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CONTROLLING THE CONSISTENCY OF ENAMEL SLIPS

BY

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By W. N. Harrison

ABSTRACT

The purpose of this work was to study vitreous enamel slips in order to develop adequate means for measuring and controlling their consistency under plant conditions.

A suitable laboratory means for determining their consistency was first selected, and the effect of various factors upon consistency determined by this means. In order to learn something of the mechanism by which changes in consistency take place, observations were made upon the physicochemical nature of the different phases of several typical slips; also, the state of flocculation of the finer particles of suspended matter was observed under different conditions known to produce slips of different consistencies.

A simplified method of determining consistency, suitable for plant use, was then devised, and the work carried into the field. This simplified means was put into use in conjunction with other tests in order to obtain data for correlating consistency as determined by this method with the working properties of the slips.

The conclusions reached may be summarized as follows:

The constitution of enamel slips.—An enamel slip has two or more solid phases, in various states of subdivision, which can be roughly classified into those particles large enough to require support to retard settling, and those small enough to contribute to this support. There is also a liquid phase made up of water with different kinds of matter in solution.

Fundamental factors governing consistency.—The major factors which control the consistency of an enamel slip are (*a*) the kind and quantity of colloidal matter present, (*b*) the degree of flocculation of this matter, (*c*) the percentage of water in the slip, and (*d*) the size of the particles which have to be supported by the colloidal structure.

Measurement of properties which describe consistency.—The effects of variations in the above-mentioned factors can be measured and expressed in terms of mobility, yield value, and "set." A special simplified method can be used for factory work to determine "relative mobility" and "relative yield value." The apparatus required for factory work consists of a graduated tube with capillary outlet, a flat metal shape with a wooden rack, a scale calibrated in tenths of an ounce or grams, and a stop watch. No calculation more difficult than simple division is necessary.

Obtaining slips of desired consistency.—Mobility is controlled by the water content. Yield value is controlled by the colloidal content and the state of its flocculation, which are dependent upon such factors as amount and kind of clay, amount of grinding, amount of aging, kind and amount of salts addition. "Set" is partially dependent upon yield value and mobility but in any given slip can be increased by adding salts or decreased by allowing the slip to stand before use.

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I. INTRODUCTION

The problem of reproducing enamel slips of a definite consistency has attracted considerable attention in the vitreous-enameling industry. Slips made by procedures considered identical in shop practice often differ widely in their working properties, and the adjustment entails delay and uncertainty of results. In order to obtain data upon which to base recommandations for the improvement of this condition, and which might at the same time lead to further beneficial modifications in present practice, the Bureau of Standards undertook a study of the factors affecting the consistency of enamel slips. In investigating this subject the author has received the generous help of various parties which he wishes to gratefully acknowledge. R. R. Danielson has given the problem the benefit of his suggestions throughout. Karl Lagenbeck and W. H. Herschel have given valuable opinions concerning colloidal phenomena and plastic flow, respectively, in their relation to the problem. R. D. Cooke, B. T. Sweely, and R. R. Fusselbaugh generously offered the commercial facilities at their disposal, and were personally responsible for procuring a large amount of the factory data.

II. REVIEW OF LITERATURE

A method for studying differences in the consistency of enamel slips was described by Shaw in 1917.[1] This method was to allow a definite quantity of material to flow from a cylinder through two tubes of different sizes. The ratio of the quantity which flowed through the large tube to the quantity which flowed through the small one was assumed to be proportional to viscosity. Without entering into the validity of this method for use with truly viscous liquids, it appears in the light of subsequent developments that it rests upon a fundamental assumption which is not applicable to enamel slips,

[1] J. B. Shaw, "American clays for floating enamels," Trans. Am. Cer. Soc., **19**, p. 349. (A review of this method appears in "Enamels for Sheet Iron and Steel," by J. B. Shaw, B. S. Tech. Paper No. 165, p. 40.)

namely, that consistency can be expressed by a single numerical value. While a single value is sufficient to express the consistency of a material such as a common mineral oil, which is deformed in amounts proportional to the stresses applied, more than one value is necessary to express the consistency of a material which does not follow this law, such as an enamel slip.[2] This criticism, of course, applies equally well to any method which rests upon that assumption.

More recently there have appeared two other notable papers concerning the consistency of enamel slips. The first, by Cooke,[3] describes an adaptation of Bingham's [4] conceptions and methods of measurement of consistency to the field of enamel slips. According to this conception an enamel slip is plastic instead of viscous, and its consistency can be expressed in terms of the two components of plasticity, namely, mobility and yield value.[5] The more important conclusions of the work were: (*a*) Raising the temperature increased the mobility without changing the yield value, (*b*) increasing the water content increased the mobility and decreased the yield value, (*c*) increasing the clay content increased yield value without materially affecting the mobility, and (*d*) the addition of magnesium sulphate and other "setting-up" agents increased the yield value without changing the mobility materially.

The other article, by Poste,[6] gives a detailed review of the literature concerning the action of electrolytes and organic matter on clays. He calls attention to the lack of a definite idea of the mechanism of changes in consistency of enamel slips and advances the hypothesis that the addition of a "setting-up" agent flocculates the colloidal matter forming a gel which, with the solid matter, forms somewhat of a continuous structure unless water is present in an excessive amount. Much of this reference relates to the electrolytic theory of the precipitation and suspension of colloids. The purpose of the presentation is stated as being "to stimulate thought and research of a fundamental nature."

