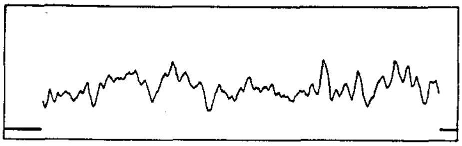
$$\text{Degree of mixing} = 1 - \frac{i_{\text{max.},c}}{i_{\text{max.},c_0}} \tag{20}$$

where $i_{\text{max.},c}$ = light intensity, *i*, corresponding to maximum concentration difference, and $i_{\text{max.},c_0}$ = light intensity, *i*, corresponding to maximum concentration difference at the start.

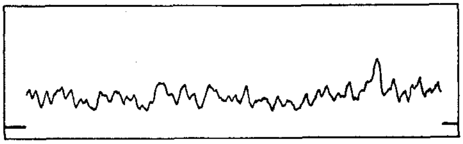
Figures 11 and 12 show graphs of *i vs.* number of revolutions for two different speeds (16-rpm and 80-rpm). In each case, the upper graph is for *c*, the lower one for *b*, and the one in the middle represents $c - b$. This difference, divided by the initial difference (at 0 revolutions) and subtracted from 1, was Oyama's degree of mixing. Realizing that the frequency of peaks and valleys was also of importance in indicating the extent of mixing, Oyama stated that if the maximum concentration difference were the same, a greater frequency would indicate better mixing. He interpreted the change in frequency as indicative of positional



7.1 revolutions



10.1 revolutions



11.6 revolutions

variation of light intensity *i*, across the cylinder end-face, as mixing progresses.

changes of particles throughout the mix, and called this the "uniform" or "total" mixing effect. The changes in maximum concentration difference can be attributed mainly to the slip, or friction among particles at localized positions, and this effect, referred to as "local" mixing, could be related to intensity. His degree of mixing is a measure of the latter type of mixing.

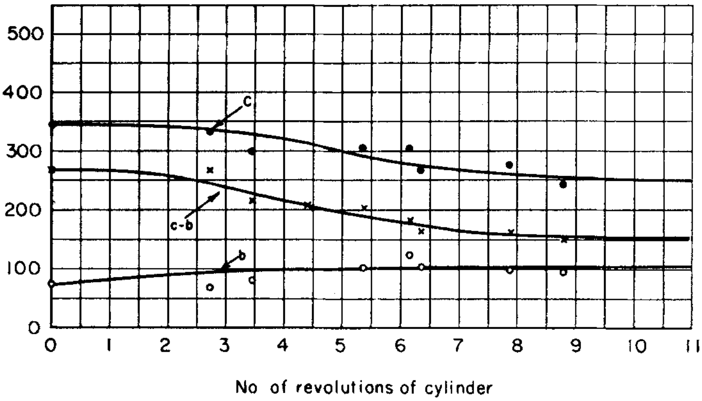


FIG. 11. Light intensity *i*, *vs.* number of revolutions. In Section III, D, 1b the procedure is described for using this graph to compute degree of mixing (O2). Cylinder speed = 16 rpm.

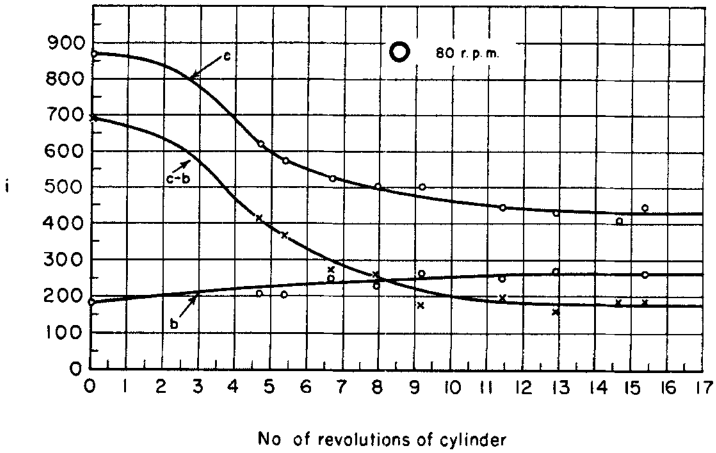


FIG. 12. Light intensity *i*, *vs.* number of revolutions. Cylinder speed = 80 rpm (O2).

c. For Mixing Particles of Two Different Sizes. Drawing on the background of packing studies provided by Furnas (F2, F3), Westman and

Hugill (W3, W4), and Kasai (K1), Oyama (O8) used the specific volume of the mixture in a term for degree of mixing for mixtures of two different particle sizes. His method involved a comparison of the specific volume of the mixed batch, with that obtained when the two materials were packed as closely as "practically attainable." The graph of specific volume *vs.* per cent composition by weight was computed for the latter case from experimentally determined data of Westman and Hugill, who

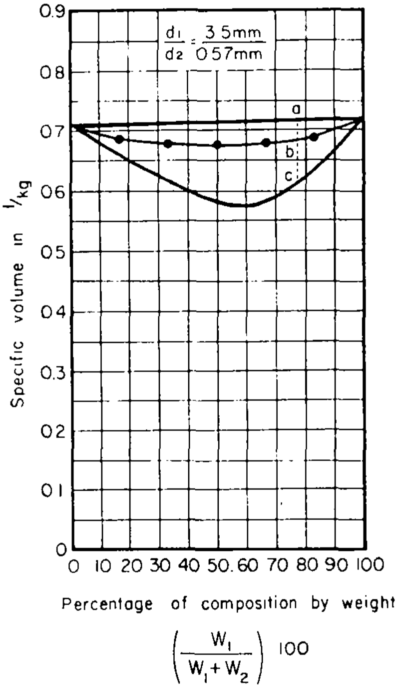


FIG. 13. Specific volume *vs.* per cent composition by weight. Used by Oyama (O5, O8) to compute per cent of mixing for a mixture of two different size particles.

used a specially designed machine to determine the minimum volume attainable in a mixture of particles of different sizes. Details of the calculation methods are given in Oyama's paper (O8) (in English). The graph of specific volume *vs.* per cent of composition by weight was also determined after mixing various weight ratios of the two materials in the cylinder. (Note: Although this is not stated in the paper, it is presumed that the figures are given for the batch after a long period of mixing, since only one figure is given for each weight per cent of W_1.) A third graph of specific volume *vs.* weight per cent, W_1, was drawn to correspond with the case where the two components were introduced separately into the cylinder without mixing; the total specific volume here would be the sum of the specific volumes of the two granular materials (i.e., apparent volumes).

These graphs are shown in Fig. 13. The per cent mixing for any weight ratio $W_1/(W_1 + W_2)$ was found as follows: (1) Determine the difference ($= ac$) between "non-mixed" specific volume and "closest packed" specific volume; (2) Determine the difference ($= ab$) between "non-mixed" specific volume and "mixed" specific volume; (3) Per cent mixed or "grade of mixing" $= ab/ac \times 100$.

2. *Beaudry* (B3)

The author presents a means for determining how well a continuous blender is operating, as compared to how well it is capable of operating. This takes into account the type of blending cycle used, the ratio of blender volume to batch volume, and for certain cycles, the ratio of inflow rate to outflow rate.

$$\textit{Blending Efficiency}\ (\text{B.E.}) = \frac{[(V_b/V_p)_{\text{actual}} - 1]}{\gamma - 1} \times 100 \tag{21}$$

where for $(V_b/V_p)_{\text{actual}}$:

V_b = variance among batches before blending

V_p = variance among batches actually obtained after blending.

Variance is defined as $\dfrac{\Sigma(c_i - c_{\text{av.}})^2}{N}$

where

$c_{\text{av.}}$ = the average value of property A

c_i = the value of property A for the i-th batch

N = the number of batches sampled

γ = limiting blending ratio $= V_b/V_p$, where V_p in this case is the variance with perfect blending, which is computed theoretically taking into account the factors mentioned above.

3. *Lacey* (L1)

Early fundamental work on the degree of mixing was performed by this author, and involved very laborious counting of all particles (0.2 in. diam.) in the mixture. Experimental work was carried out.

$$M = \sqrt{\frac{\bar{\alpha}\bar{\beta}}{n}} \tag{22}$$

where $\bar{\alpha}$ = fraction of A particles in a mixture of A and B

$\bar{\beta}$ = fraction of B particles in a mixture of A and B

n = number of particles in a cell (mixture completely divided into cells).

Plot M *vs.* $1/\sqrt{n}$: "Very probably a family of curves of characteristic shape would be obtained for each combination of mixing machine and materials" (L1).

4. *Buslik* (B10)

This paper deals with the derivation and application of a formula for computing standard deviation (σ_g) of the per cent of a given size in random samples from a granular material with a known size distribution:

$$\sigma_g{}^2 = \frac{G(100 - G)\bar{w}_g + G^2(\bar{w} - \bar{w}_g)}{W} \tag{23}$$

where $\bar{w}_g$ = average particle weight in the size fraction being considered. A range of sizes is actually included, but this size fraction is called the w_g size. (Constant density is assumed.) Methods for computing $\bar{w}_g$ to various degrees of precision are given by Buslik.

G = per cent by weight of the mixture of particles of size w_g

W = total sample weight

$\bar{W}$ = average weight of all the particles of all sizes in the entire mixture. Calculated from

$$\bar{W} = \tfrac{1}{100}(AW_a + BW_b + \cdots + GW_g + \cdots)$$

where A, B, C, . . . are the percentages by weight of the sizes w_a, w_b, w_c, . . . in the mixture.

5. *Bonilla and Crownover, and Bonilla and Goldsmith*

Results from these unpublished theses were mentioned by Weidenbaum and Bonilla (W2).

Reports of tests on a batch mixer with horizontal screw-shaped blades of opposite pitch, moving material in a trough with an approximately semi-cylindrical bottom. Graphs of $-\log M$ *vs.* $\log r$ made under different operating and loading conditions (r = number of revolutions of the mixer):

$$M = -\log\frac{a.d.}{2c(1 - c)} \tag{24}$$

where $a.d. = \dfrac{\sum_{i=1}^{N} |c_i - \bar{c}|}{N}$, which equals the mean deviation of the weight fractions of the "key constituent." (About five 5-gm. samples were taken.)

c_i = weight fraction of key constituent in the i-th spot sample

$\bar{c}$ = arithmetical mean value of c for the N spot samples

N = number of spot samples

c = weight fraction of the key constituent in the entire batch.

6. *Brothman, Wollan, and Feldman* (B5)

These workers are mainly concerned with developing a theoretical rate equation for mixing, and interpreting this equation. No experimental data are given.

P_t = proportion of v units of volume which contain some specified minimum amount of component A, where the desired goal is to effect a permeation of x units of A in a system of volume V. (Thus $v = V/x$.) The authors' rate equation is adjusted to take into account the effect of taking samples of a different size than v (say size V_0). The proportion of the total number of cubes into which the mixture has been divided, containing at least one element of the surface of separation, is used in developing the rate equation; but the above definition, in terms of the specified minimum amount of one component, is necessary for practical use of the equation experimentally.

7. *Coulson and Maitra* (C3, M2)

Experiments were performed with an inclined rotating drum to determine the effect of several equipment and material variables on rates of mixing and segregation tendencies. Also a rate equation was postulated and tested with the experimental data.

X, the percentage unmixed, was used in the rate plots. It was experimentally determined as follows: 30 samples were withdrawn from different positions in the drum and examined with an eye lens. If n samples were found to have "approximately the same composition" as the overall mixture, then the per cent mixed was defined as $n/30 \times 100$, and $X = (100 - \text{per cent mixed})$.

8. *Visman and Van Krevelen* (V1)

The authors replotted Coulson and Maitra's data on probability paper. They preferred this method of plotting to that given by Coulson and Maitra.

$100 - Z$ = percentage unmixed; it is experimentally determined as follows: A number of samples are removed. If a sample does not show any visually observable mixing when examined with a magnifying glass, it is considered unmixed. The number of these unmixed samples divided by the total number of samples and multiplied by 100, is $100 - Z$.

" . . . samples which show visible mixing are defined as samples with more than 10% and less than 90% coal or salt. The samples which do not show visually observable mixing are thought to contain less than 10% coal or salt."

9. *Stange* (S5)

A formula is presented for calculating the theoretical variance of samples taken from a randomly mixed batch of two materials (P and Q), each of which has its own size distribution:

$$\sigma_x{}^2 = \frac{PQ}{g}\,[P\bar{\nu}_Q(1 + C_Q{}^2) + Q\bar{\nu}_P(1 + C_P{}^2)] \qquad (25)$$

where P and Q are fractions by weight of the mixture components. $\bar{\nu}_P$ and $\bar{\nu}_Q$ are average particle weights for P and Q. These are measures of the *degree* of fineness of the particles. C_P and C_Q are variation coefficients for P and Q, referring to the frequency distribution of particle weights for these substances. (Note: variation coefficient equals standard deviation divided by the mean.) These are measures of the *uniformity* of fineness of the particles. g is the sample weight.

10. *Stange* (S4)

Graphical methods are presented for computing confidence limits for standard deviations that are used in plotting rate-of-mixing curves. The author gives an example of the method's use in comparing graphs of throughput *vs.* power consumption for different mixers. He also shows how to graphically compute sample size for a prescribed confidence range. (See Section III, C, 5d.)

11. *Danckwerts* (D2, D3)

In one paper (D2), Danckwerts discusses methods of measuring "goodness of mixing" which will be described. In another (D3), he gives a more general discussion on the scale of scrutiny of mixtures, and also discusses other mixing topics, which include minimum work required for mixing, scaling up from models, mechanisms of mixing, and back-mixing in continuous flow systems. His papers cover other systems besides solid-solid mixtures.

Danckwerts expresses the "goodness of mixing" by two statistically defined quantities, the *scale* and the *intensity of segregation*. He states that his treatment is suitable chiefly for mixtures where the smallest particles capable of independent movement are very small compared to the size of the portions which will normally be taken for use or analysis. For his analysis, he assumes that the mixture is uniform in texture; that is, it cannot be divided into two parts of equal size in which the mean concentration or the scale or intensity of segregation differ significantly. He further states: "This is the most important limitation on the practical value of the definitions and tests which will be proposed." He emphasizes the fact that "large scale segregation, caused for example by sedimentation, or dead space in a mixer, is of great practical importance but its study cannot conveniently be combined with that of the small-scale characteristics, or texture, . . . "

He considers that mixing occurs by two independent processes which produce distinguishable results: (1) the breaking-up process which reduces sizes of clumps and (2) the "interdiffusion" process which obliterates differences of concentration between neighboring regions of the mixture. He therefore postulates two quantities for describing the degree of mixing—namely the "scale of segregation" and the "intensity of segregation," both of which he defines by statistical methods. (Note: He generalizes these methods for mutually soluble liquids, *fine powders*, or gases.)

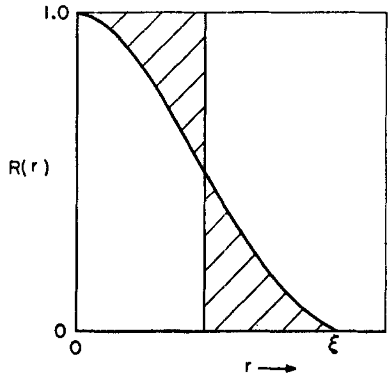


FIG. 14. Illustrative graph of correlogram (D2). Shaded areas are equal.

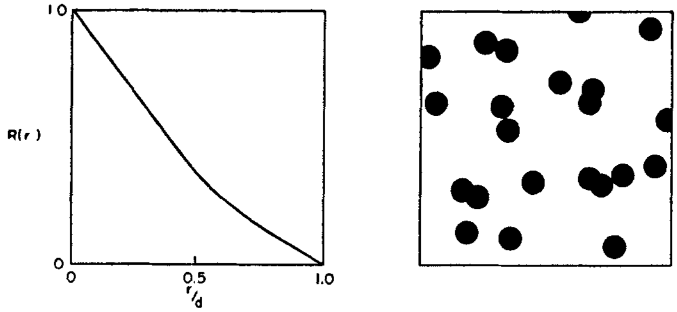


FIG. 15. Correlogram. Diameter of circles is d; $S/d = 0.42$. An analogous random collection of spheres of diameter, d, will give $S/d = 0.38$ (D2).

a. Scale of Segregation. Danckwerts considers the scale of segregation as analogous to the "scale of turbulence" used in the statistical theory of turbulence. He defines it as:

$$R(r) = \frac{\overline{(a_1 - \bar{a})(a_2 - \bar{a})}}{\overline{(a - \bar{a})^2}} = \frac{\overline{(b_1 - \bar{b})(b_2 - \bar{b})}}{\overline{(b - \bar{b})^2}} \tag{26}$$

where a_1 and a_2 (and b_1 and b_2) are concentrations measured at two points in the mixture a distance r apart, and $\bar{a}$ and $\bar{b}$ are the mean concentrations of a and b in the mixture as a whole. $R(r)$ is called the coefficient of correlation between the values of a (or b) at points separated by a distance r.

He then interprets the graph of $R(r)$ *vs.* r, known as a *correlogram*, pointing out how, as r increases, the correlation coefficient $R(r)$ will drop towards zero if there is no large scale segregation or regular periodicity in the mixture. Figure 14 illustrates a "correlogram," and correlograms for certain cases are shown in Figs. 15 and 16. Note that in the case of the circles (Fig. 15), when the distance between points r, is equal to the diameter of the circle d, i.e., $r/d = 1$, the correlation coefficient has dropped to zero. In the case of the elongated strips (Fig. 16), when the distance between points, r, is about two to three times the width of the strip, the correlation coefficient drops sharply to less than 0.1; when r is equal to the length of the strip, it drops to zero.

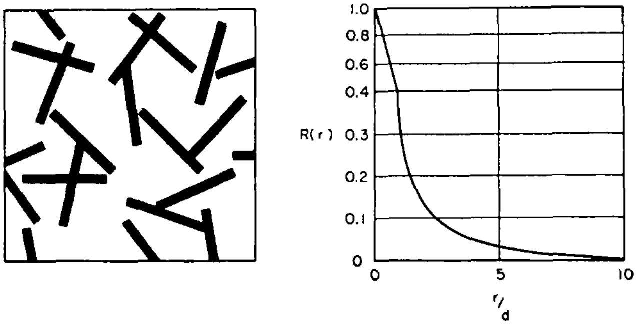


FIG. 16. Correlogram. Width of strips is d, length of strips is $10d$; $S/d = 1.1$ (D2).

Danckwerts mentions two measures of scale of segregation, (1) the *linear scale*, S, defined as the area under the correlogram:

$$S = \int_0^\infty R(r)dr = \int_0^\xi R(r)dr \tag{27}$$

where ξ = value of r for which $R(r)$ falls to zero; and (2) the volume scale, V, defined as 2π times the area under the curve of $r^2R(r)$ *vs.* r:

$$V = 2\pi \int_0^\infty r^2R(r)dr = 2\pi \int_0^\xi r^2R(r)dr \tag{28}$$

The relationship between S and V depends on the shape of the clumps and hence of the correlogram. For a random collection of spheres of diameter, d, analogous to Fig. 15, the V/S ratio is 4.7. In order to use the above theoretical relationships it is necessary to measure the scale of segregation. Danckwerts gives several ways of doing this and the computational methods for each. These involve (1) measuring concentration at a large number of points, (2) in batch-mixing, measuring the concentrations at two fixed points continuously while the mixture moves past them, (3) measuring the total content of one of the components along a straight line joining two points, (4) determining V by analyzing a number of samples of volume v taken from the mixture, and (5) other methods adaptable to continuously measuring S, as a fluid mixture flows through a pipe.

A familiar experimental technique used in solids mixing is method 4, which involves analysis of a number of samples of size v. Danckwerts computes the volume scale of segregation V, from this analysis as follows:

$$V = \frac{\sigma_K^2}{2v\sigma_a^2} \tag{29}$$

where σ_K^2 is the variance among the spot sample measurements (the content of A in each sample of size v is denoted by K). σ_a^2 is the variance of point concentrations of component A from the over-all mean concentration $\bar{a}$. This requires determination of point concentrations by special techniques, of which Danckwerts discusses a few (electrical, optical, following the progress of a chemical reaction). Although the ideas are very interesting, their adaptation to a dry solids mixing process would require considerable investigation of practical means of measuring point concentrations in a solids mixture. Of particular importance in solids mixing, the measuring techniques must not so disturb the mixing patterns, that a picture is obtained which is not truly representative of the mixer in normal operation without the interference of measuring instruments.

b. Intensity of Segregation. This is defined as:

$$I = \frac{\sigma_a^2}{\bar{a} \cdot \bar{b}} \equiv \frac{\sigma_b^2}{\bar{a} \cdot \bar{b}} \equiv \frac{\sigma_a^2}{\bar{a}(1 - \bar{a})} \equiv \frac{\sigma_b^2}{\bar{b}(1 - \bar{b})} \tag{30}$$

where σ_a^2 is, as previously mentioned, the point to point variance in concentration of a.

Although Danckwerts presents I "*in toto,*" it is actually a ratio of variances.

σ_a^2 is the variance mentioned above and $\bar{a} \cdot \bar{b}$ is the variance of the unmixed materials. ($\bar{a}$ and $\bar{b}$ are respectively the mean concentrations of a and b in the mixture as a whole.) Danckwerts states: "In general, I reflects not the relative amounts of A and B, nor the size of the clumps, but the extent to which the concentration in the clumps departs from the mean. If B is present in large excess, the value of I will depend primarily on the extent to which the clumps of A in the mixture have become diluted by B." The methods for measuring σ_a^2 have been discussed previously. In addition, Danckwerts gives an alternate method involving measurement of the chemical reaction rate which might be useful under certain conditions of mixing liquids A and B.