III. METHOD OF STUDY

The method of study used in this work was as follows: An adequate means of measuring the consistency of enamel slips suitable for laboratory use was chosen. This means was used to determine the effect of various factors not previously investigated. Also, in order to furnish actual data which might indicate the mechanism by which changes in consistency occur, some observations were made of the physicochemical nature of the different phases of several typical

[2] E. C. Bingham, Fluidity and Plasticity, McGraw-Hill, p. 215; 1922.
[3] R. D. Cooke, "The plastic properties of enamel slip," J. Am. Cer. Soc., 7 (9), pp. 651–655; 1924.
[4] E. C. Bingham, Fluidity and Plasticity, McGraw-Hill, p. 222; 1922.
[5] See Figure 2, and definitions in Section IV, 1, (*c*).
[6] E. P. Poste, "An analysis of the suspension of enamel by clay in terms of the colloid theory," J. Am. Cer. Soc. 8 (4), p. 232, 1925.

slips. Further the state of flocculation of the finer particles of suspended matter was observed under different conditions which are known to produce slips of different consistencies. These data served to suggest means of producing slips approximating the desired consistency, and to indicate the probable mechanism by which changes in consistency take place.

The work was then carried into the factory for practical application. The method of measuring consistency was simplified as much as was consistent with obtaining results sufficiently accurate for plant use. It was used in conjunction with various tests in order to correlate consistency, expressed as mobility and yield value, with the working properties of the slips.

IV. LABORATORY TEST METHODS AND RESULTS

The laboratory tests were made on ground-coat enamels, which probably give the industry more trouble than white cover coats. Three distinct types of enamels were used:

A, representing a high silica; B, a high feldspar; and C, a high borax enamel. Their batch weights and melted compositions are given in Table 1.[7]

TABLE 1

A

Batch weights		Calculated melted compositions	
Ingredient	Parts by weight	Ingredient	Parts by weight
Borax	30.0	Boric oxide	13.67
Feldspar	22.0	Sodium oxide	11.77
Quartz	29.0	Quartz	36.02
Soda ash	5.0	Fledspar	27.32
Soda niter	4.6	Fluorspar	7.46
Fluorspar	6.0	Cobalt oxide	.50
Cobalt oxide	.4	Manganese oxide	2.04
Manganese oxide	2.0	Nickel oxide	1.24
Nickel oxide	1.0		
	100.0		100.02

B

Borax	30.0	Boric oxide	14.02
Feldspar	27.0	Sodium oxide	15.83
Quartz	20.5	Quartz	26.15
Soda ash	9.8	Feldspar	34.41
Soda niter	5.0	Fluorspar	7.65
Fluorspar	6.0	Cobalt oxide	.64
Cobalt oxide	.5	Manganese oxide	1.33
Mangangese oxide	1.2		
	100.0		100.03

C

Borax	39.5	Boric oxide	19.03
Feldspar	20.5	Sodium oxide	14.51
Quartz	22.5	Quartz	29.55
Soda ash	5.0	Feldspar	26.92
Soda niter	4.7	Fluorspar	7.88
Fluorspar	6.0	Cobalt oxide	.53
Cobalt oxide	.4	Manganese oxide	1.08
Manganese oxide	1.0	Nickel oxide	.53
Nickel oxide	.4		
	100.0		100.03

[7] These compositions were taken from "A classification of sheet-steel enamels," by R. R. Danielson, J. Am. Cer. Soc., 3 (12), p. 961; 1920.

1. METHOD OF DETERMINING CONSISTENCY

(a) APPARATUS AND METHOD OF TEST

As a means of expressing the consistency of enamel slips numerically and graphically, Bingham's [8] conception of plasticity as measured in terms of yield value and mobility seemed promising. Cooke [9] showed that these principles are applicable to enamel slips, and modified the Bingham apparatus so as to be suitable for testing them. The modified apparatus was used in this work. The principle of the test is to observe the rate of flow of the slip through a capillary tube at different known pressures and at constant temperature. The apparatus is shown in Figure 1.[10] A burette, with a capillary tube attached as an outlet, is inclosed in a water jacket, through which water from a thermostat is forced by means of a gear pump. The time required for the head of the column of enamel slip to pass successive intervals on the burette is observed by means of two stop watches, used at alternate intervals.[11] When the average rates of flow in the different intervals are plotted against the corresponding "shearing stresses," a series of points in a line is obtained. If the test material is plastic, this line (when extrapolated) intersects the stress axis at some distance from the origin.

(b) CALCULATION OF RESULTS

In order to obtain the various average rates of flow for different average heights of the slip in the apparatus it is necessary only to divide the volume of material which flows between observations by the time required. In order to obtain the corresponding shearing stresses, which are plotted against rates of flow, it is necessary to consider the average height of the slip in each particular interval, its density, and the dimensions of the capillary. The shearing stress, expressed in dynes per square centimeter and designated by the symbol F, equals $\frac{RhDg}{2l}$

where:

R = radius of capillary in cm (computed from the weight of mercury held by the tube at a known temperature).

l = length of capillary in cm (measured with a vernier caliper).

D = density of slip in grams per cubic centimeter (obtained with a pycnometer).

h = average effective height of slip in cm.

g = gravitational const. = 981.

In determining the value of D the slip, at a controlled temperature of 27° C. (80.6° F.), was allowed to run from the capillary directly

[8] E. C. Bingham, Fluidity and Plasticity, McGraw-Hill, p. 217; 1922.

[9] R. D. Cooke, "The plastic properties of enamel slip," J. Am. Cer. Soc., 7, (9), pp. 651–655; 1924.

[10] The essential parts of the apparatus are shown in Figure 7, although the dimensions given in that figure are not for the laboratory apparatus.

[11] A split-second timer may be used to obtain the same readings that can be obtained with two stop watches.

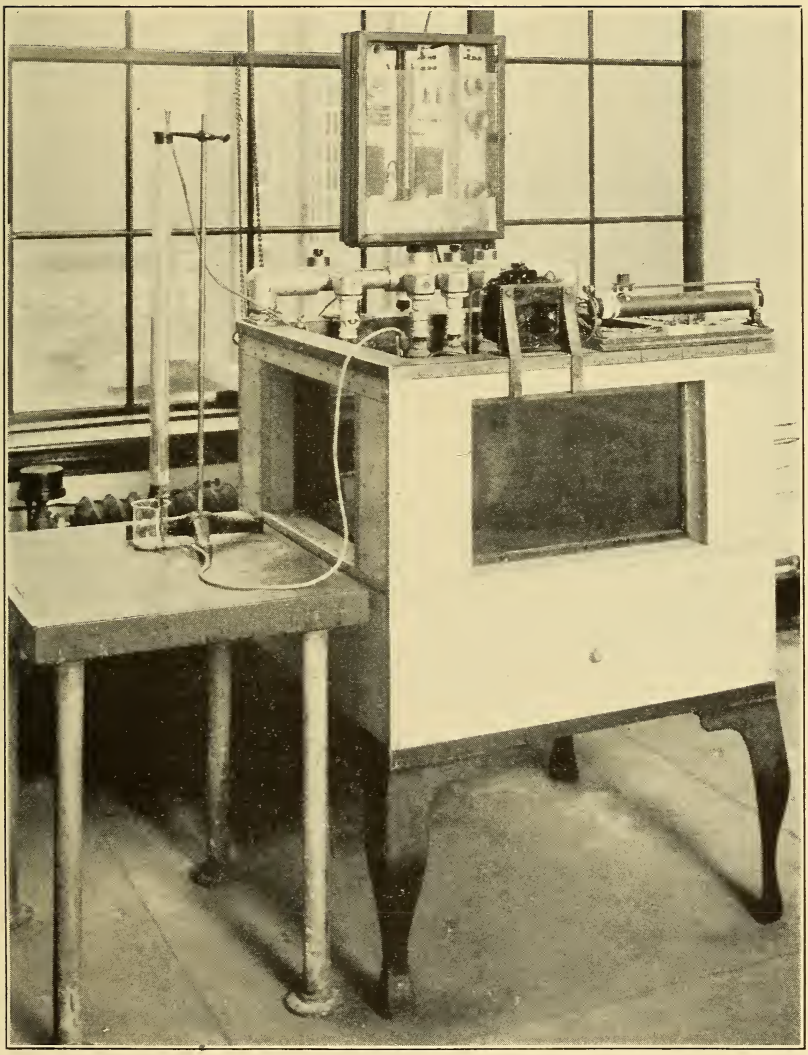


FIG. 1.—*Apparatus used in the laboratory work for measuring consistency of enamel slips*

into the pycnometer, which was immediately weighed. At the time of these tests the room temperature was never more than a few degrees lower than that of the slip under test, and it was computed that the drop in temperature of the slip in the pycnometer before weighing was not enough to cause a significant error in density.

The series of values for h were obtained through the following considerations:

The distance from successive 5 cc marks on the burette to the bottom of the capillary was measured with the aid of a vernier caliper. The arithmetical mean of the heights of two adjacent 5 cc marks may be used as h with relatively small effect on comparative results, but several corrections may be made which, combined, were considered of sufficient magnitude to warrant their use in the laboratory tests of this investigation, especially since their effect upon the position of the curve is not constant for slips of different consistency. The method of making these corrections may be summarized as follows:

The mean hydrostatic head is somewhat less than the arithmetical average and may be obtained from the formula:

$$h=\frac{h_1-h_2}{\mathrm{Log}_e\frac{h_1}{h_2}}$$ (Footnote 12)

where:

h=mean hydrostatic head,
h_1=initial head,
h_2=final head.

Additional correction may be made for the surface tension of the enamel slip, which has to be overcome before it will release itself from the end of the capillary, and which further reduces the effective head by an amount

$$\frac{H}{2}=\frac{T}{rDg}$$ (Footnote 13)

Where:

T=surface tension of the slip,
H=capillary rise,
r=outside radius of capillary,
D=density of slip,
g=gravitational const.=981.

All of these values are known except H and T. T was determined on a few samples of enamel slips and found to be close enough to the value for water so that the latter value (72 dynes per cm at the temperature used) was used throughout in the corrective formula.

Another correction, which is more important when the rate of flow is relatively high, is for internally consumed kinetic energy. This correction also tends to reduce the effective head, and may be obtained from the following formula:

$$h=h_o-\frac{B}{Ct^2}$$ (Footnote 14)

---

[12] Herschel and Bulkley, Ind. and Eng. Chem., **19**, p. 134; 1927.

[13] J. Hartmann, Phys. Rev., **20**, p. 728; 1922.

[14] Winslow H. Herschel and Ronald Bulkley, "Measurement of consistency as applied to rubber-benzene solutions," Proc. A. S. T. M., **26**; 1926. Adapted from equation (1).

where:

$$B=\frac{MQ}{8\pi l}$$

$$C=\frac{\pi gd^4}{128\,Q\,l}$$

h=mean head corrected for kinetic energy,
h_o=mean head uncorrected for kinetic energy,
Q=volume of material which flows between observations,
M=a const. (1.12),
l=length of the capillary in cm,
d=diameter of the capillary in cm.

These corrections, except that for kinetic energy, can be calculated and applied to obtain the effective heads which will be applicable as long as the apparatus (including capillary) is unaltered and slips of approximately the same specific gravity are tested. The correction for kinetic energy changes with rate of flow, but a small table is easily prepared giving the corrections applicable between various limits. Table 2 shows a sample set of data, in which the magnitude of the combined corrections for this particular case may be seen by comparing the arithmetic average heads with the mean hydrostatic heads corrected for surface tension and kinetic energy. The values given for sample No. 1 in this table are those corresponding to curve 2, Figure 2. The values given for sample No. 2 represent those obtained in the check determination, which was always made in laboratory work.