12. *Herdan* (H2)

In his chapter on "Industrial Mixing" in *Small Particle Statistics* (H2), Herdan covers ways of measuring degree of mixing, including the quality control chart. He also gives a discussion and explanation of the paper by Brothman, Wollan, and Feldman (B5).

Methods for using quality control charts, for both standard deviation and range, are discussed and illustrated with reworked data from Lowry's report (L4). This is discussed in Section III, C, 6. Numbers 13 and 14 are also mentioned in Herdan (H2) but no reference is given.

13. *Lexis*

Herdan states that the ratio given "was first introduced by Lexis for the purpose of ascertaining whether a universe from which samples had been taken was homogeneous, or whether the probability of the event in question differed significantly from place to place, or from time to time." (H2)

$Q = R/r$, where R = observed standard deviation, and r = theoretical standard deviation, calculated under the assumption of complete randomness.

14. *Charlier*

Herdan states that ρ^2 "was designed for the same purpose as Lexis' Q, viz., as a measure of heterogeneity in a denumerable population."

$$\rho^2 = \frac{S_t^2 - \sigma^2}{M^2} \tag{31}$$

where S_t^2 = observed variance at time t
σ^2 = theoretical variance for a random mix
M^2 = mean number or mean proportion of the component in question
ρ^2 = coefficient of perturbation or disturbance.

15. *Kramers*

The work of this author was not published separately but mentioned by Lacey (L2). (See 16 below.)

Here
$$M = \frac{s_0 - s}{s_0 - s_r} \tag{32}$$

where s_0 = theoretical value of s for unmixed material = $\sqrt{P(1 - P)}$. [Note: Lacey (L2), p. 259, gives $P(1 - P)$, but there should be a square root sign, as shown.]

s = standard deviation among samples of size n

s_r = theoretical standard deviation for the completely random mixture $\equiv \sqrt{P(1 - P)/n}$, where n = number of particles per spot sample.

16. *Lacey* (L2)

This author discusses several papers on various aspects of solids mixing, aiming to coordinate existing ideas, develop the theoretical aspects, and show their relationship to the few systematic practical investigations that have been considered.

He uses variance instead of standard deviation in Kramers' type of degree of mixing (see 15). This gives:

$$M = \frac{s_0^2 - s^2}{s_0^2 - s_r^2} \tag{33}$$

which Lacey states " . . . is more satisfactory statistically, since s^2, unlike s, has additive properties." He has further developed the expression to:

$$1 - M = \frac{s^2 - s_r^2}{s_0^2 - s_r^2} \tag{34}$$

which he called " . . . a fundamental equation for expressing the state of a mixture."

17. *Oyama and Ayaki* (O9)

Using a horizontal rotating cylinder and several different sand-sand systems, Oyama and Ayaki studied rate equations for mixing and the effect of rotational speed and the volume ratio of sand to mixer. Different methods of loading were also tried.

Variance of the spot sample compositions, denoted by σ^2, was called the degree of mixing of the whole mixture. Like Lacey (L2), Oyama and Ayaki considered this to be composed of two parts, σ_m^2 and σ_r^2. σ_m^2 is the variance due to local composition variations which would be independent of sample size, and σ_r^2 is the variance due to sample size.

When σ^2 is used in a rate equation and integrated to give

$$\ln (1 - M) = -\phi t$$

M is the same mixing index defined by Lacey. ϕ is the coefficient of mixing velocity.

18. *Weidenbaum and Bonilla* (W2)

A fundamental study of solids mixing is given, with experimental data for a rotating horizontal cylinder containing salt and sand. Theoretical random equilibrium mixture, chi-square test, and sampling considerations are discussed. Also rate equations and segregating effects are covered.

$$\text{The degree of mixing} = \frac{\sigma}{s} \tag{35}$$

where $\sigma = \sqrt{p(1 - p)/n}$, and p is the true particle fraction of sand in the mixture, or the mean of the binomial distribution

$$s = \sqrt{\frac{\sum_{i=1}^{N}\left[\left(\frac{x}{n}\right)_i - \left(\frac{\bar{x}}{n}\right)\right]^2}{N}}$$

$(x/n)_i$ = particle fraction of sand in the i-th spot sample
$(\bar{x}/n)$ = arithmetical mean particle fraction of sand for the N spot samples
n = total number of particles in a spot sample
N = number of spot samples taken from the mixture at any spot sampling.

Graphs of s *vs.* number of revolutions are plotted. Also, the use of the usual *chi-square* test is illustrated for comparing distributions to determine whether a batch is randomly mixed. In addition, a table is given for classifying mixtures according to the relative frequency of occurrence of chi-square values.

19. *Blumberg and Maritz* (B4)

Theoretical concepts of complete and incomplete mixing are discussed from a statistical point of view. Experimental data are given for mixing two differently colored, but otherwise identical batches of sand. Topics that are covered include the *chi-square* test and the number of samples needed to indicate completion of mixing.

For testing whether a batch is *completely mixed*, the usual *chi-square* test is used. However, for measuring the degree of mixing of an *incompletely mixed* batch, the following term was used:

$$\phi = \nu \sum_{i=1}^{k} (z_i - \zeta_0)^2 \tag{36}$$

where ν = the average number of particles per spot sample
z_i = 2 arc sin $\sqrt{x_i}$
x_i = r/n which equals the fraction of red particles in a spot sample of n particles
ζ_0 = 2 arc sin $\sqrt{0.5}$, because the fraction of red particles in the entire mixture is 0.5.

Since ϕ is also a chi-square variable, the probability that a value as large as the computed value of ϕ would occur due to chance can be looked up in chi-square tables. If this is less than the level that has been set (say one time in twenty), then mixing is considered to be incomplete. If it turns out, however, that this large a value of ϕ would occur by chance more than one time in twenty, conclude that mixing is complete, i.e., a randomly mixed batch has been obtained.

20. *Michaels and Puzinauskas* (M4)

This paper describes a study of the mixing of powdered dextrose with water-wet kaolinite in a small finger-prong mixer. The rate of homogenization, and the energy consumption during mixing are determined for clay-water systems of varying water content and total volume, other conditions being held constant. Optimum mixture volumes are given for rapidity of mixing and energy utilization.

$$I_v = \frac{D_v}{D_{v_0}} \sqrt{\frac{\sum_0^n (C_A - C_A^m)^2}{n(1 - C_A^m)(C_A^m)}} \tag{37}$$

where I_v = Uniformity Index
$D_v = \sqrt{\dfrac{\sum_0^n (C_A - C_A^m)^2}{n(C_A^m)^2}}$
D_{v_0} = value of D_v at no mixing, which can be shown to equal $\sqrt{1 - C_A^m/C_A^m}$
C_A = concentration of A in a random sample of volume v
n = the number of samples
C_A^m = the mean concentration of A in the mixture.

(Note: In their work, Michaels and Puzinauskas use $n = 6$ and $v = 1$ cc.)

21. *Adams and Baker* (A1)

Graphical and other methods are given for evaluating dry-blending equipment, by making use of accepted statistical laws. The authors discuss the effect of changes in the relative proportions of the two ingredients on variations in composition of the final mixture. Also presented, are experimental data comparing four types of blenders.

Three types of tests are discussed. The first two tests require graphs of the number of blacks *vs.* the sequence number of samples (the mixture consists of black and natural polythene colored particles). One test looks for the number of samples outside of certain control limits or confidence lines; and the other looks for the number of consecutive samples on one side of the mean. The third test requires computing $b = s^2/\bar{x}$, where $s^2 = \dfrac{\Sigma(x - \bar{x})^2}{N - 1}$; x is the number of black granules in a sample, and N is the number of samples. From a graph, the probability of obtaining this large a value of b from a Poisson distribution is obtained. This probability is used as a measure of blending in a manner analogous to that of a statistical test of significance.

22. *Smith* (S3)

Quantitative data are shown in this paper to emphasize the necessity for good mixing in treatment of soils with additives. The mixing machines, necessary to achieve this aim are also discussed.

$$R = \frac{\sigma_0}{\sigma} = \left[\frac{n\mu_a(1 - \mu_a)}{\sum_{i=1}^{n} (x_i - \mu_a)^2}\right]^{0.5} \tag{38}$$

where n = number of spot samples taken from a mix containing a mean fraction of additive μ_a

x_i = indicated content of any sample

σ_0 = theoretical standard deviation at "zero" mixing = $\sqrt{\mu_a(1 - \mu_a)}$

σ = actual standard deviation at any time = $\sqrt{\dfrac{\sum_{i=1}^{n} (x_i - \mu_a)^2}{n}}$.

23. *Gray* (G2)

The results of tests on the mixing performance of some of the common types of dry-solids mixing equipment are described by this author. A specially constructed reflectivity probe, with a light and photocell behind a glass window, is used. The intensity of light reflected from a layer of particles outside the glass window of the probe gives, via the photocell meter, an indication of the composition at the point in front of the glass window, since light and dark particles are mixed. The standard deviation s, of probe meter readings taken at several spots in the mixture, is used as a measure of the uniformity of composition.

Bullock (B8) later pointed out that the reflectivity probe is limited in its usefulness because it can not sufficiently well differentiate between mixes containing uniformly dispersed small agglomerates, and mixes in which these agglomerates have been broken down into ultimate particles.

24. *Yano, Kanise and Tanaka* (Y2)

These investigators studied the mixing of anhydrous sodium carbonate and polyvinyl chloride powders, of −100/+200 Tyler mesh, in two V-type mixers of ¼-liter and 2-liter working capacity, respectively. The variables include rpm of the mixer, volume per cent loaded, volume ratios of the feed, and method of loading.

The degree of mixing used by Yano *et al.* is the standard deviation, defined as follows:

$$\sigma = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(C_i - C_0)^2} \tag{39}$$

where C_i is the volume fraction of Na_2CO_3 in the i-th spot sample, and C_0 is the known volume fraction of Na_2CO_3 in the over-all mixture.

25. *Sakaino* (S1)[2]

An expression is developed for computing the mean size z, of randomly dispersed agglomerates, from the variance S^2, obtained with a certain sample size, R. The author postulates a rate equation for solids mixing, which he feels may also be applicable to the homogenizing process in glass melting.

The degree of mixing is defined as μ,

where

$$\mu = \frac{1}{z} = \frac{pq}{S^2R} \tag{39a}$$

p is the particle fraction of one type of particle in the mixture, and q is $1 - p$. S^2 and R are defined above.

E. Summary and Conclusions—State of Mixedness of a Batch of Solids

1. The day to day control of industrial mixing operations to obtain a desired product, with properties or composition within specified limits, is a frequently occurring problem. A variety of statistical techniques are

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[2] Prof. Sakaino kindly furnished a more detailed summary than was available in the English Abstract of (S1).

available for quantitatively determining the adequacy of the mixing operation. Included among these are: statistical tests of significance, confidence limits, and quality control charts. These can be adapted to both quantitative and qualitative measurements on spot samples.

2. There can be considerable variations from one process to the next in the required scale of uniformity. Choice of a suitable standard for a degree of mixing should take this into account.

3. To avoid ambiguity, complete details of sampling procedure should be available when spot samples are removed to measure a degree of mixing.

4. The most intelligent use of statistical techniques is made by combining them with a sound knowledge of the mixing operation and the purpose of its end use.

5. A variety of methods from the literature, for determining and expressing the degree of mixedness of a batch of solids, have been summarized. These vary from photometric methods, involving the use of a motion picture camera, to methods involving comparisons of sampling data with reference theoretical distributions.

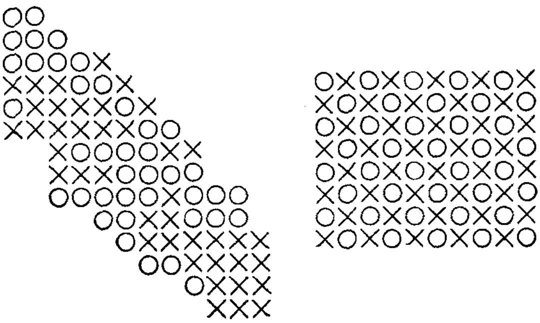
6. A good general measure of the extent of mixedness is the standard deviation among spot samples removed from the batch. The sample mean should also be reported.

IV. Theoretical Frequency Distributions

A. MIXING—ORDERLY OR RANDOM?

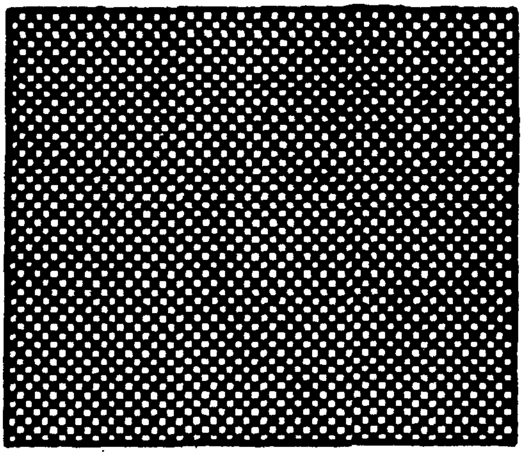
For a long time, the picture of mixing shown in Fig. 17, had been widely accepted as a guide to ideas on mixing. Such a picture would indicate that all spot samples taken from the mixed batch should give the same exact composition (or other measurement). If this were not the case, the variation between spot samples might be attributed to errors due to sampling or analysis; or perhaps to a feeling that the mixer was just not doing a perfect job, the latter statement implying that things were not quite as good as they could be. It has now been recognized and pointed out several times, that a mixture such as shown in Fig. 17(b) is not the equilibrium state of a mixing operation where tumbling motion causes the mixing. Instead, since random tumbling is involved, the mixing process is recognized as producing a random arrangement of particles, if no segregating effects are present.

The fact that the end result of a tumbling operation is not an orderly system was stated by Lacey in 1943 (L1). He considered a solids mixture from the point of view of individual particles, calling an "ideal" mixture of *A* and *B* one in which the degree of dispersal of the components is the one most likely to exist in a mixing machine after equilibrium has been established. By means of Figs. 18(a) and 18(b), he showed the difference between ordered and random arrangements of particles.



(a) "Unmixed" (b) "Mixed"

FIG. 17. Illustration entitled "The Effect of Mixing" from (P1). (b) is not the end result of random mixing, since the probability of getting state (b) by a random tumbling operation is zero for all practical purposes.

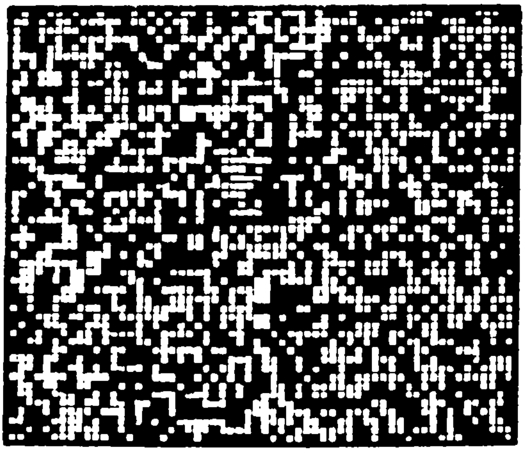


(a)

FIG. 18(a). Ordered arrangement of particles (L1).

Buslik (B10) stated that the term *random* does not describe a single specific arrangement but rather the way in which the arrangement was achieved. He showed how these ideas could be quantitatively developed to enable computation of the weight per particle necessary to achieve a certain specified uniformity of mixture. Also, he derived and illustrated the use of the formula shown in Section III, D, 4 for computing the standard deviation of the per cent of a given size in random samples from a granular material with a known size distribution.

Several others have dealt with various aspects of the development of this idea of a theoretical distribution of spot sample compositions from a randomly mixed batch. Before further discussion of the outstanding contributions of these investigators, the basic statistical concepts which underlie their work will be examined.



(b)

FIG. 18(b). Random arrangement of particles (L1).

B. BINOMIAL, NORMAL, AND POISSON DISTRIBUTIONS—GENERAL COMMENTS

The distribution of spot sample compositions of a certain size, taken from a randomly mixed batch of A and B, can be calculated theoretically. The methods of calculation are standard statistical techniques, and several papers have shown how various aspects of these basic ideas can be applied to solids mixing. Most of the calculations and discussion center around three distributions: binomial, normal, and Poisson.

The physical picture is as follows: a batch of A and B particles have been mixed until equilibrium has been reached. There are no segregating or clustering tendencies; therefore, A is considered to be randomly distributed throughout the mixture. If this is true, then *the probability of finding a particle of type A at any point in the mixture is a constant equal to the proportion of that kind of particle in the whole mixture.* This key statement immediately identifies the distribution of spot sample compositions (expressed in terms of number of A particles or "particle fraction A") as a binomial distribution, provided only a relatively small amount of material is removed for sampling. (Note: Rigorously, the multinomial hypergeometric distribution applies (W1), but if only a small amount of material is removed for sampling the assumption of constant probability is valid and for practical purposes the binomial distribution applies.) The general equation for the binomial distribution is:

$$P(x) = \frac{n!}{x!(n-x)!} p^x (1-p)^{n-x} \tag{40}$$

where $P(x)$ is the probability of obtaining x successes in n independent trials of an event, for which p is the probability of finding a success in a single trial. In the case of a random mixture of particles of A and B, n would be the total number of particles in each spot sample, p would be the fraction of A particles in the entire mixture, and $P(x)$ would be the probability of finding x particles of type A in a spot sample of n particles. $P(x)$ can also be thought of as the proportion of spot samples which will contain x particles of type A. The spot sample composition may also be expressed as "particle fraction A," rather than the number of A particles. In this case x/n is used instead of x, but the relation is not changed, i.e.,

$$P\left(\frac{x}{n}\right) = \frac{n!}{x!(n-x)!} p^x (1-p)^{n-x} \tag{41}$$

The mean of the distribution is p and the variance, σ^2, is $p(1-p)/n$. To compute values of $P(x/n)$, when n is fairly large, say 100, is a time consuming task; yet spot samples with an n of this order of magnitude are usual, even with a very small spot sample, and techniques for computing $P(x/n)$ are necessary for these cases. Therefore, approximations are used as follows:

When p is ≤ 0.5 and $np > 5$ at least, experience indicates (H5) that the normal distribution, which is a continuous function, is a good approximation to the binomial distribution, which is a discrete function. The normal distribution is:

$$f\left(\frac{x}{n}\right) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{\frac{x}{n}-m}{\sigma}\right)^2} \tag{42}$$

Since this is an approximation of the binomial distribution, the mean m, and standard deviation σ, are p and $\sqrt{p(1-p)/n}$, respectively.

Hoel (H5) states that "when p is very small, even though n is large, the normal approximation to the binomial distribution may be poor; consequently some other form of approximation is needed." This would cover the case when $np < 5$. The Poisson distribution function is such an approximation and is defined as:

$$P\left(\frac{x}{n}\right) = \frac{e^{-m}m^x}{x!} \tag{43}$$

where $m = np$.

With the above three distributions, it is possible to compute theoretical frequency distributions for the composition of samples of size n, for the case where A is randomly mixed with B. As will be shown in the following discussion, this basic theme has been developed in several different directions.

C. BINOMIAL AND NORMAL DISTRIBUTIONS: USE IN DEFINING AND ILLUSTRATING MIXING; CHI-SQUARE; ENTROPY (W2)

Weidenbaum and Bonilla made use of the normal approximation to the binomial distribution in defining mixing. They illustrated its course, as shown in Fig. 19. [Several of these items are discussed in greater detail in Weidenbaum's thesis (W1).] The limiting theoretical distribution was computed for $p = 0.53$ and $n = 133$, which were the particle fraction of sand, and the average number of particles per spot sample, respectively. By computing the theoretical standard deviation for this case, they showed that their mixing system—consisting of a small cylinder with salt and sand particles—did not give a random mixture,

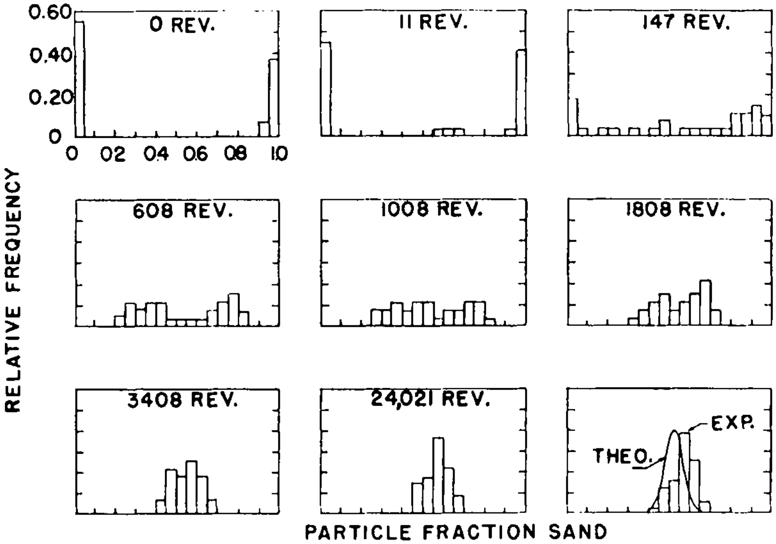


FIG. 19. Change in relative frequency histogram as mixing proceeds (W2).

but instead had an equilibrium state of segregation, as will be further described in the Section on "Equipment Performance." They also illustrated the use of the chi-square distribution to (1) compare the experimentally determined frequency distribution of spot sample compositions with that for a randomly mixed batch, and (2) as a method of rating the extent of mixedness. Also, they have introduced the concept of the entropy of the system increasing as it changes from an orderly loaded state to a random mixture. They define the change in entropy ΔS, as:

$$\Delta S_{1-2} = k'' \ln \frac{P_2}{P_1} \tag{44}$$

where P_1, P_2 are the probabilities (or relative frequencies of occurrence) of chi-square values for states 1 and 2, respectively, and k'' is a constant.

D. Binomial and Normal Distributions: Effect of Sample Size Fluctuation; Transformed Variable for Measuring Incomplete Mixing; Chi-square (B4)

Blumberg and Maritz mixed a closely sized batch of sand, half dyed red and half dyed blue. With this highly idealized case, they showed that a randomly mixed batch could be obtained in a drum rotated at 55 rpm at a 30° angle with the horizontal. By this experimental work, they confirmed the fact that where segregating forces are not present, the limiting or equilibrium mixture is a random arrangement of particles, from which the number r of particles of one kind (red in this case), in spot samples of size n, are normally distributed. They also showed, by a statistical proof, that although n might vary from one spot sample to the next, if the variance of N ($= S_n^2$) is small compared to the square of the mean ($= \bar{n}^2$), the proportion of red particles in the sample ($x = r/n$) will still be approximately normally distributed. In statistical terminology, they showed that if, instead of the equation

$$P(x) = \frac{n!}{x!(n-x)!} p^x (1-p)^{n-x}$$

the function $P(x,n) = P(x)P(n)$ were used, then assuming that the distributions of both r and n were approximately continuous, the distribution of x would be approximately normal ($x = r/n$). They later show this to be true experimentally for a ratio of $S_n^2/\bar{n}^2 = 0.005$. After their section on the completely mixed state (which concerned the random mixture), Blumberg and Maritz consider incomplete mixing. They state, "When mixing is incomplete, what appears to be important fundamentally is not the degree of mixing but rather the approach of the mixture towards the completely mixed state." Previously, for the completely mixed state, they had used a simple chi-square test to determine whether a random mixture had been achieved. This chi-square test involved a comparison, of the observed frequency distribution of x_i with the theoretical calculated frequency distribution for a random mixture. For the unmixed state, however, although a chi-square test is used as a measure of mixing, it is not based on x_i, but instead on $z_i = 2 \text{ arc sin } \sqrt{x_i}$. By introducing this transformation, they sought to obtain a variable z_i, which would be approximately normally distributed with means ζ_i and variances $1/\nu$. They also did some experimental work from which they concluded that 10 spot samples at each state of mixedness were sufficient to plot a graph of degree of mixing *vs.* time, which would accurately indicate when mixing was completed.

E. THEORETICAL VARIANCE FOR RANDOM MIXTURE OF TWO MATERIALS, EACH WITH ITS OWN SIZE DISTRIBUTION (S5)

In a paper entitled, "The Degree of Mixing of a Random Mixture as a Basis for the Evaluation of Mixing Experiments," Stange gives a formula for calculating the theoretical variance of samples taken from a randomly mixed batch of two materials (P and Q), each of which has its own size distribution (Eq. 25).

In order to determine $\bar{\nu}_P$ and $\bar{\nu}_Q$, the relative frequency distribution for particle weights must be known for each component. The variation coefficients are also determined from these distributions. Examples of the use of this formula are shown in the paper.

Special cases which enable simplification of the equation are given, e.g., the coefficients of variation are not needed in the simplified expression for the case where the initial distributions consist of almost like particles, since their squares are "small" compared with 1. Stange also shows how the confidence limit graph given in his other paper (S4) can be used to give a confidence band around the theoretically computed standard deviation for a randomly mixed batch. If the sample variation is within this confidence band, then there is considered to be no further significant change in the extent of mixedness. Variation among sample means would be accounted for by the sample size and prescribed confidence limits. Stange also gives experimental evidence to show that two substances which do not have any tendency to segregate during mixing will form a random mixture for which one can compute the standard deviation theoretically. In this case, the formula used to compute the theoretical standard deviation was a simplification of Eq. (25), because the range of particle sizes was such that the ratio of the largest particle weight to the smallest was 3.4. In Stange's paper, it was stated that if this ratio is $\leqq 3.5$, the following simplification of Eq. (25) can be used:

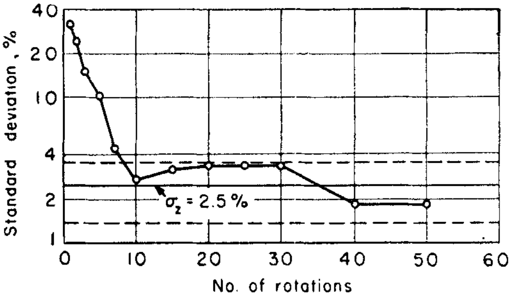


FIG. 20. Standard deviation s, *vs.* number of rotations of the mixer for experiment 1 of Table II. σ_z is the theoretical value of standard deviation computed from Eq. (45). Eight samples taken at each number of rotations. Broken lines are 90% confidence limits on σ_z for seven degrees of freedom (S5).

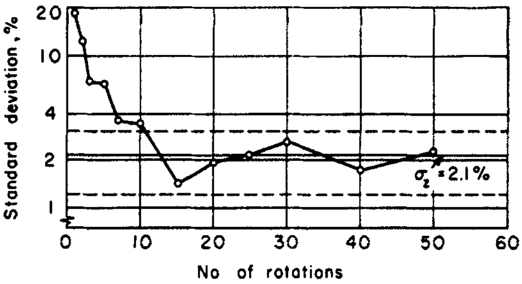


FIG. 21. Same as Fig. 20 for Experiment 2 *F* of Table II (S5).

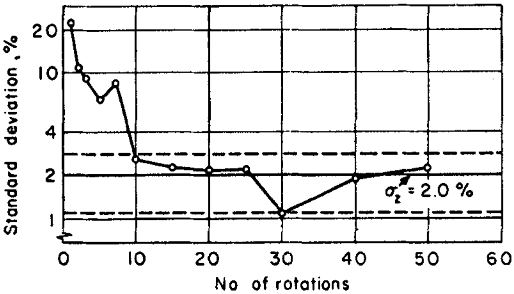


FIG. 22. Same as Fig. 20 for Experiment 3 *F* of Table II (S5).

$$\sigma_z^2 = \frac{PQ}{g}\,(P\bar{\nu}_Q + Q\bar{\nu}_P) \tag{45}$$

(See Section III, D, 9 for nomenclature.)

By applying this formula and performing experiments with the systems shown in Table II, Stange obtained the three graphs shown in Figs. 20 through 22. Further details are given in the section on Equipment Performance.

TABLE II

DATA CONCERNING MIXTURES GRAPHICALLY TESTED FOR RANDOMNESS BY STANGE[a] (S5)

		Component P				Component Q						
Experiment No.	Total wt. G[gm.]	Particle size [mm.]	Absolute wt. G_P[gm.]	Relative wt. P	Average particle wt. $\bar{\nu}_P[10^{-6}$ gm.]	Particle size [mm.]	Absolute wt. G_Q[gm.]	Relative wt. Q	Average particle wt. $\bar{\nu}_Q[10^{-6}$ gm.]	Weight of sample, g [10^{-3} gm.]	Quality coefficient of the random mixture $\sigma_z^2 \times 10^4$	Standard deviation from theoretical values P, Q σ_z, %
1	250	0.4 0.6	150	0.60	177	0.4 0.6	100	0.40	190	71	6.25	2.50
2 F[b]	250	0.2 0.3	175	0.70	24.2	0.4 0.6	75	0.30	190	65	4.53	2.13
3 F[b]	250	0.1 0.15	175	0.70	2.8	0.4 0.6	75	0.30	190	66	4.26	2.06

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[a] Stange states: "The experimental results are from the thesis of R. Schaeffer, *Mixtures of Granular Substances: Comparisons between the Variations of Samples by Calculation and Experimentation with Molding Sand Mixtures* (Technical University at Karlsruhe, 1953)."

[b] The addition of F in experiments 2 and 3 signifies an addition of 2 wt. % distilled water, in order to prevent separation of the mixture.

F. USE OF POISSON DISTRIBUTION IN EVALUATING MIXTURES (A1)

Adams and Baker have pointed out some properties of the Poisson distribution that were particularly useful in enabling them to test and compare blenders for a polythene blending problem. This involved blending a small quantity of master batch granules with natural granules, the master batch containing additives such as pigments and anti-oxidents necessary for certain uses. These properties are: (1) the Poisson distribution mean and variance are the same ($= m$), and (2) when $m \geqq 20$, the normal distribution serves as a good approximation to the Poisson distribution.

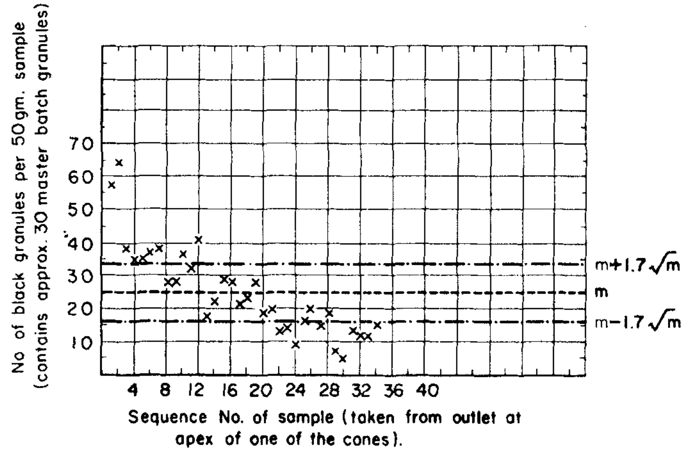


FIG. 23. Illustration of how confidence limits computed from a Poisson distribution can be used to evaluate blender performance. Double cone blender, 500 turns. Natural polythene (rough 4 mm. cubes, sp. gr. 0.92) mixed with master batch containing carbon black (3 mm. cubes, sp. gr. 1.2). Conclusion: batch not randomly mixed since probability of this graph occurring with a randomly mixed batch is less than 0.01 (A1).

Three tests were used for assessing the efficiency of blending. The first was a variation of the quality control chart or confidence band technique, which was used on individual samples rather than on means of rational sub-groups. Ninety, ninety-five, and ninety-nine per cent control lines were drawn for a mean m, which was calculated from the weight of the master-batch added, the weight of natural granules used, and the volume and density of the master batch granules. The use of the average number of master-batch granules per sample (denoted by $\bar{x}$) as an estimate of m was suggested as an alternate method which would not significantly affect the results. This test required $m \geqq 20$ and $N \geqq 10$, where N is the number of samples taken from a batch. Examples of such graphs are shown in Figs. 23 and 24; 90% control lines are shown.

The second test, which required $N \geqq 20$, is a graphical method for detecting trends in sample compositions when the latter are plotted versus sample sequence. Seven successive results on one side of the mean m, indicate that there is a trend in the sample compositions rather than a purely random arrangement. The authors advise a repetition of this test to confirm whether this trend exists. If the trend is still indicated the batch is not well blended.

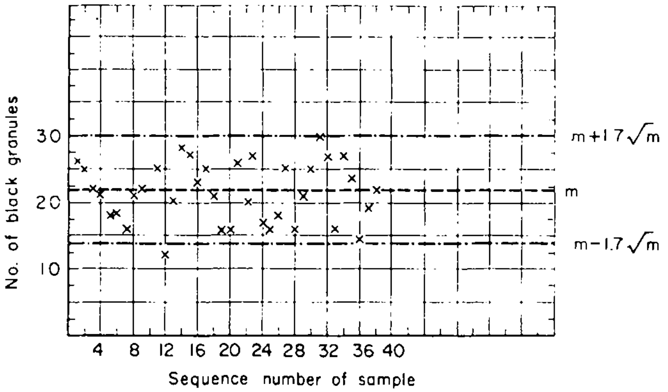


FIG. 24. Same type of graph and equipment as in Fig. 23, but with different materials. Natural polythene (sp.g. 0.92) mixed with natural polythene with black compound (sp.g. 0.922). Probability = 0.7. Conclusion: batch is randomly mixed (A1).

The third test involves use of the ratio $b = S^2/m$, where S^2 is the variance and equals $\frac{\Sigma(x - \bar{x})^2}{N - 1}$. In practice, m is replaced by $\bar{x}$ (x is the number of black granules in a sample from a mixture of natural and black granules). The probability of obtaining as large a value of b as computed, from a Poisson distribution, is plotted versus values of b. This graph is shown in Fig. 25 for sample sizes of 20 and 30, and can be used as follows:

Step 1. Calculate b from the sample compositions.

Step 2. From Fig. 25, determine the probability of obtaining this large a value of b from a Poisson distribution.

Step 3. If this probability is less than 0.05 (one chance in twenty), conclude that the samples did not come from a Poisson distribution. Thus the theoretical limiting mixture has not been reached.

This test is similar to the statistical tests of significance described earlier. In this case, the test of significance is being performed on $S^2/\bar{x}$. Instead of 0.05, some other level of significance could be used if desired.

The authors mention the fact that probability can be taken as a measure of the quality of blending. This is somewhat analogous to the Weidenbaum and Bonilla method for classifying the quality of a mixture in accordance with the probability of occurrence by chance of the chi-square value that is obtained when the mixture spot sample distribution is compared with the theoretical normal distribution (W2).

Adams and Baker illustrate a method for determining the carbon black concentration of the master batch, and also the per cent of the master batch that must be added to the natural polythene in the preblend, in order that certain specifications for variation of additive in the final compound will be met. They do this by developing and illustrating the use of an equation involving density of polythene, density of carbon black, volume per granule, average concentration of carbon black, and permitted tolerance. In deriving the equation, they use the principle that the number of granules of master batch in a weight, w, of blended granules, will be distributed according to the Poisson distribution; thus the variance of this quantity can be calculated theoretically.

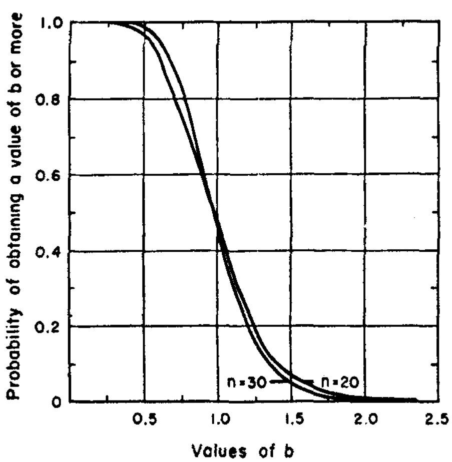


FIG. 25. Graph of probability, of obtaining a value of b or greater from a Poisson distribution, *vs.* values of b. $b = S^2/\bar{x}$, where S^2 = sample variance and $\bar{x}$ = sample mean (A1).

G. CONTINUITY OF ONE PHASE IN A POWDER MIXTURE OF TWO PHASES (F1)

In a paper dealing with the analysis of the continuity of one phase in a powder mixture of two phases, Forscher presents another approach to the use of the concept of a random mixture as a criterion of mixing.

His mathematical analysis deals with the problem of determining how much of one powder *A*, must be added to another powder *B*, to obtain continuity of powder *A* in a random mixture of the two. When more than the minimum is added, more continuity will result. Continuity is expressed as the probability that pairs of particles of powder *A* have radii, the sum of which just equals the distance between their centers. Forscher's mathematical analysis leads him to conclude that for an aggregate of equal-size spheres *A* is probably discontinuous if the ratio of *A* to *B* is below $\frac{1}{5}$. Both *A* and *B* are continuous when A/B exceeds this ratio and eventually *B* becomes discontinuous if B/A falls below $\frac{1}{5}$. In the discussion given, powder *A* is a good conductor of electricity, and powder *B*, a poor conductor. The degree of continuity of powder *A* was assumed proportional to the over-all conductivity of the compound powder mixture.

This approach has interesting potentialities as a research tool for studying mixing. Although the assumptions inherent in Forscher's article require a rather idealized system, it may be possible to determine from conductivity measurements whether very fine powders are randomly mixed with one another. This could be done, by calculating at approximately what concentration continuity could be achieved, and then determining whether this were obtained, or whether the concentration needed for continuity was far in excess of that theoretically required. Particularly where the aim of mixing is to achieve some sort of special electrical property, this approach would appear to have potentialities.

H. USE OF STANDARD NORMAL TABLE WITH RATE EQUATIONS (O9)

Oyama and Ayaki's development of their rate equation yields an expression:

$$\epsilon = \int_{-x_1}^{x_1} f(x)dx \qquad (46)$$

where ϵ = probability of a spot sample composition x, lying within the range between $a - \delta$ and $a + \delta$,

and $$f(x) = \frac{1}{\sqrt{2\pi}\,\sigma} e^{-\frac{1}{2}\left(\frac{x-a}{\sigma}\right)^2} \qquad (47)$$

The authors describe how this relation can be used to compute mixing time for the case where the equation

$$\ln (1 - M) = -\phi t \qquad (48)$$

gives a straight line.

The essentials of this method are:

1. Set the specifications to be achieved by mixing. Thus, if a is the

average composition of the whole mixture, the specifications would state that a certain fraction of spot samples taken from the mixed batch must be between $a - \delta$ and $a + \delta$.

2. Determine z_1, which is the specification expressed in multiples of the standard deviation σ, by using standard tables of the normal distribution. The area under the normal curve between $a - \delta$ and $a + \delta$ must equal the fraction of spot samples specified in step 1. This value, which equals ϵ, is just another way of looking at "the probability of a spot sample composition x lying within the range between $a - \delta$ and $a + \delta$." Thus, z_1 is the "normalized" standard deviation corresponding to this area.

3. Compute σ, $= \frac{\delta}{z_1}\cdot$ (49)

4. Use this to compute $1 - M$ in:

$$1 - M = \frac{\sigma^2 - \sigma_r^2}{\sigma_0^2 - \sigma_r^2} \tag{50}$$

(See Section III, D, 17 for further nomenclature.)

5. Using Eq. (48), compute t, the time necessary to achieve the desired degree of mixing.

Primarily, this is still only an interesting theoretical idea since ϕ, which is needed for this calculation, was obtained only for a few systems of differently colored but otherwise identical sands, loaded in a certain manner and mixed in a horizontal rotating cylinder. When two different sands were mixed, the straight line relationship did not hold, and thus no over-all ϕ could be obtained. Also, it should be borne in mind that this method assumes spot sample compositions will be normally distributed at whatever specification is set for the mixture.

I. TECHNIQUES NECESSARY FOR DIFFERENT METHODS OF ANALYSIS

The experimental work of Weidenbaum and Bonilla (W2), Blumberg and Maritz (B4), Adams and Baker (A1), and Oyama and Ayaki (O9) involved particle counting in order to test whether or not a batch was randomly mixed. If weight fraction rather than particle fraction were used as the method for expressing spot sample composition, the standard deviations based on these two different methods of analysis, might be expected to differ. Weidenbaum (W1, pp. 131–133) has shown quantitatively that the magnitude of this standard deviation difference would depend upon the magnitudes and constancies of the weight fractions, and also upon the magnitudes and constancies of the differences between the weight fractions and particle fractions. These latter differences, in turn, are contingent upon the number of particles per gram of each of the two substances being mixed, and the relative proportions of the two materials in the spot sample. Hatch's equations relating count and weight distributions, which are summarized by Dallavalle (D1), may also be of use in this area.

Adams and Baker mention some variations of the particle count technique for cases where counting is tedious. One entails cutting down the number of counts, which involves using the square root of the count as the variable rather than the count per sample. The other involves spreading the sample over a flat surface and placing a transparent covering with grid markings above it, and then counting the number of squares which contained none of the additive. They then used the transformation of Blumberg and Maritz to obtain a new variable which is approximately normally distributed. It is stated that in both cases, tests can be developed with these new variables, similar to those which are illustrated in their paper (A1) using the number of master batch granules per sample as the variable.

J. Summary and Conclusions—Theoretical Frequency Distributions

1. It has been shown, both theoretically and experimentally, that with certain systems of particulate solids in which precautions were taken to prevent segregation, a randomly mixed batch was achieved from a mixing process.

2. The distribution of spot sample compositions from such a mixture can be computed from the binomial distribution, and closely approximated by either the normal or Poisson distributions, depending on the relative amounts of the two materials in the mixture and the size of the spot samples taken.

3. Several methods for using the above principles to evaluate mixing machines have been developed and illustrated. To a certain extent, the above ideas have been applied to systems where the two types of particles differ in size distributions.

4. Examples have been given illustrating criteria for deciding whether a specific mixing operation turns out a random mixture. Also the principles have been applied to planning how best to prepare quantities of coarse particulate ingredients for blending in a mixture to meet specifications as to variability.

5. In order to increase the usefulness of this type of approach, techniques should be developed to extend the application, of both the experimental and calculation methods, to much finer mesh materials. Some

equations for doing this are available, but these are still in early exploratory stages.

6. A recent paper mentions an approach—involving continuity of one ingredient throughout a mixture—which although purely theoretical, offers a potential method for ascertaining whether random mixtures of fine particles have been achieved. The conductivity of the mixture could be studied in such work.

V. Rate Equations

A. THE VALUE OF RATE STUDIES

The attempt to find rate mechanisms for solids mixing is important for several reasons. First, and most obvious, is the fact that if a method were available for calculating how long it would take to mix materials in various mixers, the amount of time necessary for testing could be reduced considerably. At present, there is no general way of calculating the optimum mixing time accurately from such data as have been reported. Another value of rate studies is that they throw light on the basic mechanisms of the mixing operation, thereby pointing to ways in which mixing machines and techniques can be improved.

In the summaries of rate studies which follow, both these considerations should be borne in mind.