TABLE 2.—*Showing a sample set of data for two check tests. Aging test, ground coat A, seven days aging. (See fig. 2)*

5 cubic centimeter marks	Distance in centimeters from bottom of capillary	Arithmetic average heads	Mean hydrostatic heads corrected for surface tension and kinetic energy	Time of flow in seconds		Rate of flow in cubic centimeters per second		Shearing stress $F=\frac{RhDg}{2l}$
				Sample No. 1	Sample No. 2	Sample No. 1	Sample No. 2	
5	61.85							
		59.57	59.2	16.8	16.6	0.298	0.301	304
10	57.29							
		54.99	54.6	19.6	19.6	.255	.255	281
15	52.69							
		50.39	50.1	23.0	22.7	.217	.220	258
20	48.09							
		45.77	45.5	28.8	28.2	.174	.177	234
25	43.44							
		41.10	40.9	36.6	35.6	.137	.140	210
30	38.76							
		36.41	36.2	54.2	53.2	.092	.094	186
35	34.05							
		31.69	31.5	109.0	101.5	.046	.049	162
40	29.32							
		26.98	26.8	233.0	217.0	.021	.023	138
45	24.64							
		22.27	22.1	373.8	355.0	.013	.014	114
50	19.89							

R=0.0812 cm. D=1.644. l=12.75 cm. $\frac{RDg}{2l}$=5.14.

(c) DEFINITION OF TERMS

The curves shown in Figure 2 are typical of those obtained with enamel slips. Two features of such graphs are important. One is the distance from the origin to the intersection of the "*F* axis" with the line drawn through the series of points. This distance indicates the "yield value." The other important feature is the slope of the line, which represents "mobility."

(1) YIELD VALUE—The yield value is the number of units of stress necessary, under certain assumptions, to start the flow, and is given by the intercept of the straight part of the experimentally determined graph with the *F* axis. For example, the yield value is 133 for graph 2 (fig. 2), but there is in reality some movement of material through the tube at forces less than the yield value.[15]

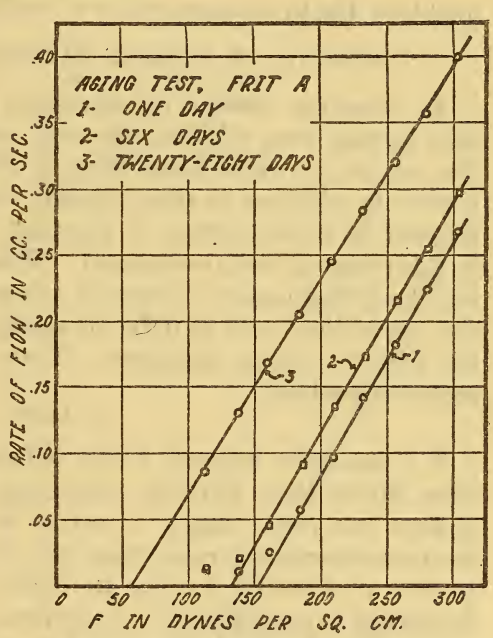


FIG. 2

A high yield value indicates the necessity of a comparatively large force to cause the slip to flow. Of two slips, the one having a higher yield value will, therefore, adhere in a thicker coat to the metal base because it will offer more resistance to removal by gravity and centrifugal force. A very definite picture of the effect of increasing the yield value of a slip can be obtained by any one familiar with enamels when it is realized that the effect of the commonly used magnesium sulphate, and other "setting up" agents, is to increase the yield value of a slip. The quantitative determination of yield value is only an exact measure of a property which has been estimated by rule-of-thumb methods for many years.

(2) MOBILITY.—The difference between two slips having the same yield value but different mobilities would be plainly visible in a comparison of their graph lines, which would intersect the *F* axis at the same point but would have different slopes. Two such

[15] This becomes noticeable in slips of high yield value. It is attributed variously to slippage, seepage, and movement of a solid plug through the tube, so that the considerations involved in normal flow are not applicable. See Fluidity and Plasticity, page 222. Some materials have been shown to have a definite "starting pressure" or force which is necessary to start flow which is lower than yield value, but for the purposes of this work it was not believed necessary to enter into this phase of consistency measurements.

enamels would adhere to the metal base in approximately the same thickness, but the more mobile would drain more easily and quickly, other things being equal, and would have less tendency to clog a spray gun. When two such enamels were given to an experienced sprayer for use, he described the more mobile one as "lighter" and easier to work with.

The slope of the curve varies with the dimensions of the capillary,[16] but for the same capillary a greater slope indicates a greater mobility. In this work all comparative readings were taken with the same capillary in order to obviate any difference in results that might be due to changes in size of capillary.

2. EFFECTS OF VARIOUS FACTORS UPON CONSISTENCY

An adequate method of comparing the consistency of different slips having been selected, the next step was the determination of the manner in which consistency is affected by changes in various factors in addition to those already reported in the literature and referred to in the review of literature. Four factors were studied in this phase of the investigation. These were: (*a*) Aging, (*b*) varying the concentration of certain solutes in the liquid phase of the slip, (*c*) adding borax at different stages of grinding, and (*d*) grinding the frits to various finenesses. These topics are discussed under separate headings.

(*a*) AGING

It is generally believed in the industry that the aging of enamel slips affects their working properties, although the nature of the change has been largely a matter of conjecture. Securing more accurate information concerning this change is of primary importance in any work which has for its object the control of the working properties of enamel slips. Accordingly, the following series of tests was made: A sample of enamel A, with a mill batch of frit 100, water 55, clay 7, and borax 15 (parts by weight) was prepared and divided equally among several closed jars for storing. After periods of 1, 6, and 28 days, respectively, the "mill liquor" was pipetted off from the top of one jar, where it collected, and the remaining thick slip was mixed well, and its moisture content determined. A definite weight was then placed in a flask, and sufficient mill liquor returned to the sample of slip to bring it to a definite water content (35.6 per cent of total weight). After coming to temperature in the thermostat (see fig. 1), the sample was ready for test. The same was done with frits B and C.