B. GENERAL DISCUSSION

Solids mixing rate theory has been discussed in papers by Brothman *et al.* (B5), Coulson and Maitra (C3, M2), Visman and Van Krevelen (V1), Weidenbaum and Bonilla (W2), Weidenbaum (W1), Lacey (L2), and Oyama and Ayaki (O9). In all of these papers, some sort of a rate equation has been postulated. These are tabulated in Table III, which is an expanded version of a similar one from Weidenbaum and Bonilla (W2).

Lacey (L2) points out that simply finding an exponential law of mixing rate in practice, must not be taken by itself as substantiation of a theory without considering its range of agreement. He indicates how theories for the rate of mixing can be developed by assuming one or more of the following three mechanisms: (1) convective mixing—transfer of groups of adjacent particles from one location in the mass to another, (2) diffusive mixing—distribution of particles over a freshly developed surface, and (3) shear mixing—the setting up of slipping planes within the mass. Later, in discussing the analysis of incomplete mixtures, he states that $1 - M$ (see Section III, D, 16) should be independent of sample size for diffusive mixing, but greatly dependent on sample size for convective mixing. The importance of using the most meaningful term in a

TABLE III

RATE EQUATIONS AND PLOTTING METHODS PROPOSED BY VARIOUS INVESTIGATORS[a]

Investigators	Original rate equation proposed in derivation of final equation[b]	Final equation given[b]
Brothman *et al.* (B5)	$y_{t+1} = y_t + \phi(1 - y_t)$	$P_t = 1 - e^{-kS_p(1-e^{-tc})}$
Coulson and Maitra (C3)	$\frac{dS}{dt} = k(S_0 - S)$	$\ln \frac{100}{X} = kt$
Bonilla and Crownover, and Bonilla and Goldsmith [mentioned in (W2)]	Not given	Data plotted as $-\log \frac{a.d.}{2c(1-c)}$ *vs.* $\log r$
Visman and Van Krevelen (V1)	Not given	Data plotted as $(100 - Z)$ *vs.* t on linear probability paper using the probability scale for $(100 - Z)$
Weidenbaum and Bonilla (W2)	$\frac{d\left(\frac{\sigma}{s}\right)}{dt} = k'\left[\left(\frac{\sigma}{s}\right)_{\text{eq.}} - \left(\frac{\sigma}{s}\right)\right]$	$\ln\left[\frac{1}{\left(\frac{\sigma}{s}\right)_{\text{eq.}} - \left(\frac{\sigma}{s}\right)}\right] = \ln\left[\frac{1}{\left(\frac{\sigma}{s}\right)_{\text{eq.}} - \left(\frac{\sigma}{s}\right)}\right]_0 + k't$
Weidenbaum (W1) and Lacey (L2)	Diffusion equation—see Table IV	
Oyama and Ayaki (O9)	$\frac{\partial\sigma^2}{\partial t} = -\phi(\sigma^2 - \sigma_r^2)$	$\ln \frac{\sigma^2 - \sigma_r^2}{\sigma_0^2 - \sigma_r^2} = -\phi t + c'$
Sakaino (S1)	$-\frac{dz}{dt} = c(z - z_f)$	$\ln\left(\frac{z - z_f}{z_0 - z_f}\right) = -ct$

[a] This is an extension of a similar table given by Weidenbaum and Bonilla (W2).

[b] Nomenclature: t = time; ϕ, k, k', c' = constants; y_t = proportion of the maximum theoretically possible surface of separation, S_p, that has been developed in t units of time; $c = \log 1/1-\phi$; S = interfacial area of surface per unit volume of the mix; S_0 = maximum surface per unit volume that can be achieved with the given system; r = number of revolutions of the mixer; $\left(\frac{\sigma}{s}\right)_{\text{eq.}}$ = value of $\frac{\sigma}{s}$ for theoretical random equilibrium mixture = 1; z = mean size of "agglomerate" which is being distributed throughout the batch ($-dz/dt$ = rate of decrease of size of unit); z_0 = initial value of z; z_f = equilibrium value of z. As previously given, the definition of c applies to Brothman *et al.* However, c is also a constant in Sakaino's equation. Also for Bonilla and Crownover and Bonilla and Goldsmith, c refers to weight fraction of the key constituent in the entire batch. *a.d.* is mean deviation and σ and s are standard deviations defined in Section III, D under the various authors who use them. P_t, X, and Z are also explained in Section III, D.

rate plot is thus stressed. Weidenbaum and Bonilla (W2) also emphasized this point by showing how the integrated form of the simple first-order rate equation $dA/dr = K(A_p - A)$, can give different plots simply by changing the definition of A, which is a term expressing degree of mixedness. A_p is the value of this term for perfect mixing (definitions of the latter also vary), r is the number of revolutions of the mixer and K is a constant.

The Brothman *et al.* (B5), and Coulson and Maitra (C3, M2) rate theories have been analyzed in several other articles (W2, L2, H2). As Table III indicates, these papers start with essentially the same original rate equation concerning the rate of change of the surface of separation, but they end up with different forms of the final equation. The lack of data for testing the theory by Brothman *et al.*, plus the obviously curved initial portions in the Coulson and Maitra plots of log $100/X$ *vs.* t, still leave much to be desired before either of these theories can be accepted. The work of Weidenbaum and Bonilla (W2), although indicating a straight line initially in a plot of $\ln (1/1 - \sigma/s)$ *vs.* t, gives an irregularly shaped portion thereafter due to segregating effects, thus limiting the area of usefulness of this rate equation. Their method of loading, which was similar to that shown in Fig. 26, probably affected the shape of their rate plot, since the original rate equation would more likely be followed in such a system, than in an irregularly loaded one. However, this is an idealized situation which probably does not arise in most commercial mixing applications. It should be noted that Weidenbaum and Bonilla's original equation, although similar in form to those of Brothman, *et al.*, and of Coulson and Maitra, differs from them in that it does not involve surface of separation, but instead uses a ratio involving the standard deviation among spot samples from a randomly mixed batch, divided by the experimentally determined standard deviation.

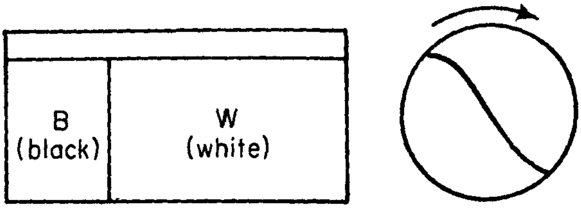


FIG. 26. Starting point for pure diffusive mixing (L2).

Visman and Van Krevelen (V1) replotted the data of Coulson and Maitra on linear probability paper, using $100 - Z$ (which they called the per cent unmixed) on the probability scale, and time t, on the arithmetic scale. Probability paper changes one of the scales, so that the cumulative normal distribution curve appears as a straight line. Thus, if there were a straight line from such a plot, its equation would be:

$$(100 - Z) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{t} e^{-\frac{y^2}{2}} dy \tag{51}$$

where y is a dummy variable. Differentiating this with respect to t gives

$$\frac{d(100 - Z)}{dt} = \frac{1}{\sqrt{2\pi}} e^{-t^2/2} \tag{52}$$

which is the rate equation giving a straight line on such a graph.

Blumberg and Maritz (B4), while not covering rate theory, provided data on a system of two otherwise identical, but differently colored sands, which were mixed. Lacey has shown that if their degree of mixing, ϕ is replaced by $(\phi - s_r^2)$, then a plot of $-\log(\phi - s_r^2)$ *vs.* time will give a comparatively straight line over the range of 100 to 1. (All terms are defined in Section III, D, 15, 16, 19.)

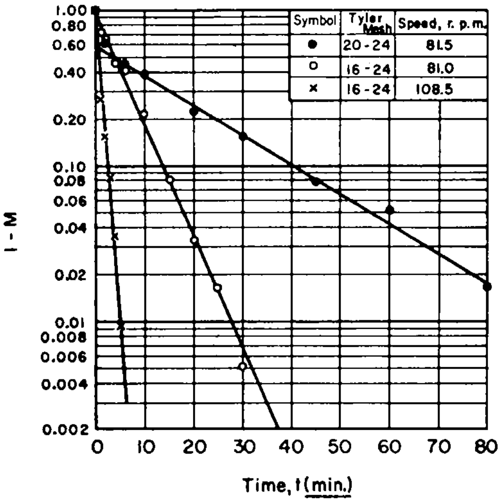


FIG. 27. Log $(1 - M)$ *vs.* time. Horizontal cylindrical mixer rotated at indicated speeds. Sōma standard sand of indicated mesh sizes was mixed. Half was dyed red, the other half blue, and initially the colored sands were loaded on opposite sides of the mixer. Analysis performed by particle counts. Mixer 30% full (by volume); total charge = 6 kg. (O9). Spot samples taken of approximately 108–118 particles each.

Oyama and Ayaki (O9) performed experiments in a small cylinder, with otherwise identical but differently colored sands, in which they tested the rate equation

$$\frac{\partial\sigma^2}{\partial t} = -\phi(\sigma^2 - \sigma_r^2) \tag{53}$$

which was integrated to give

$$\ln\frac{\sigma^2 - \sigma_r^2}{\sigma_0^2 - \sigma_r^2} = \ln(1 - M) = -\phi t + c' \tag{54}$$

(Note: The background for M is given in Section III, D, 16 under Lacey.)

They found that graphs of log $(1 - M)$ *vs.* t were straight lines for the cases where identical (except for color) sands were mixed, indicating

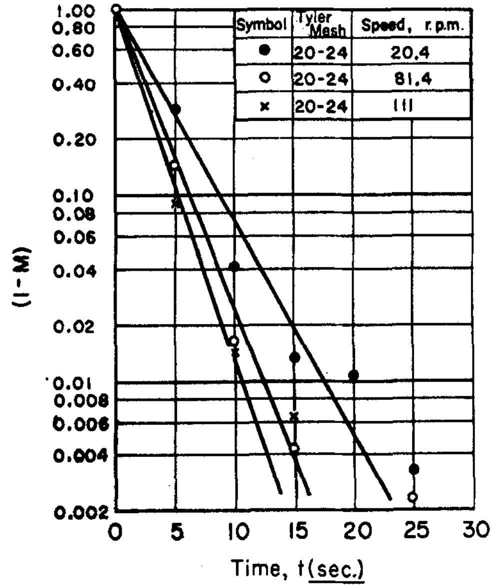


FIG. 28. Log $(1 - M)$ *vs.* time. Horizontal cylindrical mixer rotated at indicated speeds. Sōma standard sand of 20–24 Tyler mesh was mixed, 20% differently colored from the other 80%; initially loaded one on top of the other. Analysis by particle counts; spot samples taken of approximately 118 particles each. Total charge = 6 kg. (O9).

that their proposed rate equation applied here. Figures 27 and 28 show such graphs. The data for Fig. 28 are rather sketchy.

However, where two different sands were mixed, this rate equation did not hold, as shown in Fig. 29.

Michaels and Puzinauskas (M4) studied the mixing of powdered dextrose with water-wet kaolinite in a small finger-prong mixer. Using the Uniformity Index, I_v, shown in Section III, D, 20 as the degree of mixing, the mixing rates and energy requirements were determined for systems of different water contents and total volumes.

The authors stated that graphs of I_v *vs.* θ (time) on logarithmic coordinates approximate straight lines in the interval $10 > I_v > 1$, which can be expressed by $I_v = k\theta^n$, the exponent n varying between -0.7 and -1.2. Although they realize that this is insufficient to prove any of the rate theories which have been proposed, they feel that the trends of the Uniformity Index with time are qualitatively in agreement with the equation of Brothman, *et al.*, predicting that the logarithm of mixture uniformity will be an exponential function of time.

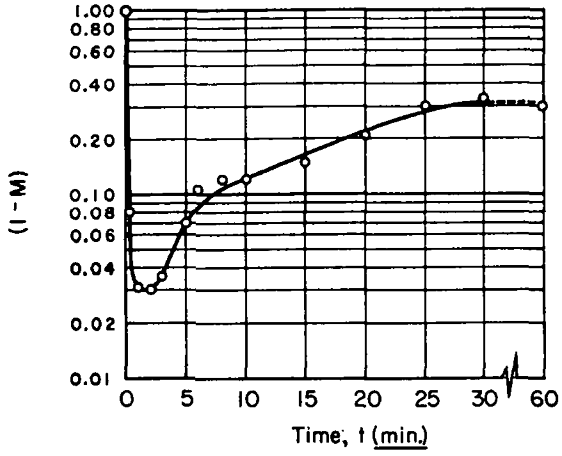
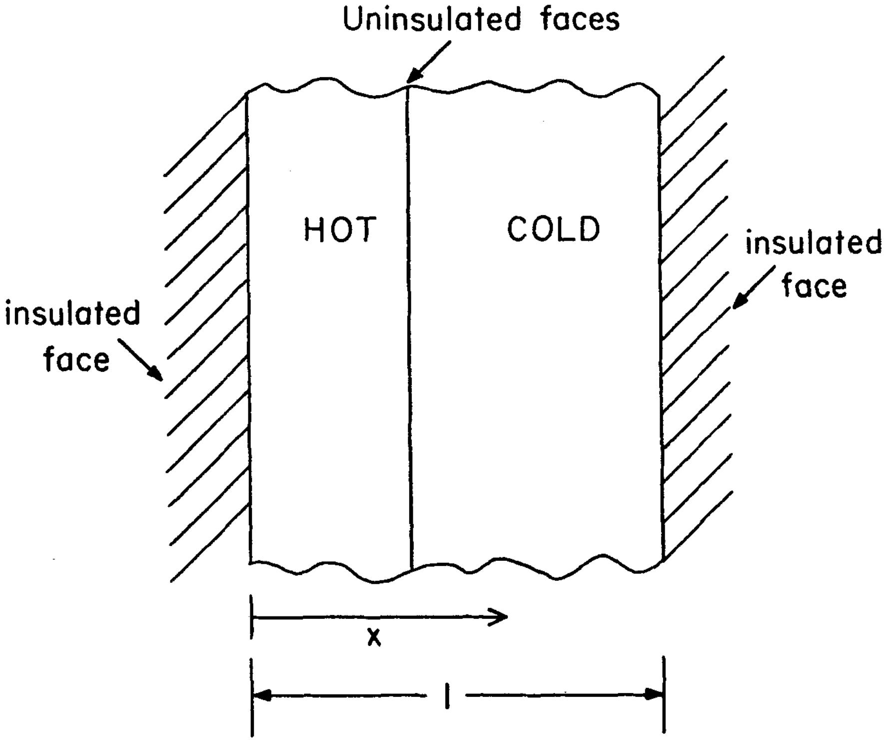


FIG. 29. Log $(1 - M)$ *vs.* time. Horizontal cylindrical mixer rotated at 54.5 rpm. Equal weights of 80–100 Tyler mesh Toyouro standard sand and 35–42 Tyler mesh Chigasaki sand were mixed, initially loaded on top of one another. Mixer 25% full (by volume). Total charge is 5 kg. Samples of about 0.45 gm. each were taken (O9).

Sakaino (S1) has attempted to utilize the same type of rate equation for explaining both solids mixing rate theory and the homogenizing process during glass melting. Drawing on data from Tooley and Tiede (T1), he uses their plot of density spread *vs.* melting time to illustrate his theory. His equation, as shown in Table III, deals with the rate of decrease in size of agglomerates, of size z, which are distributed throughout the mixture. "Apparent sample size" is denoted by R/z, where R is the actual sample size. It is used in computing the limiting variance for a pseudo-perfect mixture, which is considered a mixture in which agglomerates have reached their limiting size and are randomly dispersed. In the case where agglomerates reduce to individual particles and the sample size is so large that the variance due to theoretical random variation may

TABLE IV

Analogy for Heat Conduction, Molecular Diffusion, and Diffusive Mixing



Heat conduction

A hot and a cold infinite slab, each with a single face insulated, have their *un*insulated faces brought into perfect thermal contact at time zero.

$$\frac{\partial \theta}{\partial t} = \frac{k}{\rho c_p}\left(\frac{\partial^2 \theta}{\partial x^2}\right)$$ (M1, with some changes in nomenclature)*

$\frac{k}{\rho c_p}$ = thermal diffusivity

where k = thermal conductivity of the solid, $\frac{\text{B.T.U.}}{(\text{hr.})(\text{sq. ft.})(^\circ\text{F. per ft.})}$

c_p = specific heat of solid, $\frac{\text{B.T.U.}}{(\text{lb.})(^\circ\text{F.})}$

ρ = density of solid, $\frac{\text{lb.}}{\text{ft.}^3}$

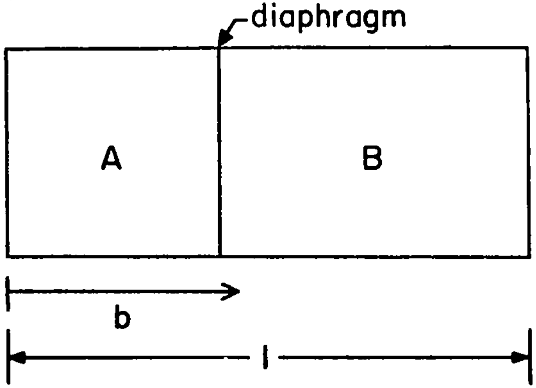
θ = temperature, °F.

x = relative distance in the direction of flow of heat, and

t = time, hr.

* For consistency with the rest of the table, t is used here for time and θ for temperature although in (M1) just the reverse is done.

TABLE IV (*Continued*)



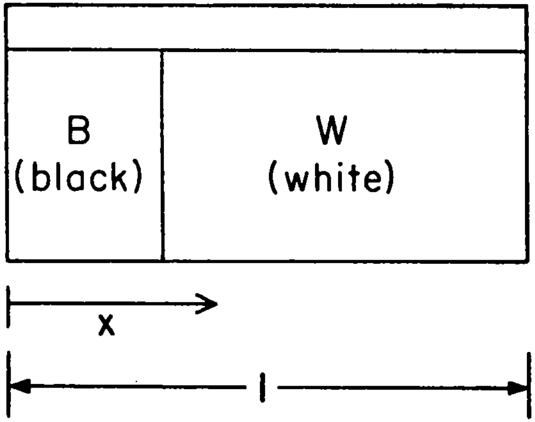
Molecular diffusion (W1)*

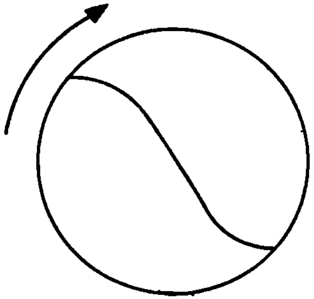
A thin diaphragm separating gases A and B is suddenly removed, and the gases are allowed to diffuse.

$$\frac{\partial y_A}{\partial t} = D\frac{\partial^2 y_A}{\partial b^2}$$

y_A = mole fraction A
b = relative distance in the direction of diffusion of A molecules, as shown
D = molal diffusivity
t = time

* (D4) gives basic reference material on diffusion.





Diffusive mixing (W1, L2)

A mixing cylinder is loaded with particulate solids and separated by a partition as shown.* The partition is removed and the cylinder is rotated around its horizontal axis.

$$\frac{\partial p}{\partial t} = D\frac{\partial^2 p}{\partial x^2}$$

where p = per cent black,
t = time,
x = relative distance in the direction of movement of black particles, as shown
D = mixing diffusivity.

* In (W1) the partition is in the center of the cylinder.

Lacey's nomenclature is used here for ease in following the discussion of Eqs. (55–58) which he gave (L2).

In Weidenbaum's terminology (W1):

y_A (= particle fraction of component A) replaces p and b replaces x.

In Eqs. (56–58), P is the value of x at the initial boundary, or the final per cent black in the overall mixture.

be neglected compared to the experimentally determined variance, Sakaino's final rate equation becomes log $S^2 = kt$ (k = a constant). He shows a straight line plot of log S *vs.* time for Lowry's data (L4), the latter being taken from Herdan (H2). This is the same as the standard deviation line in Stange's plot (S4) which is shown in Fig. 6.

C. DIFFUSION ANALOGY

Considering mixing in an analogous manner to molecular diffusion has led Weidenbaum (W1) and Lacey (L2) to investigate the use of Fick's second law of diffusion:

$$\frac{dy_A}{dt} = D\frac{d^2y_A}{db^2} \tag{55}$$

as a rate equation for the mixing of solid particles.[3] The ideal case, which has been separately considered by each of them, is that where a mixing cylinder is loaded, as shown in Fig. 26. If the mixer is revolved as shown, then the motion of the particles of the two substances being mixed can be considered as analogous to the motion of molecules of two different gases, which are allowed to diffuse after a partition separating them has been removed. The above equation is for the case where diffusion is considered in the plane perpendicular to the axis of rotation of the cylinder. In order to more clearly illustrate the analogy with other unit operations, Table IV illustrates how similar equations can be applied to heat conduction, molecular diffusion, and diffusive mixing.

Lacey has shown how the solution of the differential equation for the stated boundary conditions gives:

$$(p - P) = \frac{2}{\pi}\sum_{q=1}^{q=\infty} e^{-q^2\pi^2T}\,\frac{\sin\,(qP\pi)}{p}\cdot\cos\,(qx\pi) \tag{56}$$

where $T = Dt/L^2$, L is the actual length of the mixer, and q is an integer. (Table IV gives further nomenclature.)