---

[16] The numerical expression for mobility equals the slope of the line $\frac{r}{F-f}$ multiplied by a constant equal to $\frac{4}{\pi R^3}$, where r=rate of flow at any point on the graph, F=the shearing stress required to produce the rate of flow r, f=yield value, and R=radius of the capillary. Reference, R. D. Cooke, "The plastic properties of enamel slip," J. Am. Cer. Soc., 7, (9), p. 654; 1924.

The results of this experiment for enamel A are shown graphically in Figure 2. The reltive effects of aging for enamels B and C were the same, but the extent of the change in yield value was progressively smaller from A to C. These results indicate that aging a ground coat containing the usual borax addition (1.5 per cent) causes a marked decrease in yield value which is approximately proportional to the time of aging, within the limits studied, which are wide enough to cover commercial practice. The mobility undergoes a slight reduction, but remains practically unchanged. The decrease in yield value for the 28-day period amounted to 96 units for enamel A, 62 units for enamel B, and 33 units for enamel C. From these figures it is apparent that the composition of the frit affects the rate of change of consistency, a high silica ground coat changing considerably more rapidly than one high in borax, and a high soda enamel falling between the two.

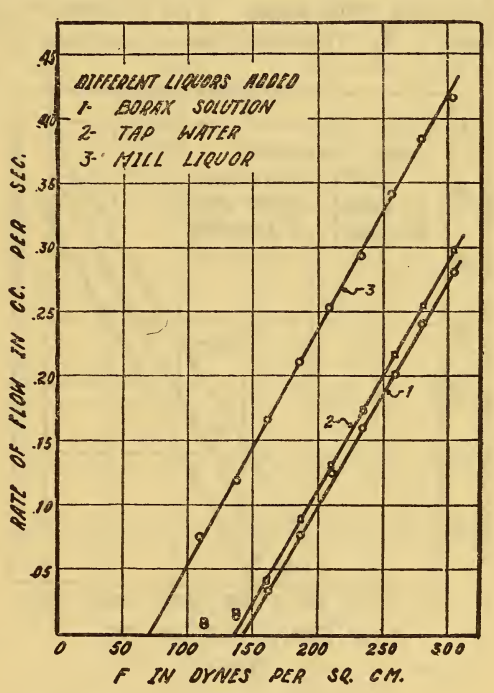


FIG. 3

(*b*) VARYING THE CONCENTRATION OF CERTAIN SOLUTES IN THE LIQUID PHASE

It was pointed out by Poste [17] that the effect of materials dissolved from the solid phases of an enamel slip can not be overlooked, although no actual data had been published showing the effect of changes in concentration of these solutes. In order to obtain such data, a batch of frit B was prepared. After it had stood a week, the liquor which had separated was pipetted off, the remaining thick slip was mixed well, and the water content was found to be 29.9 per cent of the total weight. Three portions of this slip were placed in separate flasks, and a different liquor added to each in amounts calculated to bring the total liquid content to 35.6 per cent. To the first was added a solution of borax, having a concentration equal to that resulting from the usual mill addition of 1.5 parts by weight of borax to 50 parts of water in the mill. To the second was added tap water.

[17] E. P. Poste, "An analysis of the suspension of enamel by clay in terms of the colloid theory," J. Am. Cer. Soc., 8, (4), p. 232; 1925.

To the third was added a solution obtained by concentrating liquor from a batch of enamel B ground without borax and which had also stood a week. This liquor, in process of evaporating to one-seventh its original volume, apparently became supersaturated with respect to some of its solutes, forming a precipitate which was removed by filtration, before the liquor was added to the slip. These three samples were tested for yield value and mobility, and the results are plotted in Figure 3. The difference between the slips from which curves 1 and 2 in this figure were obtained is that the concentration of borax was greater in slip 1. The additional borax caused an increased yield value. The difference between slips 2 and 3 (curves 2 and 3, fig. 3) is that the concentration of matter dissolved from the solid phases is greater in slip 3. Since a variety of materials are dissolved from the solid matter, it is probable that some of them have conflicting influences upon the consistency of a slip. The net result of the concentration was, however, to greatly lower the yield value, without materially affecting the mobility of the slip. This evidence substantiates previous suggestions that the material dissolved from the solid phases influences the consistency of a slip, and shows in what manner the consistency is influenced.

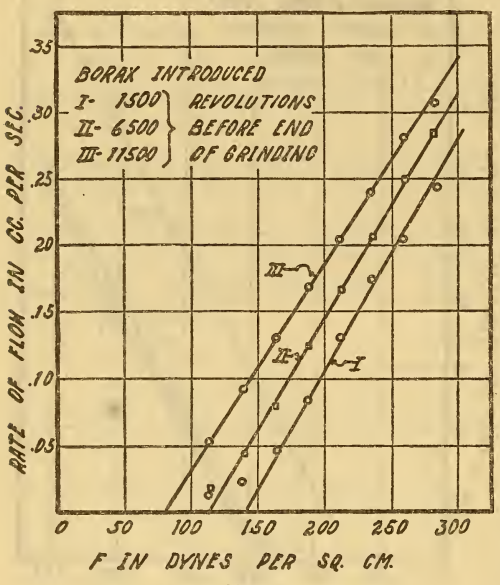


FIG. 4

(c) ADDING BORAX AT DIFFERENT STAGES OF GRINDING

There is a difference of opinion in the industry regarding the stage of grinding at which borax should be added. Some plants make a practice of adding it near the end of the process and some at the beginning. The effect upon mobility and yield value of adding borax solution at different stages of grinding a ground coat was studied. Three batches of frit B were prepared, each receiving 26,500 revolutions in a ball mill. The usual 1.5 per cent of borax in solution was added to the first 1,500 revolutions before the end of the grinding, the second 6,500 revolutions, and the third 11,500 revolutions before grinding was stopped. The effect of this variation on mobility and yield value is shown in Figure 4. It is apparent from this figure

that yield value was lowered as the borax solution was added nearer the beginning of the grinding operation. Mobility was only slightly affected. Microscopic examination disclosed an increasing grain size corresponding to earlier additions of borax.