From Eq. (56), the variance can be theoretically computed as:

$$s^2 = \frac{2}{\pi^2}\sum_{q=1}^{q=\infty}\left(\frac{\sin\,qP\pi}{q}\right)^2 e^{-2q^2\pi^2T} \tag{57}$$

Therefore a plot of $-$ log s^2 *vs.* T should be a straight line if the original equation was valid. Lacey has plotted this graph, as shown in Fig. 30. The initial portion in all cases is curved, which Lacey attributes to initial

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[3] See Table IV for nomenclature.

transients that are indicative of the distance that the black particles have to travel to the middle of the mixer. The transients assume more importance at low values of P, but the graphs all have the same slope for the linear portion, showing that the final rate of mixing does not depend upon composition. Using a simplified equation for the post-transient period:

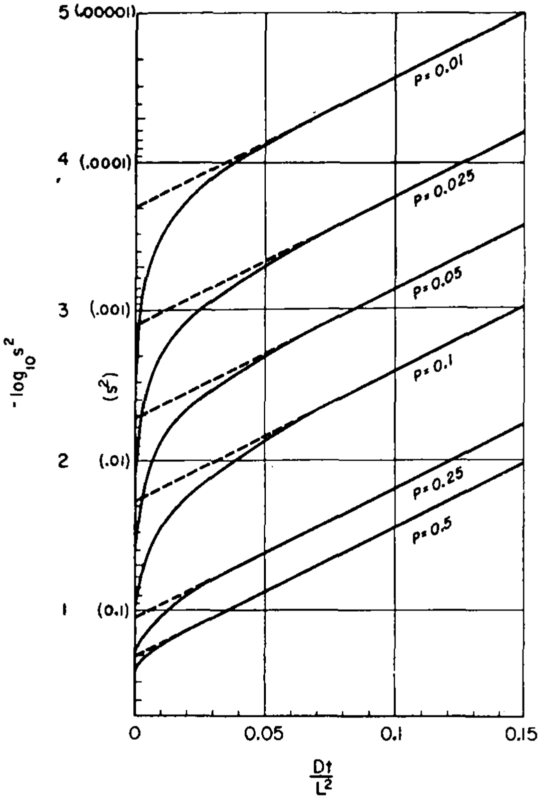


FIG. 30. Logarithmic plot of sample variance s^2, computed according to Eq. (57), *vs.* Dt/L^2 (L2). P = proportion of black particles in the overall mixture, D = diffusion coefficient, t = time, L = length of mixer.

$$s^2 = \frac{2}{\pi^2} e^{-2\pi^2 T} \sin^2 P\pi \tag{58}$$

and dividing s^2 by $\sin^2 P\pi$ gives a corrected s^2, denoted by s_c^2. When this is plotted against T, the straight line portions all eventually reduce to one line, although there is still divergence in the transient region (Fig. 31).

It should be noted that Oyama and Ayaki (O9) arrive at an expression similar to that of Eq. (58), by developing the idea of mathematically formulating the probability, that any particle would transfer from one location to another in the mixer at any particular rotation. They mathematically summed up the product of probability × concentration for the N cells into which they had divided the mixture volume, in order to get concentration at any time. By then assuming that the particles being mixed have the same physical properties, and that the mechanism of mixing is independent of the locations of cells in the mixer, the authors simplified the mathematical expression and obtained the equation for a horizontal rotating cylinder initially loaded as shown in Fig. 26. They assumed the motion of the particles in the mixer to be similar to what they referred to as "rodinal one-dimensional Brownian motion in a finite domain."

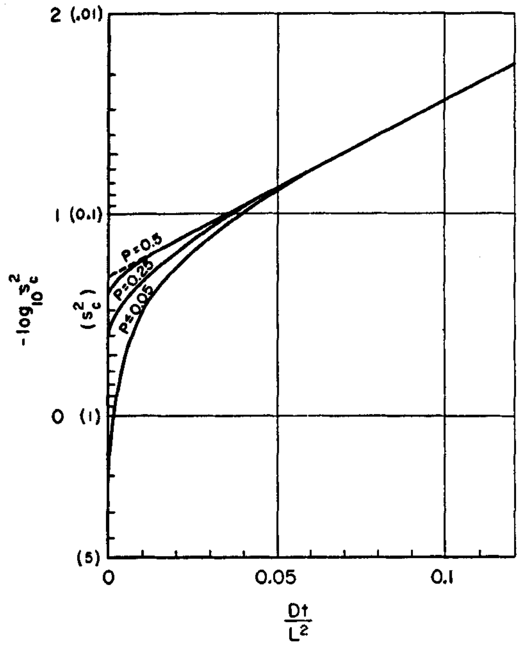


FIG. 31. Same as for Fig. 30 except that "corrected" variance, s_c^2, is used in place of s^2. (See Section V, C.) This shows the elimination of the effect of P, except in the transients (L2).

Lacey (L2) concludes from this that the straightness of a plot of this type for any machine is an indication of how uniformly the machine in question acts upon its contents. He states that straightness of such a plot implies "that either D is independent of position, or else there is good circulation which evens out variations in D; and thus that the design is an optimum for the type of mechanism in use." He further concludes, "If there is curvature, this indicates that there are regions of poor mixing (or even 'dead' spots), which control the mixing time, owing to the absence of good circulation. Such regions can then be looked for and the defect remedied."

Lacey gives some sketchy data from Blumberg and Maritz (B4), and a private communication from Kramer which, although somewhat indicative a compatibility with diffusion theory, still leave several phenomena that require more investigation and experimentation before this theory can be confirmed. In applying diffusion theory it is well to bear in mind Weidenbaum's comments (W1) concerning the solution of Eq. (55) for any boundary conditions. He states that it " . . . has in its derivation two assumptions which are probably not true for the physical situation in most cases. They are: (*a*) 'equimolal' counterdiffusion of A and B. (*b*) D is a constant independent of concentration." Mole fraction is replaced by particle fraction when using the diffusivity concept for solids mixing. He (W1) further states that the diffusion analogy " . . . might eventually lead to a way of summing up the effects of the particle properties which affect the rate of mixing, i.e., the D might be used as an ultimate variable in a correlation of the variables involved in mixing particulate solids."

Extension of these ideas on diffusion, to cases where there are differences in diffusivity between the materials, would be of interest. Barrer's chapter (B2) on the solution of the diffusion equation may be of use here.

D. Summary and Conclusions on Rate Equations

1. Coulson and Maitra's rate equation (C3), although resulting in straight lines in the latter parts of the rate plots for certain systems, was not followed during their initial portions.

2. The rate equation of Visman and Van Krevelen (V1) gave two straight line portions in their rate plots for certain systems, the change in rate being attributed to a de-mixing effect setting in after a certain time of mixing.

3. Weidenbaum and Bonilla's rate equation (W2) was followed at the beginning of mixing, but not all the way to the end of mixing. The authors explain this as due to random motion being the initial driving force with the later appearance of an additional driving force, namely, a segregating tendency in the particular system they used.

4. Oyama and Ayaki's first-order type of rate equation (O9) was followed when two substances, identical except for color, were mixed. The major mechanisms of mixing were diffusion and shear, in this case. However, when two different substances were mixed, the equation was

only followed at the beginning, later deviation from it probably being due to segregating tendencies.

5. The equation of Brothman, Wollan, and Feldman (B5) was not supported with any experimental evidence when first postulated. Lacey's further analysis of this equation (L2), which he illustrated with a hypothetical graph, led him to conclude that the apparent rate constant should increase with increasing proportions of the constituent being analyzed for, and with decreasing particle size. He considers the fact that Coulson and Maitra's rate constants follow this pattern as some confirmation of the Brothman theory. Michaels and Puzinauskas' rate plots (M4) lead them to feel that the trends of changes in the Uniformity Index with time are qualitatively in agreement with the Brothman, *et al.* equation, which predicts that the logarithm of mixture uniformity will be an exponential function of time. (Note: Shearing forces would probably be very important in the mixer used by Michaels and Puzinauskas.)

6. Weidenbaum and Bonilla's data indicate that a first-order rate equation can give either a straight line or a curve depending on the term chosen for the degree of mixing. Lacey's logarithmic rate plot of Blumberg and Maritz' data indicates that a straight line over a wide range is obtained if the variance of a random mixture is subtracted from their expression for the degree of mixing, whereas a curved line is obtained if that expression alone is used.

7. Lacey's plot of a theoretically calculated variance based on a diffusion equation, *vs.* time, has an initial curved portion after which a straight line is obtained. Lacey concludes that the straightness of this latter part is an indication of how uniformly the machine in question acts upon its contents; curvature indicates that there are regions of poor mixing which control the mixing time, owing to the absence of good circulation.

8. The rate studies thus far described have dealt with mixers in which the predominant mechanisms of mixing were diffusion and shear, rather than large scale turbulence. Rate studies in a machine where the latter was predominant would be of interest.

9. Bearing in mind the three types of mixing previously mentioned, namely, convective, diffusive, and shear mixing, and the wide variety of results obtained in the various rate studies, the following picture emerges: In any but an extremely idealized system, numerous driving forces are at work to cause mixing. When the materials are loaded, groups of similar particles will be thrown around. At the same time, they will be broken up into smaller groups. The means of distributing the larger groups of particles to the different parts of the mixing vessel may involve shearing or convective mechanisms, whereas the smaller scale mixing

which causes the clusters to decrease in size, involves a diffusion-type mechanism. When the larger groups of particles have been distributed throughout the vessel, the most rapid mixing will then be obtained, if the scale of turbulent movement of particles is the same as the scale of segregation.

With large-scale and small-scale random movement going on, and considerable differences in the initial method of loading the material, any single rate mechanism will not be able to adequately cover all cases. In addition, the forces acting upon the particles will affect the rate of mixing. Some of these are gravitational and centrifugal forces, frictional forces between particles and between particles and equipment, and surface forces on particles such as electrostatic forces. Differences in properties between particles being mixed may cause segregating tendencies which affect the rate of mixing. Rate data thus far mentioned apply only to the specific systems of machine and materials used. While some of the above conclusions indicate their possible usefulness as a guide to improving the performance of mixing machines, they are not enough to enable any general theoretical calculations of mixing times. However, as more data on different systems and machines are acquired so that the above equations may be further tested, more light will be thrown on the controlling mechanisms for different machines mixing different materials. This information will aid in analyzing mixing motion and improving mixer design by enabling the determination of the major mixing mechanisms in different types of mixing systems. It would be interesting to see what type of rate equations best describe the mixing action of various types of mixers with different materials, and how closely this classification compares with Scott's (S2) grouping of mixers according to the category of predominating action. By determining which rate mechanisms best describe the action of various mixers, it would be possible to group the mixers according to predominating mechanisms. The rate constants for any type of mixing action could then be compared in order to determine which of the mixers in that category gave most rapid mixing.

VI. Equipment

A. DESCRIPTION

The one phase of solids mixing which has been treated at length in the literature is the description of equipment. In textbooks, reference books, and review articles, pictures of equipment are shown and tables or charts given, which list suitable equipment for various applications. Also, details of machines, diagrams of their shapes, and practical construction data are available, including approximate power requirements.

Should one want any further information on a specific type of mixer shown, he need only write to the manufacturer for a detailed bulletin concerning construction, operation, and applications of that mixer. In many cases a description of the motion during mixing is also given. Some of the standard references describing solids mixing equipment are the Chemical Engineers' Handbook (P1) (very brief) and the Encyclopedia of Chemical Technology (K2). The latter lists several types of dry solids mixers and has a table listing types of machines that can be used for various specific applications. Brown (B6) has discussed five types of tumbling mixers and tabulated various construction details. For a de-

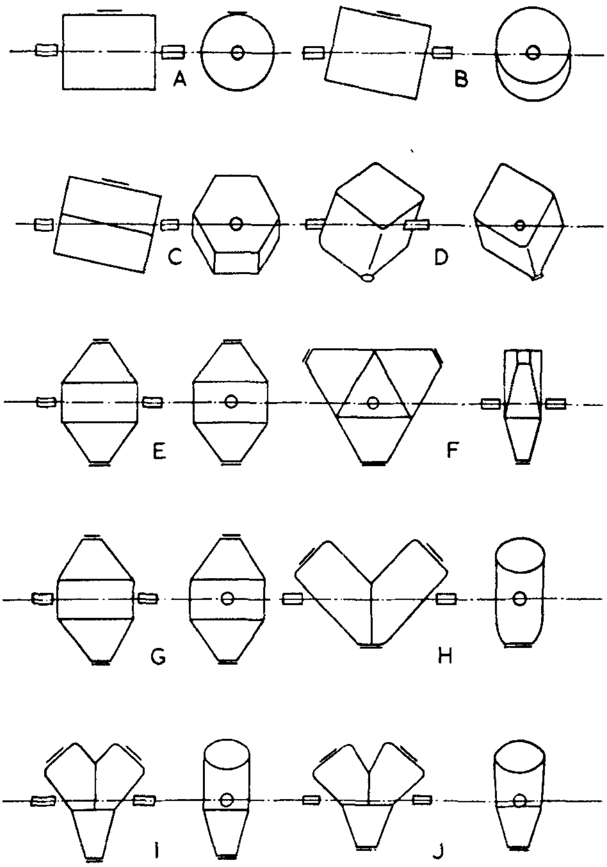


FIG. 32. Diagrammatic outlines of powder mixers (A1). A, horizontal rotating cylinder; B, cylinder—off center axis of rotation; C, similar to B but hexagonal shape; D, rotating cube; E,G, double cone; F, pyramid; H, twin shell; I,J, "Y" cone.

scriptive summary of a large number of pieces of dry mixing equipment, Quillen's article (Q1) is available. Work (W5) has discussed some of the considerations involved in solids mixing and prevention of subsequent segregation. In particular, he has discussed the concept of systems mixing whereby, instead of a specific mixer, various process steps, such as dumping in rotation, and grinding, are used to further the mixing of ingredients. Scott (S2) has described several kinds of mixers, indicating which of the several mechanisms mentioned by Lacey (L2) are predominant in them. Wornick (W6) has summarized characteristics of several dry solids mixers in connection with their use in premixing micro-ingredients for feed-stuffs. Young and Snaddon (Y3) have described an adjustable angle mixer which they found of use in mixing laboratory samples preparatory to analysis. Bullock (B7) has discussed the types of material for which muller type mixers are applicable and described the action of mullers. He cautions against trying to use the muller for materials which are too fluid or too sticky. However, he states that if used in the proper ranges, mullers are well suited to breaking down aggregates. Pierce (P2) has mentioned a vertical helical screw mixer with planetary movement in a conically shaped vessel. In the discussion of the paper by Adams and Baker (A1), several new shapes are illustrated (Fig. 32), and the mixing action of these plus other shapes is discussed. It is unnecessary to duplicate here descriptions of equipment which are readily available in the above sources.

B. PERFORMANCE

1. *Introduction*

In contrast to equipment description, the subject of equipment performance has few available published references. This has probably been due, at least in part, to the lack of quantitative methods for testing, which requires certain theoretical and experimental tools. Also, because a machine can be used to turn out a product which can either be further processed or sold at a profit, it might be thought of as a "satisfactory" machine. However, it may still not be giving the best mixture attainable; the rest of the process may be making up for its deficiency, possibly at a decreased profit. Higher off-specification losses than necessary may be occurring in the finished product, without realization that the solids mixer is contributing to them. As has previously been mentioned, there are often many steps following the mixing operation, so that irregularities in the final product may not be traced to improper mixing unless they become so serious that the plant may have to shut down if their cause is not found.

Burton (B9) points out that unmixing is nothing new, giving as an example what he calls " . . . the first recorded instance of its importance in industry," which was in 1910. It relates to a problem that the Rumford Chemical Works had concerning the control of baking powder uniformity. After considerable fruitless checking of weighing accuracy, research discovered the cause of variation to be improper mixing in the 5000-lb. capacity mixers. This example deals with the mixer itself. Burton gives other examples concerned with segregation after mixing due to free fall; one of these, he reports, caused the loss of a chief engineer's job in a munitions plant producing electronic cores for military equipment. "Absolutely uniform and perfect magnetic requirements" were demanded in the cores, which were made of thermosetting resin and powdered iron of high purity. Evidently the trouble-shooting did not go back far enough: a free fall from the mixer had been causing segregation which resulted in non-uniformity. Still another example of unmixing was given by Burton, this case leading to non-uniformity in the height of material in packages. These phenomena emphasize the need for starting with a good mixture and making sure that it stays that way. Certainly the first step would appear to be the choosing of mixing equipment which will not have inherent tendencies to cause segregation of the components and which will give the most uniform product most rapidly, making most efficient use of power. The following paragraphs will aim to present a coordinated picture of such work as has been done to further our knowledge along these lines.

2. *Horizontal Rotating Cylinder* (O1–O8)

A comprehensive study of solids mixing in rotating cylinders was made by Oyama between 1933–1940. Later, in 1956, Oyama and Ayaki (O9) did some further work concerning mixing in a rotating cylinder. Some of the highlights of the above papers, most of which are in Japanese, will be discussed below.

a. State of Motion of Materials. Oyama observed the state of motion of materials in a rotating horizontal cylinder under various conditions of speed and volume per cent loaded, using black and white sand of particle diameter equal to about 1.3 mm. (between 12 and 16, U.S. mesh size). He described the various states of motion by the terms "cascade," "cataract," and "equilibrium." The *cascade* state, which he reported for low speeds, consisted of particles rolling down the inclined surface after leaving their circular paths. At a certain speed, the motion changed to the *cataract* state, which consisted of particles close to the cylinder walls adhering to it until they reached a certain height, whereupon they were thrown onto the inclined surface and rolled down the remainder of the way. The state at which this changeover occurred was called the *critical* state. When the speed was increased sufficiently, the particles finally reached a state such that they remained on the cylinder wall until they fell upon the bottom edge of the inclined surface, thus bypassing the process of rolling down the inclined surface. In this state, called the *equilibrium* state, the particles in motion were considered to always keep their own fixed paths in flight and circular motion. The best operating conditions existed between the *equilibrium* and *critical* states, the particular optimum speed for Oyama's system being 80 rpm. Oyama gave an empirical relationship, by which the rotational speed of the mixer which would give a certain state of motion could be computed as shown below:

$$N = \frac{C}{D^{0.47}X^{0.14}} \tag{59}$$

where N = speed in rpm
D = inner diameter of cylinder in meters
X = per cent of mixer volume occupied by batch;
and C = a constant as follows: 54 for the *critical* state, 72 for the *equilibrium* state, and 86 for the state in which the whole mass of particles was almost in contact with the inner wall of the cylinder.

It is interesting to see how Oyama's empirical relationship compares with the type of relationship derived from model theory. This can be done by assuming that the ratio of centrifugal to gravitational forces is the only thing that would be changed by varying only the cylinder size (frictional forces, electrostatic forces, etc., would not change). The Froude number = N^2L/g expresses the ratio of centrifugal to gravitational forces. Therefore, to produce the same state of motion in two different cylinders (say 1 and 2), their Froude numbers, V^2/Dg or N^2D/g, should be the same.

Therefore
$$\frac{N_1{}^2D_1}{g} = \frac{N_2{}^2D_2}{g} \tag{60}$$

or
$$N_1/N_2 = \sqrt{D_2/D_1} \tag{61}$$

where V = linear velocity, ft./sec., and g = acceleration of gravity, 32.17 ft./sec.^{2}

Thus the speed required to give a certain state of motion should be inversely proportional to the 0.50 power of the cylinder diameter. Oyama's relationship shows that speed is inversely proportional to the 0.47 power of the cylinder diameter, and in addition, is inversely proportional to the 0.14 power of the volume per cent loaded.

The above relationship might serve as a "guesstimate" for scaling up any type of tumbling mixer, where centrifugal and gravitational forces are of primary importance. It would be necessary to use the proper characteristic dimension for the various sizes of geometrically similar equipment.

b. Mechanisms of Mixing. Oyama listed two mechanisms of mixing for the cylinder, based on analytical analysis and visual observations. These he called "local" mixing and "whole" or "total" mixing. The former he attributed to the scattering of particles as they roll down the surface in a "cascade" motion, whereas the latter was ascribed to positional changes of particles by circulation throughout the mixture. In terminology later used by Lacey (L2), these would correspond to the "diffusion" and "shear" mechanisms, respectively, for Oyama's system. By observing that the state of motion with the lowest dynamic angle of repose also gave the slowest mixing, Oyama pointed out the importance of the diffusion mechanism in promoting mixing.

His photographic method of measuring degree of mixing gives a visual means of illustrating the "diffusion" and "shear" mechanisms. Figure 10 mentioned in Section III, D, 1b showed a maximum intensity difference and a frequency difference on the various photographs. The drop in maximum intensity difference with mixing means a breakup of large groups of particles of one type, and the increase in frequency means a greater distribution of these groups throughout the mixture. These illustrate, respectively, the effects of the diffusion and shear mechanisms previously described.

In a paper by Oyama and Ayaki (O9), the authors point out the perfectly reasonable fact that radial mixing in such a cylinder is extremely rapid in comparison with longitudinal mixing, so that the controlling factor in determining mixing time is the coefficient of longitudinal mixing.

c. Performance Tests. Graphs from some of Oyama's tests with a cylindrical mixer of 20 cm. diameter and 40 cm. length, are shown in Figs. 33 and 34. This was for a system of black and white sand of approximately 1.3 mm. diameter (12–16 U.S. mesh size). The total weight of the mixture in the cylinder was 8 kg. The degree of mixing was measured photometrically, as described in Section III, D, 1b. For this system, the optimum speed is seen to be approximately 80 rpm. Equation (59) would permit calculation of the range of speeds between the "critical" and "equilibrium" states, which would include the optimum operating speed.

In a more recent paper, Oyama and Ayaki (O9) reported the results of some experimental work in connection with testing a rate equation (see Section V, B). Using a cylinder, 20.4 cm. in diameter and 39.6 cm. in height, they mixed several combinations of sand—sand systems. Employing 20–24 mesh, differently colored Sōma sand, they measured the coefficient of longitudinal mixing, ϕ_L, *vs.* rotational speed, with 6 kg. of

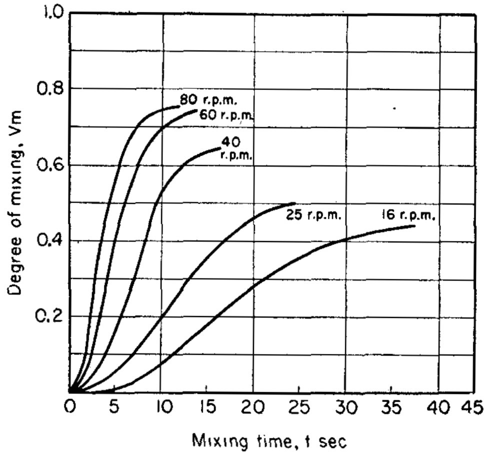


Fig. 33. Relation between the degree of mixing and mixing time. From (O2, p. 581). Horizontal rotating cylinder. Degree of mixing determined photometrically as described in Section III, D, 1b; 12–16 U.S. mesh, black and white sand. Total weight of mixture is 8 kg.

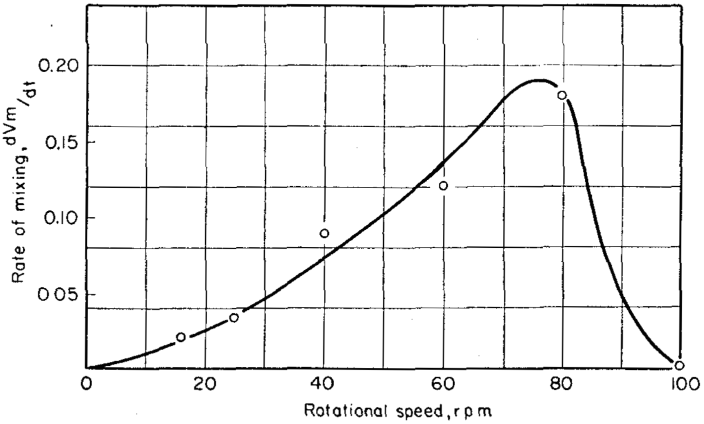


Fig. 34. Relation between the rate of mixing and rotational speed of mixer. Same materials and equipment as for Fig. 33 (O2). Values of rate of mixing are obtained from the slope of the linear portions of Fig. 33.

material in the mixer, corresponding to 30% loaded by volume. The degree of mixing was based on quantitative particle counts rather than photometric methods. The results, shown in Fig. 35, again indicate an optimum speed, although it differs from that shown in Fig. 34 due to differences in experimental conditions and the methods of measuring degree of mixing. Also, using a speed of 81.4 rpm, the curve in Fig. 36 was

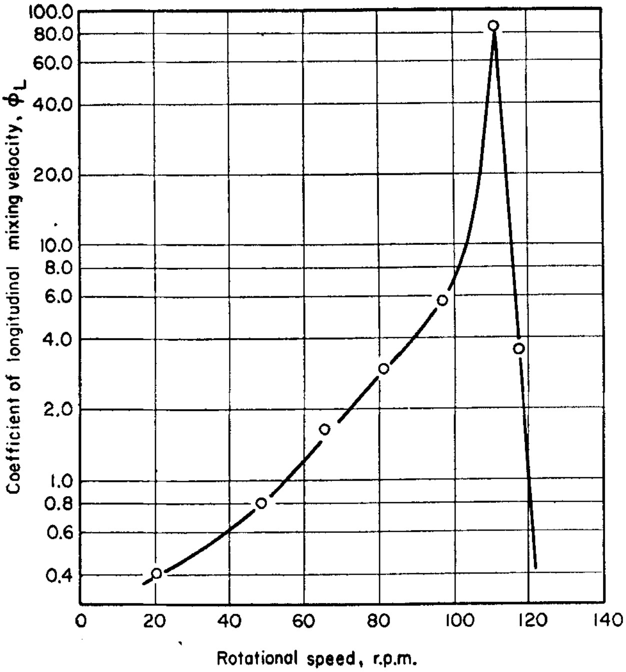


FIG. 35. Effect of rotational speed on values of ϕ_L. Horizontal rotating cylinder. 20–24 mesh sand. Degree of mixing from particle counts on spot samples (O9).

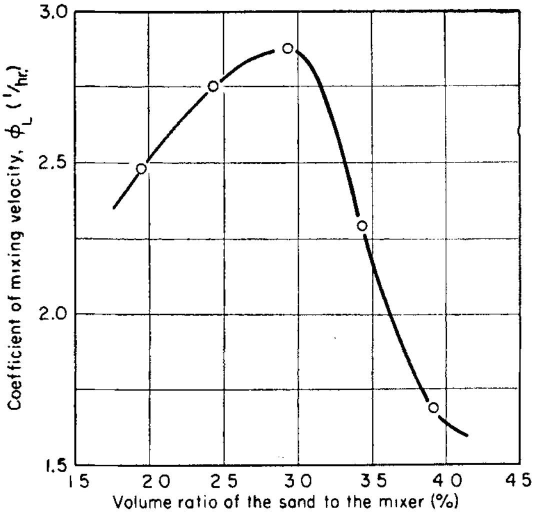


FIG. 36. Relation between volume ratios of the sand to the mixer and values of ϕ_L. Same equipment and method of measuring degree of mixing as used for Fig. 35. Speed = 81.4 rpm (O9).

determined. This indicates that the optimum volume ratio of sand to mixer was about 30% for the conditions shown.

d. Mixing of Solids of Two Different Sizes. A very interesting series of experiments by Oyama (O5) showed that the equilibrium state, when solids of different sizes are mixed in a horizontal rotating cylinder under certain conditions, is associated with a definite type of segregation. In fact, even if a well-mixed batch is put into the cylinder, it will end up in the segregated state after mixing. When Oyama mixed black and white limestone, he found that there were alternately arranged strips of black and white particles perpendicular to the horizontal axis of the cylinder, when the mixer had been stopped. These strips, which were visible on the inclined surface of the bed in the cylinder, were reproducible for the same conditions and appeared to get sharper with longer mixing.

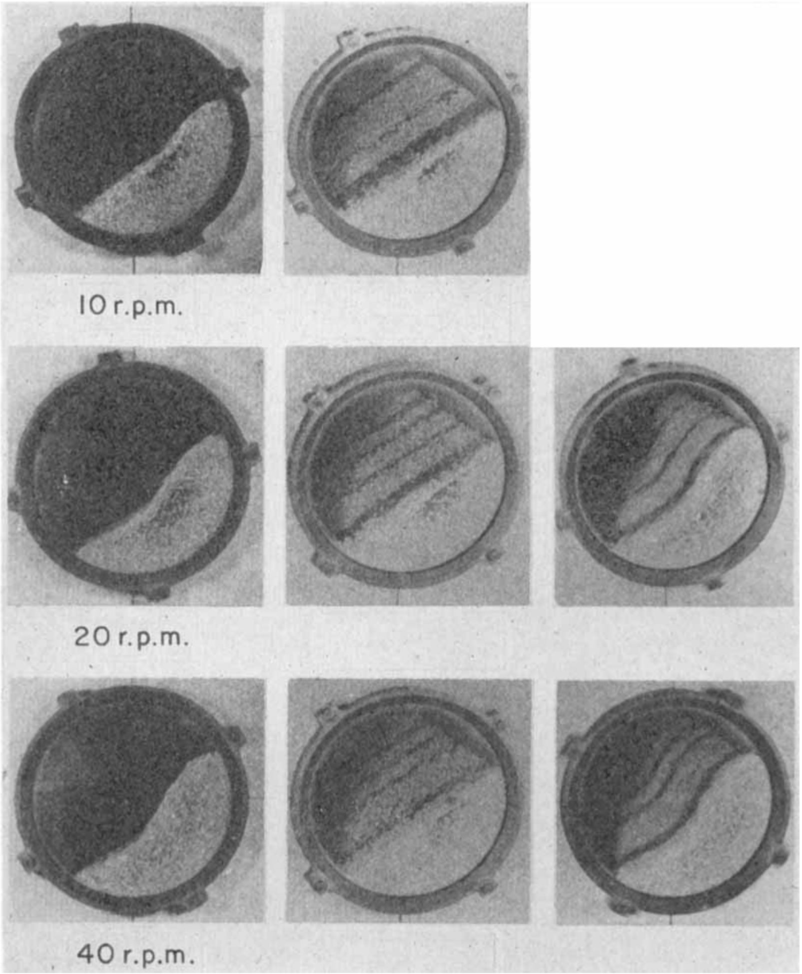
The strips became clearer with decreasing weight ratio of the two components (W_1/W_2), where $d_1 = 3.5$ mm. (diameter of white limestone particles), and $d_2 = 0.57$ mm. (diameter of black particles). He reported that they were easily produced at low speeds of the cylinder, even with a larger weight ratio W_1/W_2, and that the frequency of their appearance decreased after this, but again increased at the speed corresponding to the equilibrium state. In Fig. 37, are shown pictures of these strips for certain conditions of rpm, d_1/d_2, and W_1/W_2. The total charge was $W_1 + W_2 = 6$ kg.

These results certainly would indicate, that when two differently sized solids are mixed in a cylinder, some sort of segregation is likely to occur. Testing for the above type of effect where such a system is in use, would be strongly advisable. As has been pointed out in the Introduction to Section VI, B the results of segregation may result in trouble later on in the process.

e. Effect of Baffle (or Flight) in a Cylindrical Mixer. In another part of his work, Oyama (O4) studied the effect of a flight (or baffle) in a cylindrical mixer, using the same photometric method previously mentioned to measure degree of mixing. His graphs indicate that when an unbaffled cylinder was run at other than the optimum speed (80 rpm in this case), much was to be gained in improved mixing by the use of a baffle plate, provided it was not too high in relation to bed depth. At the optimum speed, the unbaffled cylinder gave more rapid and uniform mixing than for any baffled condition. In cases where the baffle can improve mixing, the h/R_f' ratio is important; here h is the height of the baffle, and R_f', the maximum bed depth. Oyama reported that the best results were obtained when this ratio was less than 0.9. An example given for a specific case where the baffle improved mixing is shown in Fig. 38. Note that h/R, rather than h/R_f', is used on the graph. The bed depth was constant for all runs.

These results indicate that a baffle would be most advantageous when its use causes the motion in the cylinder to be as close as possible to that existing at the optimum speed in the unbaffled cylinder.

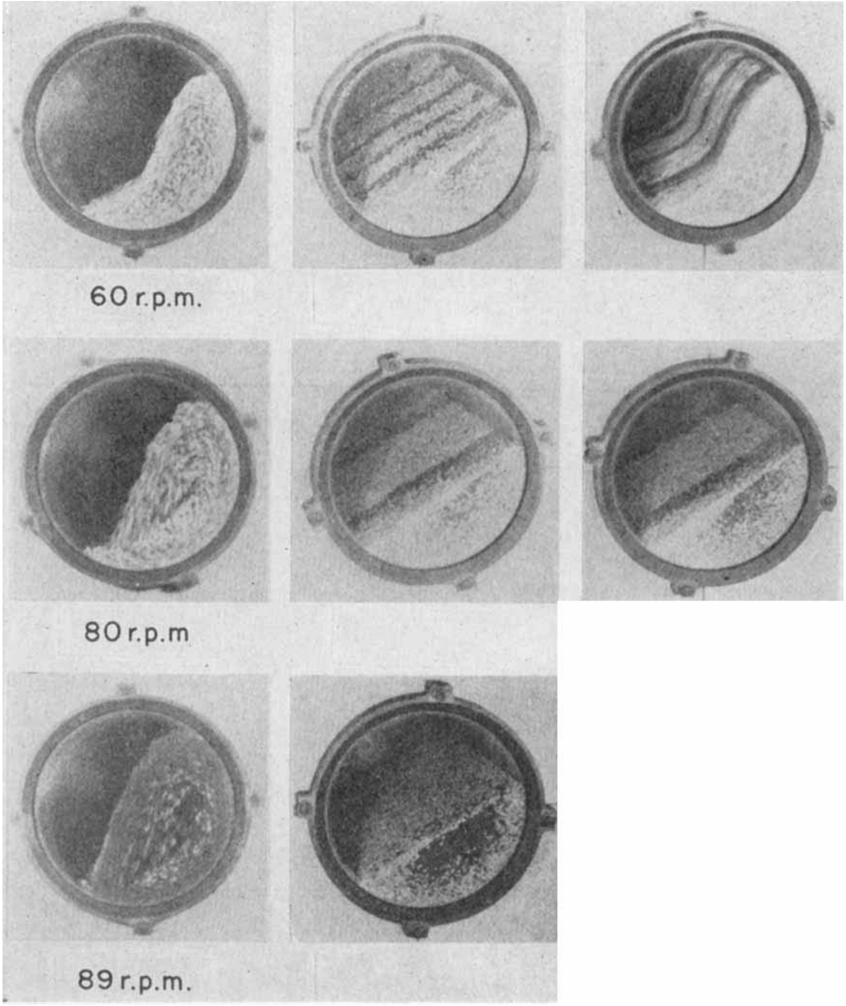
(Note: In the discussion of the paper by Adams and Baker, Johnson (J1) mentions a horizontal rotating drum, approximately 21 in. long and about 1 ft. in diameter, which was used for fundamental studies. He notes that without baffles, when the drum was one-third full, mixing was far from perfect, even after 81 hours. A specific kind of baffling,



[Fig. 37. Photographs illustrating segregation of a mixture of two different sizes limestone the coarser one. Cylinder rotated at indicated speeds. $d_1/d_2 = 3.5$ mm./

which is not elaborated on, managed to improve mixing so that a fairly wide specification could be met.)

f. On Power Consumption of Horizontal Rotating Cylinder (O7). Oyama measured the power consumption under various mixing conditions for certain systems. Some of his results are illustrated in Fig. 39, which gives plots of power in kg.-m./sec. *vs.* rpm. Each graph covers three different diameter cylinders at a certain volume per cent loaded. A major point is that the maximum rate of mixing occurred at a different speed



of particles into strips upon mixing. Black limestone is the finer component, and white 0.57 mm., $W_1/W_2 = \frac{3}{8}$, $W_1 + W_2 = 6$ kg. (O5).

from that which required the most power. Thus, highest power consumption does not necessarily mean highest rate of mixing. Specifically, the "equilibrium" state of mixing required the highest power consumption although the maximum rate of mixing occurred *between* the "critical" and "equilibrium" states.

3. *Cylinder Rotating at Various Angles with the Horizontal* (C3, M2, V1)

Using a small drum mixer, 6 in. diameter and 9 in. long, Coulson and Maitra investigated the effect of several equipment and material varia-

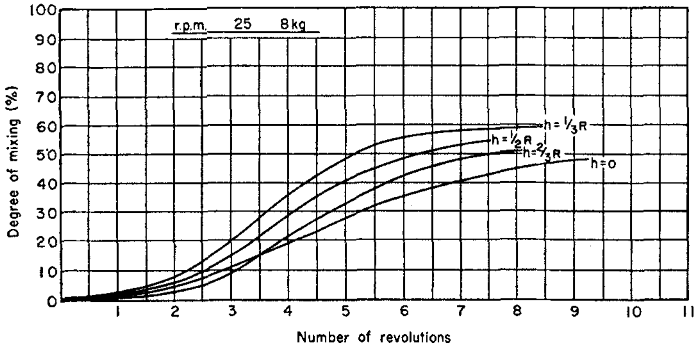
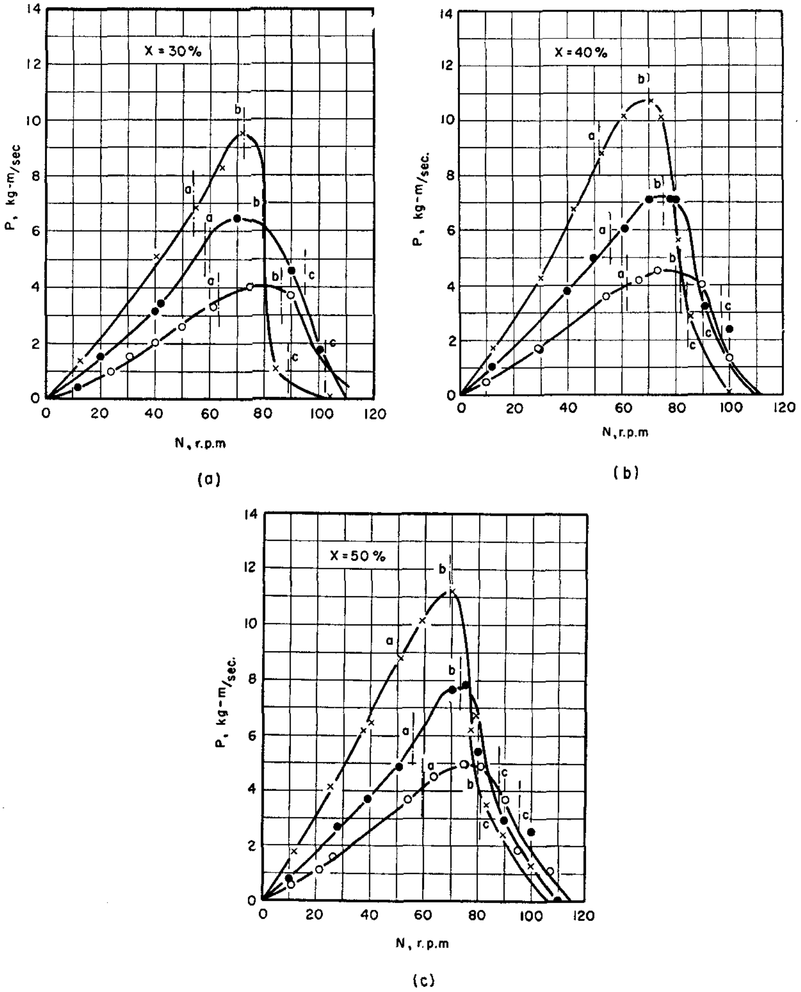


FIG. 38. Relation between degree of mixing and number of revolutions for various conditions of baffling. 20 cm. × 40 cm. horizontal cylinder rotating at 25 rpm. Black and white particles of about 1.3 mm. diameter mixed. Degree of mixing measured photometrically. Total weight of solid is 8 kg. h = height of baffle plate, R = radius of cylinder (O4).

bles on rates of mixing and segregation tendencies. As mentioned under Rate Equations, they used graphs of ln $100/X$ *vs.* kt to plot the data, ignoring the initial curved portions of these graphs. The k's, obtained from the latter straight-line portion of these graphs, were determined for various systems. From preliminary experiments with black and white glass spheres in a glass drum they concluded that the maximum quantity of material that can be effectively mixed is that which forms an elliptical surface with one apex at point A of the drum shown in Fig. 40. They also stated that if a free surface such as A_1A_1 is formed, then virtually no mixing will take place. The effect of several other variables will be separately discussed. Before this, however, some qualifying remarks are necessary in order to point out the limitations of these results.

First of all, the variables were changed one at a time using an arbitrary condition as standard, and then a number of rate constants were



(a)

(b)

(c)

Fig. 39. Power consumption *vs.* rotational speed of a rotating horizontal cylindrical mixer. Limestone was mixed, particle size about 1.35 mm. Experimental conditions varied as shown (O7). a = rotational speed corresponding to critical state; b = rotational speed corresponding to equilibrium state; c = rotational speed corresponding to the state when all particles tend to rotate with the inner wall of mixer; D = diameter of mixer, m.; ○:D = 0.25; ●:D = 0.30; ×:D = 0.35. N = rotational speed of mixer, rpm; P = power consumption of the horizontal cylindrical mixer, kg.-m./sec.; X = per cent of mixer volume occupied by batch.

obtained as mentioned above. By changing one variable at a time, the effects of varying two quantities simultaneously cannot be determined. Thus the optimum angle of inclination which was determined at a certain speed may not be the same at another speed. (The statistical term for these effects is "interaction.") Also, extreme care is necessary when generalizing from these results to larger or smaller equipment. Furthermore, as was previously mentioned, the k's are based on the latter part of the rate plot, since there is a curved initial portion.

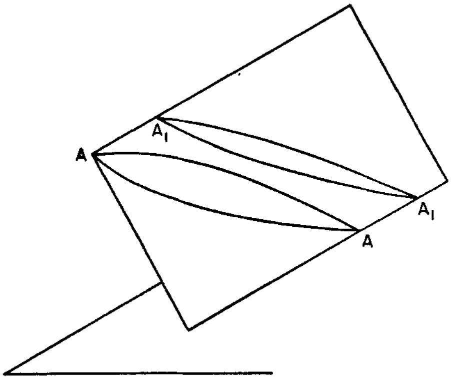


FIG. 40. Diagram showing maximum quantity of material which Coulson and Maitra felt could be effectively mixed (C3). This has surface AA. With surface A_1A_1, the authors state, "virtually no mixing will take place."

Yet, despite these limitations, there is some worthwhile information contained in a study of the rate coefficients. Graphs of these for different conditions are shown in Fig. 41. Figure 41(a) points to an optimum angle of inclination of approximately 14°, which the authors state can be shown to correspond with the maximum free surface. Furthermore, they state, that for angles less than 8° and greater than 30°, the mixture never achieves a high degree of dispersion. Figure 41(b) shows the effect of speed of rotation on k for an angle of 23°. (The authors do not explain why they chose this rather than the optimum of 14°.) Approximately 55 rpm was the optimum, although no runs were made at rpm's between this value and 80 rpm. Poor mixing was obtained at both very low speeds and very high speeds. Here a parallel can be drawn with Oyama's work, where the "cascading" motion at low speeds did not give good dispersion, and at high speeds the whole mass rotated, thus not promoting mixing.