(*d*) GRINDING THE FRITS TO VARIOUS FINENESSES

The difference in grain size noted above suggested that the reduction in yield value might be due to a retardation in grinding in the presence of borax. It seems natural that fineness of grinding should affect consistency, since a continuation of grinding effects a diminution in size of the relatively coarse grains and an increase in the number of particles of colloidal dimensions. In order to study the effect of increased fineness of grinding upon mobility and yield value, a series of tests was made upon batches of a single frit ground to various finenesses. Four samples of frit B were prepared, each with a mill batch of frit 100, water 55, clay 7, and borax 1.5 (parts by weight), the latter being added at 1,500 revolutions (about one-half hour) before the end of each run. They were ground 10,000, 20,000, 30,000, and 40,000 revolutions, respectively, in a mill in which ordinarily about 25,000 revolutions were required for satisfactory grinding. After grinding, all were passed through a 60-mesh sieve before testing. In the case of the sample ground only 10,000 revolutions, about 35 per cent of the frit remained on the sieve, but only a negligible per cent of the others. Before testing, the samples were all brought to a liquor content of 35.6 per cent in the manner previously described. The results are shown in Figure 5. From these graphs it can be said that an enamel slip having a mill batch as described above decreases in mobility and increases in yield value (the latter at an

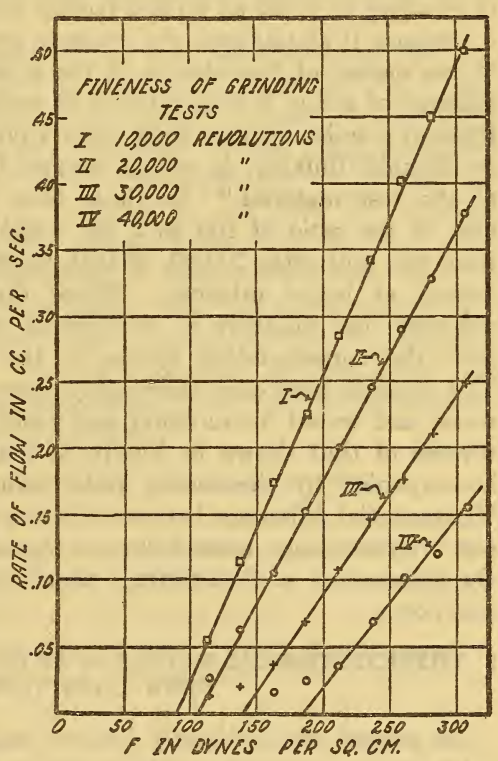


FIG. 5

accelerated rate) with increased grinding. It is worthy of emphasis that the effect of grinding upon consistency was accelerated as the grinding continued. If consistency is a function of total surface of the solid particles, it is natural that this should be true.

This effect is contrary to the general idea obtained from the fact that continued grinding has a decelerated effect upon the per cent of solid matter which is too coarse to pass a given sieve. The data obtained indicate that sieve tests are not a true measure of the effect of grinding in so far as surface factors are concerned.

Because it emphasizes the extreme importance of a consideration of the degree of flocculation of the collodial matter upon the consistency of a slip, it is of interest to compare the above results with those of a series of tests made from a purely academic point of view by Ronald Bulkley, in which enamel frit happened to be chosen as the test material.[18] In those tests frit and clay were ground dry, in the ratio of 100 to 7 by weight. Samples were removed from the mill after 20,000, 50,000, 95,000 and up to 700,000 revolutions at larger intervals. (Since the grinding conditions were different, the numbers of revolutions are not entirely comparable with the corresponding figures in the work already mentioned.) The samples were each thoroughly mixed with equal percentages of water and tested for mobility and yield value. The effect was the reverse of that shown in Figure 5; that is, increased fineness was accompanied by decreasing yield value and increasing mobility. The essential difference between the two series of experiments is that one, representing enamel slips as actually used, was performed in the presence of a flocculating agent; namely, borax, and the other was not.

3. PHYSICOCHEMICAL NATURE OF AN ENAMEL SLIP—ITS INFLUENCE UPON CONSISTENCY

An enamel slip ordinarily has one liquid phase and two or more solid phases, consisting of frit particles, clay particles, and possibly particles of insoluble mill additions. Soluble matter, drawn into solution from the solid phases or added purposely to control the consistency of the slip is dissolved in the liquid phase and probably adsorbed on the surfaces of solid particles. In order to formulate a definite conception of the mechanism of changes in consistency, so that it might be more intelligently controlled, it seemed desirable to obtain some fundamental information concerning the physicochemical nature of the various phases of an enamel slip, and correlate these data with observed changes in consistency.

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[18] "Consistency as a function of particle size," a thesis presented as one of the requirements for the degree of M. S. at George Washington University, June, 1926.

(a) DETERMINATION OF ELECTRICAL CHARGES CARRIED BY MINUTE FRIT PARTICLES

Several theories concerning the behavior of colloidal particles are based on the presence of an electric charge, and some of these have been used in forming hypotheses concerning the mechanism of changes in an enamel slip.[19] It is already widely accepted that minute clay particles carry negative charges, and a series of experiments was performed for the purpose of detecting and determining the nature of these charges (if present) on the fine particles of frit as well as on the clay.

Samples of the finest particles of frit were easily obtained for test due to the fact that, when clay is excluded from the mill batch, the liquor which segregates at the top of the slip is densely clouded with suspended particles and does not completely clarify upon prolonged standing. As a description of this test it is sufficient to say that the apparatus used was similar in principle to one used by Whitney and Blake,[20] but the procedure differed from theirs in that they determined changes in concentration of the colloidal solutions by measurement of change in conductivity, while in this case the concentration of the particles was determined more directly by counting with an ultramicroscope.[21] The data obtained indicate that the frit as well as the clay particles are repelled from a negative electrode and, therefore, carry a negative charge.

(b) OBSERVATIONS OF HYDROGEN ION CONCENTRATION

The character of the electrical charges carried by the minute particles of frit and clay having been established, a logical question which arises is whether a change in consistency is actuated by a change in hydrogen ion concentration in the liquid phase of a slip. The presence of a considerable amount of borax renders it impossible to materially change the hydrogen ion concentration until a disturbing factor is introduced in such magnitude as to exhaust the buffering ability of the borax. Without entering into a rigorous investigation of the subject, it was possible to determine by a few experiments that broad changes in consistency of enamel slips can and do take place with no significant change in hydrogen ion concentration. In order to do this it is only necessary to measure the hydrogen ion concentration before and after a considerable change in consistency, and if the

[19] E. P. Poste, "An analysis of the suspension of enamel by clay, in terms of the colloid theory," J. Am. Cer. Soc., 8, (4), p. 233, 1925.

[20] W. R. Whitney and J. C. Blake, J. Am. Chem. Soc., 26, p. 1339; 1904.

[21] For description of the ultramicroscope see Colloids and the Ultramicroscope, by R. Zsigmondy, trans. by J. Alexander; J. Wiley & Sons, publishers.

pH value remains constant proof is obtained that a change in consistency is not necessarily accompanied by a change in pH. Changes in consistency could be effected by various means, but the most appropriate seems to be aging, since during that process nothing is added to or subtracted from the system. Since enamel A changed in consistency most rapidly with aging it was used for these tests. The liquor had a pH value of slightly over 9, which remained practically unaltered throughout the aging period of four weeks. Thus, although a change in consistency may in some cases be accompanied by a change in pH, it is evidently possible for a slip to change in consistency through some other mechanism. Since the borax would prevent small changes in the concentration of any given ions from changing the pH, it seems probable that the mechanism of changes in consistency is intimately connected with the process of selective adsorption. Further indication that it is not necessary to change pH in order to alter consistency is found in the fact that sodium chloride, a neutral salt, causes an increase in yield value.[22]

(c) RELATION BETWEEN DEGREE OF FLOCCULATION AND YIELD VALUE

The effect of the state of flocculation of the fine particles of frit and clay upon the consistency of an enamel slip has been a matter of some speculation, but the previous literature lacks data on the subject. This phase of the work was studied by first bringing about conditions that resulted in a wide difference in consistency for a given slip, and then observing the respective states of flocculation of the fine particles. The variation in consistency produced by adding borax solution, tap water, and mill liquor, respectively, which was reported under the head, "Varying the concentration of certain solutes," was chosen as a suitable basis for study. In order to observe the effect of this change in the liquid phase of the slips upon the smaller grains of the solid phases, the following test was made:

Five cubic centimeters of slip from frit B, which had been prepared in the customary manner, were placed in each of six graduated cylinders. Two of these were filled to the 50 cc mark with a borax solution of a concentration equal to that resulting from the usual mill addition, two with tap water, and two with mill liquor containing no borax. After being thoroughly shaken they were allowed to stand two hours, with the result shown in Figure 6. The most deflocculated (or best suspended) samples contained the liquor which produced a slip of low yield value; namely, mill liquor to which there had been no mill addition of borax. In order to determine whether or not the particles of clay and frit were affected alike by this treatment, a sample of frit B was prepared without clay or borax, and a sample

[22] R. D. Cooke, "The plastic properties of enamel slip," J. Am. Cer. Soc., 7, (9), pp. 651–655; 1924.

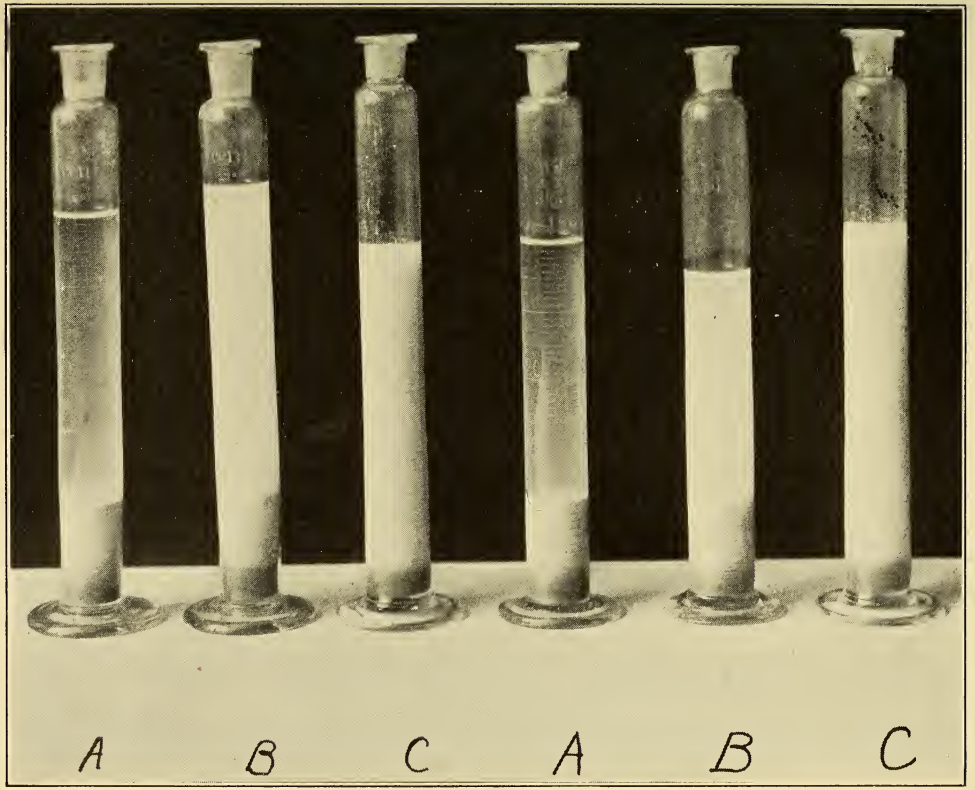


FIG. 6.—*Showing effect upon the degree of deflocculation of the finer particles in a slip, caused by varying the concentration of specified solutes in the liquor*