Figure 41(c) indicates that faster dispersion was obtained with smaller particle sizes, both components having the same size. Where particles of different sizes were mixed, if the fines were put on the bottom no mixing was reported. With coarse material loaded on the bottom of the mixer, mixing reached an optimum degree of dispersion, followed by

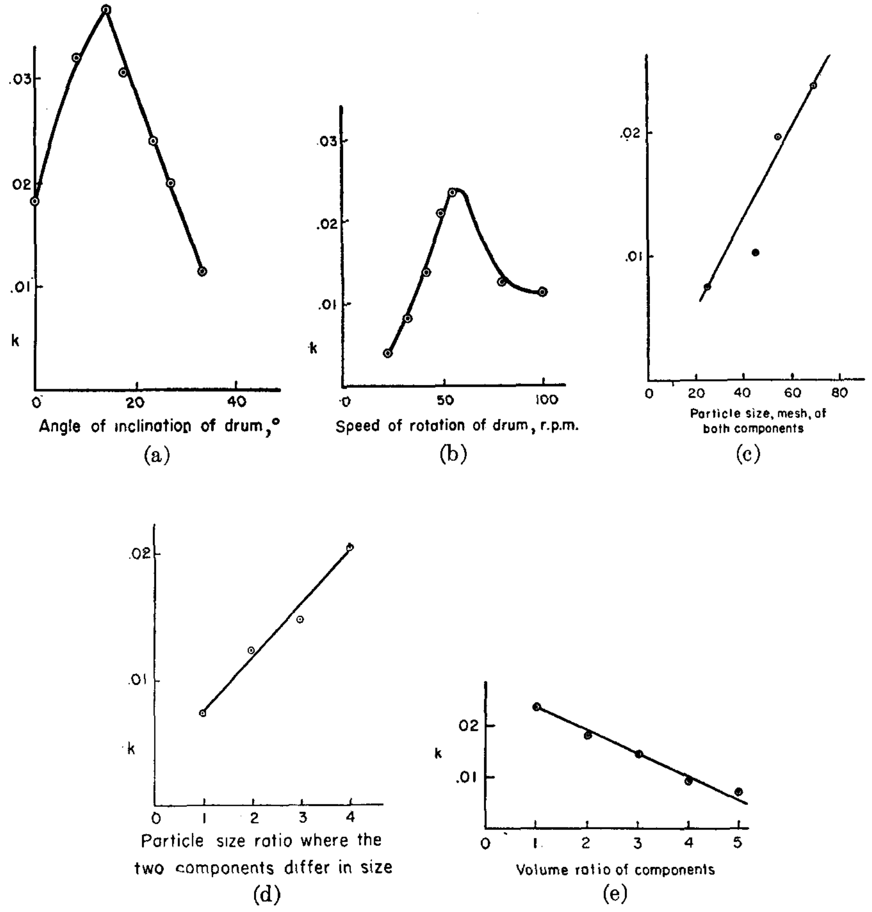
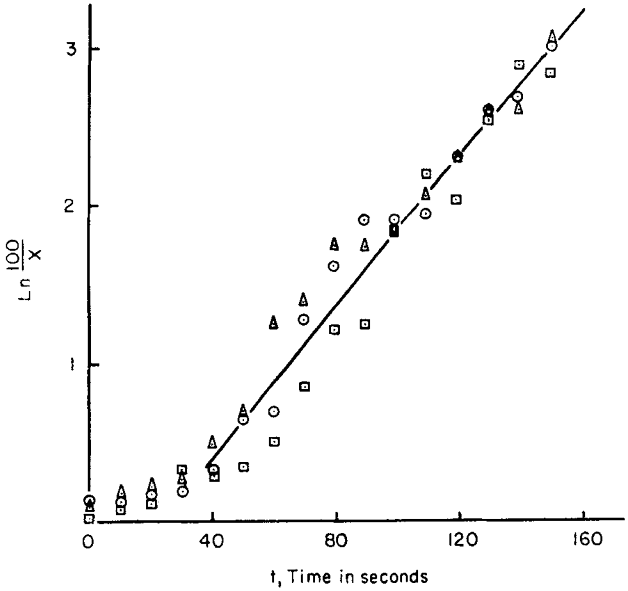


FIG. 41. Manner in which rate constant k, of Coulson and Maitra (C3), changes with different equipment or material variables.

unmixing, the rates of mixing and unmixing being approximately numerically equal. Thus, while a greater size ratio between the two materials being mixed would speed up mixing (see Fig. 41(d)), it would also speed up unmixing. These tests were made with 25-mesh coal, and salt ranging from 25-mesh in some tests to 95-mesh in others. The effects of density differences on mixing were determined with lead nitrate-coal and barium nitrate-coal systems, particle sizes being 70-mesh. The latter system gave better dispersion than could be obtained with the lead nitrate and coal. Also, with the lighter material (coal) loaded on the bottom, the lead nitrate-coal system went through a maximum degree of dispersion, and segregated upon continued mixing. A well mixed coal-lead nitrate system which was put into the mixer segregated upon mixing.

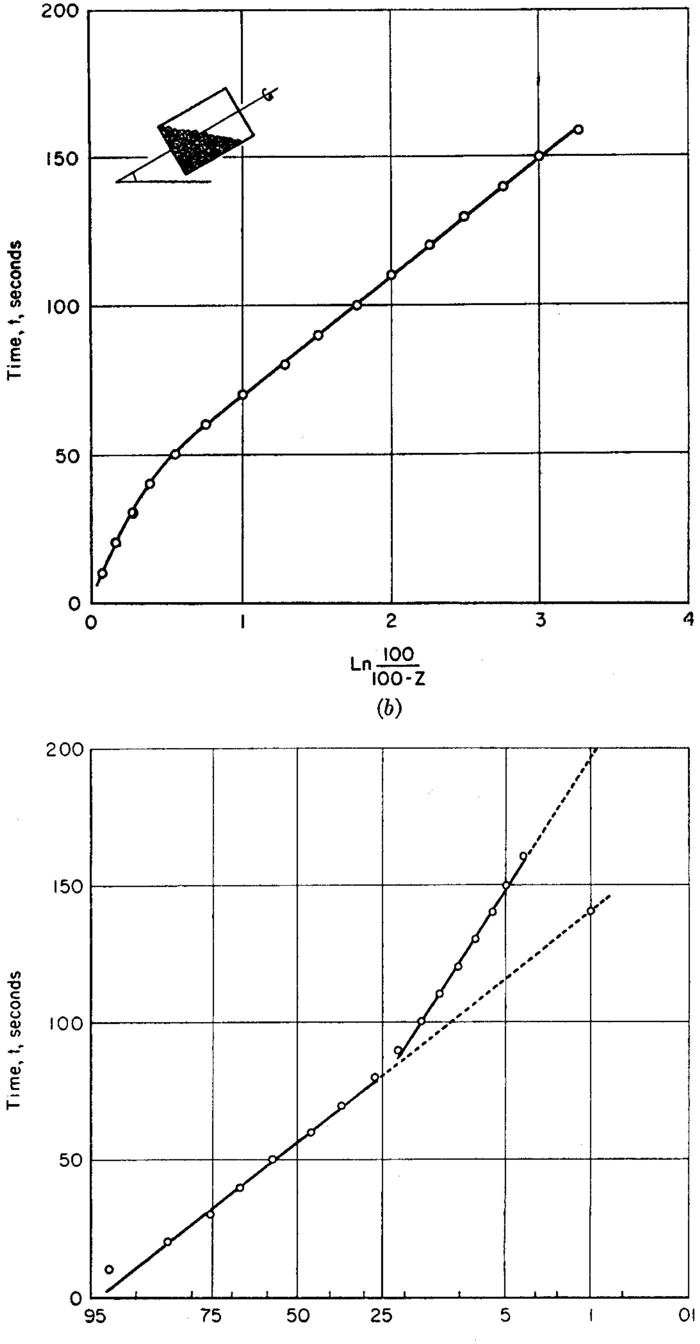


(*a*)

FIG. 42. Data from Coulson and Maitra (C3) plotted in several different ways. System: 70 mesh coal and 70 mesh salt mixed in a cylinder at a 23° angle with the horizontal. Speed 55 rpm. (a) Original graph given by Coulson and Maitra showing replications. X = per cent unmixed (C3). (b) Replot by Visman and Van Krevelen using Coulson and Maitra's method but with horizontal and vertical axes switched (V1). (c) Visman and Van Krevelen's probability paper replot of Coulson and Maitra's data (V1).

Figure 41(e) shows that increase in volume ratio of the two components causes k to decrease.

Although primarily concerned with a certain type of rate plot, Visman and Van Krevelen, in replotting the data of Coulson and Maitra, have postulated a reason why a break in their rate plot occurs. Since this has a bearing on equipment performance, it will be discussed here even though Visman and Van Krevelen did not actually perform any experiments themselves. Figure 42 shows the probability paper plot of Coulson and



(*b*)

(*c*)

FIG. 42 (*Continued*)

Maitra's data, together with the original method of plotting, for a 70-mesh coal-salt system in a rotating drum at an angle of 23° with the horizontal and a speed of 55 rpm. Visman and Van Krevelen explain the break as follows: at the start of mixing one substance was loaded on top of the other so that the top surface of the sloping portion was almost entirely made up of one substance. When however, sufficient mixing had been obtained to give a mixture of two kinds of particles on this surface, an unmixing effect became appreciable due to differences in the manner in which the two substances roll down the surface. This segregating tendency slowed down the subsequent rate of mixing.

4. *Horizontal Rotating Cylinder* (W2)

Although this paper has been mentioned in several other sections, the segregation phenomenon reported warrants a separate discussion here under Equipment Performance. Using a horizontal rotating cylinder of $5\frac{13}{16}$ in. in diameter and $8\frac{5}{16}$ in. long, Weidenbaum and Bonilla mixed 40 to 50 mesh (U.S.) salt and sand, initially loaded on opposite sides of the cylinder. After a long period of mixing, it was found that the sand concentration was higher in the center of the mixer than at the ends. This segregation was attributed to differences in tumbling properties between salt and sand and to tumbling surface curvature near the end faces. The higher angle of repose of salt was believed to give a smaller horizontal component towards the center of the mixer to the salt particles than to the sand particles as the materials tumbled, thus giving more salt near the end faces and more sand in the center portion. Figure 43 illustrates the concentration gradient existing after mixing.

5. *Cylinder Rotating at Angle with Horizontal* (B4)

By using identical sands (except for color) in a cylinder inclined at an angle with the horizontal, Blumberg and Maritz (B4) showed that a random mixture of the two colored sands could be obtained. This is one further piece of evidence which, together with other similar studies of cylinders mentioned, points out that the problem in achieving a good mixture arises when there are dissimilar substances with segregating tendencies. When the substances are identical, except for color—as was the case here—a random mixture can be produced.

6. *Horizontal Rotating Cylinder* (O9)

Again, while phases of this work have been mentioned elsewhere, it is worth emphasizing one aspect related to equipment performance. This is the fact, that when identical but differently colored sands were mixed (Sōma sand—half colored with Rhodamine B and the other half colored with methylene blue), the rate equation mentioned in Section V, B was followed throughout mixing. However, when two different sands were mixed (Toyoura sand and Chigasaki sand), an irregularly shaped graph of $1 - M$ *vs.* t was obtained, rather than a straight line. Although large spot samples were taken in the case where two different sands were mixed, and small ones where sands differing only in color were used, these differences should not cause the change in the rate curve which occurred.

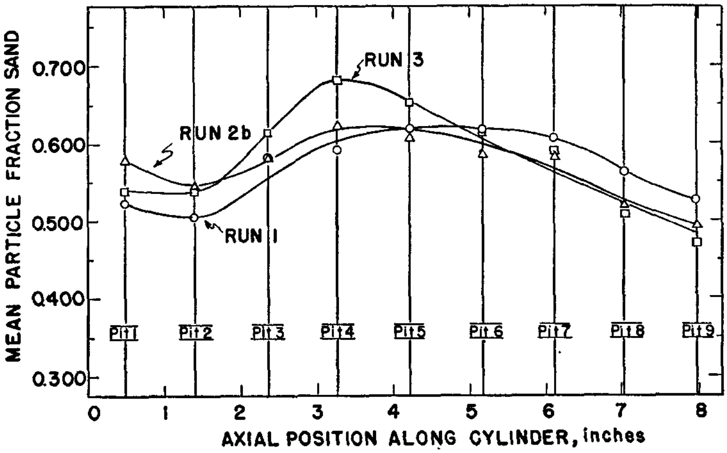


FIG. 43. Axial concentration gradient after a long period of mixing (W2). System: −40 to +50 (U.S.) mesh sand and salt in a horizontal cylinder rotating at 45 rpm; approximately one-third full.

Rather this is indicative of a segregating tendency between the two sands in this particular mixing system, and appears to be similar to the effects reported by Weidenbaum and Bonilla (W2).

7. *Comparison of Several Mixers* (A1)

Adams and Baker used the methods previously described in Section III, D, 21 and Section IV, F to test four common types of blenders. They blended natural polythene granules with black granules which contained additives. The particles were cubes of $\frac{1}{8}$-in. side, or cylinders or spheres about $\frac{1}{8}$ in. in diameter.

Their results, using the three test criteria, are summarized in Table V. The large rotating cubes are seen to have given the best results. However, since several sizes were not tried for the other types of equipment, no positive conclusions can be made on the basis of the data presented.

8. *Sigma Mixer* (S5)

In testing an equation which he gives for calculating the theoretical variance of samples taken from a randomly mixed batch of two materials, P and Q, Stange uses data for a laboratory mixer which he refers to as "an older model of the Werner & Pfleiderer firm, Stuttgart." This is a sigma-blade mixer, which ordinarily is used for sticky materials rather than dry solids. The systems mixed are shown in Table II. Using a simplified version of the equation for the standard deviation for a random mixture, Stange calculated this quantity for the three systems. He then showed graphically, using 90% and 98% confidence limits, that in all three cases a random mixture of the systems shown was achieved. The fact that this could be done even in the system for 3 F, in which there was a particle size ratio of approximately 4 to 1, is worthy of note. This was achieved, according to Stange, by the addition of 2 wt. % distilled

TABLE V

DATA ON THE PERFORMANCE OF DRY SOLIDS MIXING EQUIPMENT[a]

[System: Natural polythene granules (sp. g. = 0.92)—black polythene granules (sp. g. = 1.2) containing additives.
Size: Cubes of ⅛" side, and cylinders or spheres about ⅛" in diameter.]

Type of blender	No. of turns	Fraction of samples outside of 90% "control" limits	If trend was indicated, No. of consecutive samples either above or below mean	Probability that the distribution of black particles in the samples came from a random mixture
Double cone	500	0.55	12 above mean 15 below mean	<0.01
Double cone (control)[b]	500	0.02	no trend	0.7
Ribbon blender, type A	not given	0.37	9 above mean 9 below mean	<0.01
Ribbon blender, type B	not given	0.22	7 below mean	<0.01
Twin-shell blender	100	0.18	7 above mean	0.025
Twin-shell blender	300	0.31	no trend	0.005
12" cube	320	0.25	no trend	<0.01
18" cube	250	0.14	no trend	0.2
48" cube	—	—	—	0.2 to 0.75 (range over a dozen results)

[a] Tabulated from Adams and Baker (A1).

[b] Materials mixed were almost identical except for color.

water to those systems in which there was a difference in particle sizes between the two components being mixed.

9. *Comparison of Several Mixers with Different Materials* (G2)

Gray presented performance data for the mixing of three types of particulate solids in several of the commonly used kinds of dry solids mixing equipment. A probe containing a light and photocell was used for obtaining measurements related to composition of the material adjacent to the photocell, and the standard deviation of the reflectivity probe readings was used as a measure of the uniformity of composition of the solids mixtures. Three solid-solid systems were used as follows: sand-ilmenite, barium sulfate-ilmenite, and aluminum oxide–ilmenite. The principal conclusion reached was that the rate of mixing obtained depended on the properties of the solids mixed, as well as the type of equipment. When segregating tendencies were diminished, there were fewer differences among the various pieces of equipment. Detailed graphical and tabular comparisons were given by Gray for the various machines, and a summary of some of the highlights of Gray's data is shown in Table VI. The method of loading the materials was shown to affect the rate of mixing in the ribbon mixer.

An analysis of this work indicates the complexity and large number of variables involved in mixing. For example, Table VI shows that a V mixer rapidly mixed sand and ilmenite to a degree of mixing which did not change appreciably with further mixing. However, in the case of aluminum oxide and ilmenite, after 92 minutes the mixing still seemed incomplete. This apparent enigma might be explained by the possible segregation tendencies of sand and ilmenite balancing out the mixing effect after a certain level of mixedness was reached. However, where segregating tendencies were probably not as great (as with aluminum oxide and ilmenite), mixing would continually improve, although much more slowly as the driving force decreased due to the batch becoming better mixed. This one item, of which there are probably several others that careful scrutiny of the original paper will reveal, illustrates the complexity of analyzing the solids mixing operation.

10. *Finger-Prong Mixer with Materials Having Varying Moisture Content* (M4)

Using a small finger-prong mixer (7.2 cm. wide × 10 cm. long × 10 cm. deep), Michaels and Puzinauskas studied the effect of water content and volume of solids on mixer performance. Their work involved mixing a water soluble powder (dextrose), with a clay (kaolinite), and water. The material consistency varied from a dry powder to a liquid.

TABLE VI

DATA ON PERFORMANCE OF DRY SOLIDS MIXING EQUIPMENT[d]

Type of mixer	Volume (cu. ft.)	Speed (rpm)	Total lbs. of material mixed	Range of % ilmenite in spot samples after 10 min.[a]	Minimum range obtained, % ilmenite[a,b]	Time to obtain this minimum, minutes[b]	Did unmixing occur after this minimum?[b,c]
System 1:[e] sand (65–200 mesh)—ilmenite (150 mesh–10 μ)							
(Weight ratio $\frac{\text{sand}}{\text{ilmenite}} = 10$, except where otherwise noted)							
Ribbon—ilmenite loaded at one end	3.2	90	174.9	2.3	2.2	22.3	Not continued much past minimum.
Ribbon—ilmenite loaded on top	3.2	90	108.3 to 174.9	2.3	2.2	22.3	Not continued much past minimum.
Muller	2.75	33.3	108.9	2.8	2.1	108	No, range still decreasing.
V mixer	0.5	32.6	18.15	3.2	3.0	1.22 to 1.84	Slightly, to about 3.6%.
Concrete mixer (sand/ilmenite wt. ratio = 9.1)	15	16.2	269.9	3.6	3.0	3.65	Yes, to about 6.0%.
Planetary paddle	0.42	60 (planetary speed)	17.71	4.2	3.8	38.4	No, range still decreasing.
Conical	3.2	25.8	145.2	5.0	4.7	12.2 to 18.4	Yes, to about 6.0%.
Cylinder	0.67	40	39.6	5.8	5.8	8.7	No
Conical	0.45	32.6	18.15	7.1	7.0	1.84 to 2.45	No

System 2:[e] aluminum oxide (100–270 mesh)—ilmenite ore (65–270 mesh)							
(Weight ratio $\frac{Al_2O_3}{\text{ilmenite}} = 4.0$)							
V mixer	0.5	32.6	18.1	3.6	3.1	92	No, range still decreasing.
Conical mixer	0.45	32.6	18.1	4.1	3.8	2.75 to 3.08	Yes, to 6.3.
System 3:[e] barium sulfate (20 μ to finer than 0.5 μ)—ilmenite (80 μ to finer than 1.8 μ)							
(Weight ratio $\frac{BaSO_4}{\text{ilmenite}} = 5.0$, except where otherwise noted)							
V mixer ($BaSO_4$/ilmenite wt. ratio = 4)	0.5	32.6	8.01	2.1	1.8	21.5	No, range still decreasing.
Muller	2.75	33.3	48.0	2.1	2.1	6.1	Yes, to 3.0.
Ribbon mixer	3.2	90	67.2 and 94.1	1.0	1.0	8.9 and 10	Very slightly, to 1.1%.
Hammer mill	—	single rapid pass	27.2 (mixture from ribbon mixer)	—	about 0.9	—	—

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[a] For 90% of readings; based on interpolated standard deviation of meter readings and assumption that they are normally distributed. Because of the limitations of the photoelectric probe, small agglomerates may still be present even when a very low range is obtained.

[b] Read from graphs and converted by chart given in Gray's paper.

[c] The percentages given here are the ranges in % ilmenite after unmixing occurred.

[d] Tabulated from Gray (G2).

[e] Detailed size distribution of materials are available in (G2). Predominant size ranges are listed here.

going through the intermediate states (in the order of increasing water content) of pellet and powder, pellet, plastic state, and sticky state. Table VII summarizes the general trends in mixing characteristics. The method of measuring degree of mixing is shown in Section III, D, 20. The authors concluded that there was an optimum mixture volume at which *most rapid* mixing occurs for each clay system at a given water content, although the maximum efficiency of utilization of *mixing energy* was achieved at mixture volumes far below this optimum. As indicated in Table VII, the dry solids mixing operation gave the most rapid mixing with the most efficient utilization of energy.

TABLE VII

RELATION OF MIXING CHARACTERISTICS TO WATER CONTENT OF THE MIXTURE[a]

[System: dextrose-kaolinite-water.
Powder A to be blended with a mixture of B + liquid.]

Increasing liquid content of B →

Physical appearance	powder	pellet + powder	pellet	plastic	sticky	liquid
Rate of homogenization	rapid	slow	very slow	rapid	slow	rapid
Power input	low	low to moderate	moderate	high	moderate	low
Efficiency of utilization of mixing energy	very high	fair	fair to poor	very poor	poor to fair	high

[a] From Michaels and Puzinauskas (M4).

The high liquid content system, if run at the proper mixture volume, also gave rapid mixing with efficient utilization of energy. However, the graphs show that at lower mixture volumes the high-liquid content system gave the poorest uniformity after mixing. Since the mixture volume was not varied for the dry solids condition, it was not possible to determine whether this state would have been as sensitive to changes in mixture volume. A variety of graphs is given to enable determination of the optimum conditions, when neither dry solids nor high-liquid content is used. For these intermediate cases, the most rapid mixing occurred when the water-clay ratio was in the neighborhood of 0.3, although this gave low utilization of energy efficiency. More efficient use of mixing energy and mixer capacity could be made at higher water contents without great sacrifice in rapidity of mixing.

This paper gives useful methods for aiding in the selection of optimum conditions for mixing. Also, the observations concerning the physical nature of solid systems of different water contents are of general use. Concerning the specific data given for this mixer, a quote from the paper is worth repeating (M4): "It should be kept in mind, however, that extrapolation of such data to mixing operations carried out in different-size or different-type apparatus, or with different solid-liquid systems, is open to serious objection." In particular, it is well to bear in mind the *small size of the mixer* used in this work.

11. *Machines to Mix Additives with Soil* (S3)

This paper gives performance data for machines used to mix additives with soil. Both batch and continuous mixers are discussed. Details of various mixer characteristics are given and their mixing action discussed. Using the measure of mixing defined in Section III, D, 22, Smith has tabulated mixing coefficients for the various mixers with natural soils.

TABLE VIII

MIXING COEFFICIENTS[a] FOR VARIOUS NATURAL SOILS IN SEVERAL MIXERS[b]

Soil	Plasticity index	Batch mixers, 3 min. mix		Continuous mixers		
		2-arm kneader	Muller	Centrifugal disk	Reducing helix	Reciprocating conveyor
Sand (91% below 5 mesh, 12% below 200 mesh)	0	100	125[c]	15.9	—	38.5
Silt	3	67	29.4	22.2	20.4	45.5
Dunkirk clay	15	28.5	26.3	18.2	22.7	50
Marshall clay	33	20.8	16.7	—	27.8	83

[a] Crudely hand-mixed soil, with the additive still plainly visible, gave mixing coefficients of 7 to 12.

[b] Compiled from data of Smith (S3).

[c] 1.5 min. mix.

Table VIII, which is a combination of two of Smith's tables, shows the necessity for choosing the proper mixer for the particular soil to be mixed; for example, although the two-arm kneader and muller mixed very well with sand, they did not do well with the Marshall clay. The reciprocating conveyor, however, while it did not mix sand too well, did the best job on Marshall clay.

Smith also gave mixing coefficient *vs.* time graphs for the soils in a laboratory kneader. He stated that whereas small quantities of soil for laboratory or small-scale field tests are mixed in stationary batch mixers such as tumbling drums, mullers, finger-prong mixers, or two-arm kneaders, the large quantities involved in field mixing require continuous machines such as continuous tumbling drums and pugmills, either single-shaft or twin-shaft.

Along with his own experimental results, Smith summarizes other papers related to soil mixing. He gives graphs from papers which, although evidently unpublished, had been presented at various meetings dealing with road construction problems. These graphs, from papers by Baker (B1) and Clare (C2), give quantitative evidence that the strength and performance of soil-cement improves with increasing thoroughness of mixing. Again referring to Clare, Smith discusses when it is economically justifiable to incur added expense of thorough mixing, and when it is not.

TABLE IX

Dimensions of Machines Used for Mixing Additives with Soil[a]

Mixer type	Dimensions
Centrifugal disk	14-inch disk rotating at 1750 to 3500 rpm.
Reducing helix	Chamber: 14 in. maximum diameter 4 in. diameter at discharge. Agitator driven at 228 rpm by a 5 hp motor.
Reciprocating conveyor	Cylinder: 4 in. diameter and about 4 ft. long. Motor size: 10 hp. Shaft speed: 39 to 69 rpm.
2-arm kneader	No dimensions given, but it was called a laboratory kneader.
Muller	No dimensions given.

[a] Compiled from data of Smith (S3).

He states that excessive amounts of power are not required to achieve high uniformity, even in plastic soils, in the appropriate mixer, although the mixing of dry, free-flowing soil requires less power than that of wet plastic soil. The maximum energy used for mixing by the *Ko-Kneader*, at various conditions of plasticity and at throughput rates between 200 and 750 pounds per hour, was 1 HP-hr. per ton of soil mixed (power load on the empty machine was 2 HP). Traveling in-place road mixers use less energy for mixing, Smith reported, the *Madsen Road Pug* requiring about 0.5 HP-hr. per ton and the *Wood Roadmixer* 0.75 HP-hr. per ton, for both mixing and propelling the vehicle. The *P and H Stabilizer* was reported as using 1 HP-hr. per ton for propulsion, excavation of the soil, and mixing.

Since mixer size was not varied for any machine, the effect of this variable on performance cannot be determined, although it probably would affect the mixing performance. The dimensions of the mixers tested are therefore listed in Table IX.

In his conclusions, Smith also covers some general information, besides the specific tests on mixers and soils of Table VIII. He states that a stationary mixer is preferable to a traveling mixer for treating heavy soils, especially with trace additives; and also that variation in consistency and moisture content of soils, plus the presence of occasional large stones, must be handled by a commercial mixer. He also states that precrushing of soil fed to a mixer with close clearance is needed, and that good control of the feed rates is important.

12. *Comparison of Muller and Ribbon Mixer* (L3)

In a study prepared for a muller manufacturer, Lofton *et al.* compared the ability of a muller and ribbon mixer to mix minerals, and also dairy and poultry feeds. They concluded that for the particular systems used, the muller produced greater uniformity in a shorter time, and that feeds mixed in the muller had less of a tendency to segregate upon further handling than those mixed in the ribbon mixer. Six of the 25 runs tabulated in the report (L3) are summarized in Table X, to give some idea of the type of data taken and the method of expressing results. There were several instances where the average of the samples was higher than the per cent tracer added, indicating that more representative sampling would have been desirable.

The segregation tendencies of the mixed feed materials were studied, utilizing the dry dairy feed for the test, and by employing a *Ro-Tap Soil Analyzer* and nested screens upon which the mixture was placed. On the basis of analysis for NaCl in one sample for each mixer, before and after shaking, it was concluded that there is considerably greater tendency for the feed mixed in the ribbon mixer to separate on handling than for that mixed in the muller. More samples would have been desirable in order to get an idea of the variation in NaCl content within the mixtures from each mixer, both before and after "tapping." This would have permitted a better evaluation of the significance of the difference between the mixtures after tapping.

Lofton *et al.*, mention some theoretical background for the case of mixing two materials, each with a known content of a common tracer material. In their introductory portion, they show diagrams to illustrate the effect of mixing on the distribution of tracer fraction in spot samples from a batch in which each of the two materials being mixed originally had a different fraction of a common tracer.

TABLE X
Data on Performance of Dry Solids Mixing Equipment[a,b]

Type of mixer	Dimensions	Material mixed	Rated capacity, lb.	Number of lb. mixed	Speed (rpm)	% Tracer added	Number of samples taken	After 1 minute mixing time, % tracer in samples	
								Average	Range
Muller	mixing chamber, 48″ diam.	limestone (mineral feed)	500	500	42	0.90 KI	4	0.93	0.04
	depth 32″	dairy feed	200	190	25	1% NaCl, 5% molasses	4	0.97 (NaCl)	0.31
	2 rollers with 25″ diam. and 5″ face	poultry feed	200	200	39	1% NaCl (dry run)	4	1.05	0.04
Ribbon	36″ long 20″ wide at the top	limestone (mineral feed)	cover axle by approx. one inch	400	35	0.90 KI	3	1.18	0.48
	21¾″ deep-dished bottom	dairy feed		100	35	1% NaCl, 5% molasses	3	0.90 (NaCl)	0.43
		poultry feed		100	35	1% NaCl (dry run)	3	1.39	0.27

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[a] Only a few of the 25 runs are summarized here. Further details are given in the report (L3).

[b] Tabulated from Lofton *et al.* (L3).

13. *Helical Flight Mixer* (G3)

Data concerning helical flight mixers with a magnesium sulfate–sodium bicarbonate system were given by Greathead and Simmonds, together with a description of the types of particle movements which they felt occurred in this type of mixer. They mention coarse mixing, which takes place by movement of slugs of powder through the material, and fine mixing, which occurs at the boundaries between moving and stationary material. They postulate that local bulk density changes in the wake of the moving blades may cause segregation as the powder settles back behind the blade. This they compare to the ore-dressing operation known as "jigging."

The effects of several variables are depicted by plots of all the individual sample compositions *vs.* time. Although this procedure does have certain advantages in following changes in composition at individual sample locations, it is difficult to use in making overall comparisons. Thus, for example, it is not clear how the conclusions concerning the effects of particle size and density were arrived at. By computing standard deviations and using statistical methods to determine the significance of differences, a clearer picture of the effects of the several variables could be obtained. Where this was done, e.g., following the change in standard deviation during the further handling of the batch after mixing, the manner in which the conclusion was arrived at that there was segregation due to subsequent dumping and conveying, could be understood.

14. *Twin Shell Blender* (Y2)

In a paper dealing with the V-type mixer, Yano, *et al.* studied the mixing of $-100/+200$ mesh (Tyler) anhydrous sodium carbonate (Na_2CO_3) and polyvinylchloride. Two very small mixers were used, with working capacities of ¼ liter and 2 liters respectively. Several graphs were plotted to illustrate the influence of the per cent of the total volume occupied by the mixture, relative amounts of the two ingredients, method of loading, and rpm of the mixer. The optimum rpm for obtaining the smallest standard deviation among spot samples was reported at about 50 rpm for the larger mixer and about 60 rpm for the smaller one. Details on the other variables are given in graphs for which there are English titles, although the article is written in Japanese.

The graph of speed *vs.* degree of mixing, which, for the small mixer, extended from 7.8 to 158 rpm, showed that rather poor mixing was obtained at either very low or very high speeds. Although both of these mixers are on a laboratory scale, it would be of interest to see whether the actual operating speeds of the commercial units of comparable sizes are close to the optima reported by Yano *et al.* Of course, their optima apply to the specific system tested.

To help in evaluating this paper, the writer checked the speed of an available commercial unit which handles five laboratory sizes of the above type of blender. It ran at 34 rpm, which is a constant speed for all five sizes, since the same motor and gear drive are used in all cases; only the method of mounting the different size blenders varies. The commercially available blenders corresponding to the sizes mentioned by Yano *et al.* were about one-third full when loaded to the stated working capacity. A subsequent paper by Yano, Kanise, Hatano, and Kurahasi (Y1), indicated that an F/V percentage of 13.5, which was used throughout most of this study, would correspond to loading the mixer about one-third full. (F = real volume of the charged powder and V = inner volume of the mixer.) It might be worth investigating whether drives for several sizes of small blenders should have adjustable speeds to enable choice of the optimum speed for any size.

15. *Comparison of Several Mixers* (Y1)

A study of the comparative performance of several types of mixers was made by Yano *et al.* (Y1). They worked with two small sizes of each of the following: cube, double cone, horizontal cylinder, and twin-shell types. A short summary, as well as the titles of the figures and tables, were in English, but the remainder of the paper was in Japanese. Study of the graphs, tables, and English summary revealed a certain discrepancy between Conclusion 3 in their English summary and that indicated from their Table 2. Conclusion 3 stated that the cube and V-type (twin-shell) blender gave lower values of standard deviation than the double cone or horizontal cylinder mixers, but took a larger number of revolutions to reach their minimum standard deviations: Table 2 of the same paper indicated that a typographical error may have been made in that conclusion, since the opposite was the case.

From Table 2 of the above paper (Y1), the following conclusions were drawn:

1. In the very small sizes (inner volume = 741 cc.), the horizontal cylinder mixer gave the lowest standard deviation (1.1%), and the twin-shell blender the highest (2.6%). In the larger sizes (inner volume = 5,630 cc.), the lowest standard deviation attainable for the various blenders ranged from 0.9 (double cone) to 1.4 (twin-shell). It is not clear from visual observation alone which differences are significant. Confidence limits would have been helpful here for the interpretation of results. Thus, an approximately eight-fold increase in volume of all the blenders greatly reduced optimum standard deviation differences among them. For all

but the horizontal cylinder, which was not affected, this increase in volume was associated with a cut in the standard deviation of roughly half. This emphasizes the dangers of attempting to apply directly the results of experiments on small blenders to large ones, without adequate scale-up information.

2. The range of optimum volume per cent charged for the four types of mixers includes 31% in all cases.

Graphs were given to show the effect of rotational speed and volume per cent loaded, although they do not reveal how the values in Table 2 of (Y1) were arrived at, in certain cases.

C. CRITICAL EVALUATION OF PUBLISHED PERFORMANCE DATA

Because of the dearth of objective published data on the comparisons of various blenders, one may be tempted to place undue emphasis on the few papers that have been published. This may be harmful, because scrupulous attention to one or two particular tests, without considering the broader view of the capabilities of certain types of mixers, can lead to just as erroneous a conclusion as blindly choosing whatever particular mixer is handy when a certain job must be done. Just as certain questions should be asked when choosing a degree of mixing, as was previously pointed out, so should the following questions be asked when attempting to use published data as a guide to choosing a particular mixer for a specific application:

1. What are the major conclusions of the study? For example, although Gray (G2) did rate several mixers for several systems, his principal conclusions were that the rate of mixing depended on the properties of the solids mixed, as well as the type of equipment, and that when segregating tendencies were diminished, there was less difference in performance among the various pieces of equipment. Therefore, to attempt to use the graphs and tables given by Gray as a general guide to which mixer is "best," is to go far beyond the limitations of Gray's exploratory study.

2. Is the type of mixer used in a particular test best suited for the materials? For example, Bullock's discussion of mullers (B7), cautions against their use for materials which are too fluid or too sticky, although he states that if used in the proper ranges, mullers are well suited to the breaking down of aggregates. Obviously, therefore, a study of the mixing action of a muller, made on materials outside of the ranges advised for them, would not prove that the muller was not a good mixer just because the results of such a test indicated poor mixing.

3. Has the effect of size been considered in the comparisons of mixers? For example, in Adams and Baker's paper (A1), the larger cube machines

gave better results than the smallest one, but the size of the other blenders was not varied, and in fact, was not even stated.

4. Is the mixer being run at optimum conditions? For example, in the case of a commercial mixer which is not run at the recommended speed and volume fraction loaded, poor blending does not necessarily mean that the mixer is no good.

5. What method was used to measure the degree of mixing and how does this relate to the needs of the particular mixing operation for which the published data are being studied? For example, Bullock (B8) pointed out the limitations of the reflectivity probe used by Gray (G2) in differentiating between uniform mixes of aggregates and mixes of ultimate particles.

Despite the above precautions that are necessary in evaluating the published data, there is considerable value in the latter in providing objective bases for the choice of mixers. Because of the large variety of machines and materials, much more data on the performance of various solids mixing machines with different types of materials is desirable. A standard testing procedure for dry solids mixing equipment would help in the most efficient accumulation of meaningful data of this type. Such a procedure should pool the knowledge of equipment building and process points of view.

D. Summary and Conclusions and Related Thoughts—Equipment Performance

1. Several criteria have been used in various studies to judge the performance of dry solids mixing equipment: *a.* the uniformity of the batch with regard to either composition or some other property, *b.* the time required to achieve a certain uniformity, and *c.* the power required to mix the batch to a certain degree of uniformity. Most studies have dealt with either *a.* or *b.* Complete quantitative performance criteria should cover all three of these aspects.

2. There are several other factors besides these, however, which will influence the suitability of a particular mixer for a specific application. Such things as ease of cleaning in a case where contamination can be ruinous, or dust proofing, are typical practical considerations which must be taken into account. Although these were not discussed for the various performance tests, it should be borne in mind that they must automatically be considered before choosing a mixer.

3. Ambiguities in certain previously reported test results stress the need for using clear cut objective methods for determining mixing performance. (See Section III.)

4. Several tests on the performance of rotating mixing cylinders, both horizontal and inclined, have been made. A correlation, involving speed, diameter, and volume per cent loaded, has been given for horizontal cylinders. Conditions under which segregation during mixing has occurred are reported for several cases. This segregation is attributable to differences in properties between the materials being mixed. Such things as size, shape, and density differences can cause segregation. Where differently colored but otherwise identical sands were mixed in an inclined rotating cylinder, statistical tests on the data proved that a random mixture was achieved (B4). Graphical evidence has been published (O9) which indicates that, where differently colored but otherwise identical sands were mixed in a horizontal rotating cylinder, a randomly mixed batch was achieved.

5. A few equipment comparison studies have been made. In evaluating these, it is important to bear in mind certain check points which bring out limitations to the studies as well as to their use as guides. These studies do not all clearly point to any particular piece of equipment as being consistently superior. Rather, their careful scrutiny indicates that relative performance varies with the materials mixed as well as equipment size. Therefore, while the comparative studies may serve as rough guides for similar systems, the present limited published knowledge along these lines requires that an individual test be made when considering a particular application. It is very dangerous to generalize from the few reported results to other situations, since it is clear that the material to be mixed, as well as the kind of machine to be used, affects the flow patterns and effectiveness of mixing.

6. The effects of many different variables on the performance of different pieces of dry solids mixing equipment have been shown. Some of these are particle size, shape, density, and mixer speed and volume fraction loaded. Also the relative proportions of the materials being mixed has been studied for certain cases.

7. Published performance data on various pieces of equipment and different materials is still relatively scarce. More of this work would help in the selection of equipment and in the understanding of the effects of equipment and particle variables. Examples which clearly illustrate sound methods of measurement, calculation of product uniformity, and control of product quality; and photographs of mixing and particle movements, would also be helpful in developing this area.

8. A standard testing procedure for dry solids mixing equipment which was available as a means of evaluating equipment performance would help in the most efficient accumulation of meaningful data of this type. Points of view of the men who build and sell the equipment and of

those who must use it in processing should be taken into account by such a procedure. It would, of necessity, have to be flexible.

9. Scale-up relationships should be developed and experimentally investigated. Performance studies, in which various sizes and types of blenders have been used without provision for determining the effect of size, leave a big question mark as to the true relative merits of the different types of blenders.

10. Much can be gained in industrial practice by simply checking operational procedures where solids mixers are concerned. For example, a mixer rated at a certain capacity may, due to production expansion, be overloaded—with detrimental effects on the blend it produces. Or somehow, it may be underloaded, which, besides giving a less than optimum operating condition, can also be costly in that it does not make the fullest use of available plant capacity. These conditions may sometimes also affect related labor costs. Other "obvious" factors, such as making sure that the correct weights of materials are going into the mixer, are worth checking on. The possible loss of material as dust is another good point to check, particularly if there is strong suction in the dust collection apparatus for the mixer. And, as previously stated, the solids mixing operation must be checked from the point of view of delivering a well mixed batch to a certain point. Although this work has mainly dealt with the mixer itself, the subsequent travel of the mixed batch must be scrutinized for possible segregating points, such as long drops or flow through silos.

VII. Overall Concluding Comments

The published literature concerning the field of dry solids mixing is presently emerging from a primarily descriptive explanation of the equipment used, to methods for quantitatively dealing with this unit operation. Several points of view are involved in this transition. The process control point of view looks for statistical ways to treat the solids mixing operation, so as to produce an output within certain specifications. The equipment building point of view has tended to rely heavily on individual tests, with non-statistical judgment as to whether the final product is well mixed. A number of publications have dealt with the development of methods for evaluating extent of mixedness. Some of the concepts most fundamental to chemical engineers in other unit operations have barely been touched upon. Rate constants are still largely academic. Mechanisms of mixing are only sketchy hypotheses. However as more of the pieces of the puzzle are put together, usable methods are emerging which will enable a systematic attack on improving solids mixing performance. Elimination of inefficient mixers with dead spots may yet come out of rate studies. Easy check methods for quantitatively determining optimum operating conditions are breaking through the complicated and sometimes not too easily understood statistical procedures. Theoretical frequency distributions, which permit an understanding of the equilibrium state of the randomly mixed batch, have been investigated and checked against experimental data. They are no longer an oddity, but are on the threshold of broad application, and their proper use in certain problems, for example, the nut problem mentioned in Section III, C, 2, c, iv, can avert unnecessary experimental work and, perhaps, striving for impossibilities. Performance data, after years of neglect, are beginning to appear in increasing amounts in the published literature.

This all adds up to the following picture. Useful methods are now available to carry out fruitful investigation of both the experimental and theoretical aspects of the unit operation of solids mixing. They are still not widely used, but rather appear to be considered a novelty by many people with great practical experience who might make the best use of them. This is not surprising, because their presentation has not been in a streamlined, easy-to-use form, but rather it has involved a groping attempt to apply ideas without too much concern for making them easily understood and used.

What is now needed is much more performance data for many different types of mixers and combinations of materials, properly collected and interpreted, so as to put to effective use for industry the considerable amount of exploratory knowledge now available.

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Nomenclature

Symbols are defined at the point of their introduction in the text.

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