A—Borax soln.; *B*—Tap water; *C*—Mill liquor (without borax)

of enameling clay was ground with water in the ratio used in a slip. Each of these was mixed well, and 5 cc placed in each of three graduated cylinders. The borax solution, tap water, and mill liquor were added to these as in the previous tests. The larger particles of clay settled within a few hours in all three cases, leaving liquors of approximately equal cloudiness for the borax and tap water, but much greater cloudiness for the liquor containing matter dissolved from the frit. In the case of the frit the largest particles settled almost immediately, and the cloudy liquors above were not readily distinguishable from each other at first. After several days, however, there was a decided difference in their appearance, the cloudiest liquor again being the same as that which caused a decrease in yield value. The settled-out particles of frit were loosely packed in the bottom of the cylinder containing borax solution, and could be poured out with the liquor. The frit in the other two tubes was tightly packed and had to be forcibly dislodged.

Attention is called to the fact that in all cases the largest particles settled out rapidly in these dilute suspensions, and that an enhanced suspension (deflocculation) of fine particles does not necessarily indicate the same effect on the whole solid content. The indication is, rather, that in a properly "set up" enamel the finer particles are in a flocculated condition on or about the coarser grains. This flocculation, through increasing the yield value of the slip as a whole, would tend to retard the settling of the coarser grains.

(*d*) MECHANISM OF CHANGES IN YIELD VALUE—DISCUSSION OF RESULTS

The experiments reported in the preceding pages, together with data contained in the literature referred to, point to the conclusion that the major factors controlling the yield value of an enamel slip are: (*a*) The amount of the several kinds of colloidal matter present, and (*b*) the state or degree of flocculation of this matter A greater abundance of colloidal matter makes the slip as a whole more sensitive to changes in its state of flocculation. Given a sufficient amount of colloidal matter to make the system sensitive, yield value will be relatively low if the colloidal matter is deflocculated and will increase as it becomes more and more flocculated. Once it has reached maximum flocculation, addition of salts can not raise the yield value.

V. FACTORY TEST METHODS AND RESULTS

1. DEVELOPMENT OF FACTORY METHODS FOR MEASURING MOBILITY AND YIELD VALUE

It is realized that the method of determining yield value and mobility which was used in the laboratory work is not the most convenient for ordinary plant use. Too much equipment is required and

the method of calculation too involved to appear attractive to the shop man for a control test. The task of simplifying the method so that it is easy to use and at the same time gives information which is sufficiently accurate for plant needs may be accomplished by simplification of the apparatus itself, elimination of as much calculation as possible, or both. In this process of simplification it is to be borne in mind that a substitution of empirical for scientific units should not affect the actual utility of the test.

(a) SIMPLIFICATION OF EQUIPMENT

The only part of the equipment which is not easily and cheapl obtainable is adequate means for temperature control. It is especially fortunate, therefore, that in ordinary plant work the temperature control can be disposed of not only with no ill effect but with positive beneficial effect. This is true because the operator wants to know the consistency of the slip as it is being used and not its consistency at some other, arbitrarily chosen, temperature. The small variations in temperature such as are likely to exist between the vat and the sample under test will be unimportant, provided the apparatus is given an opportunity to come to approximately the same temperature as the vat before testing a sample. With the greater variations in temperature, such as that from a hot summer day to a cold winter day, it is important that the slip be tested to determine its consistency under the influence of the temperature at which it is being used.

(b) CHOOSING PROPER DIMENSIONS

To obtain greatest simplicity it was deemed desirable to so regulate the dimensions that the same apparatus would be suitable for testing enamel slips covering the whole range of consistency from the slowest running to the fastest running. Another requirement is that the feed tube should be long enough to permit readings to be taken over a relatively wide variation in height of the enamel slip, in order to minimize the error of any individual reading. Further, it was reasoned that an apparatus which requires a sample of only 100 or 200 g would be preferable to one requiring a considerably larger sample, provided satisfactory results could be obtained with the former.

After trying capillaries and feed tubes of various dimensions, a combination was chosen which satisfactorily filled the above requirements. The capillary was 0.16 cm in diameter and 12.0 cm in length. The feed tube, of heavy Pyrex, was 1.3 cm in diameter and 90 cm in length. A sketch of the apparatus selected is shown in Figure 7.

(c) CALIBRATION OF APPARATUS

A simple and easily removable joint for the two parts was made with a rubber stopper fitting into the feed tube, and through which the capillary passed. A mark was filed on the feed tube as a guide

for inserting the capillary a proper distance. The feed tube was then calibrated at intervals of 10 cc, a small strip of gummed label being pasted at each interval, and coated over with shellac. The calibration was accomplished accurately enough by using a 10 cc pipette to put the proper volume of water into the tube, the meniscus serving as a guide for attaching the calibration strips. In order to minimize the length of tubing over which the introduced water was compelled to flow after leaving the tip of the pipette, the feed tube was half filled with water to start with, and calibrated toward the upper end. Then the tube was reversed and the other end calibrated. In this process care was taken that when the paper strips had all been pasted on and the tube righted, the upper edges of the strips represented the 10 cc marks. The distance from each of these to the file mark near the bottom of the feed tube was measured with a meter stick to the nearest millimeter.

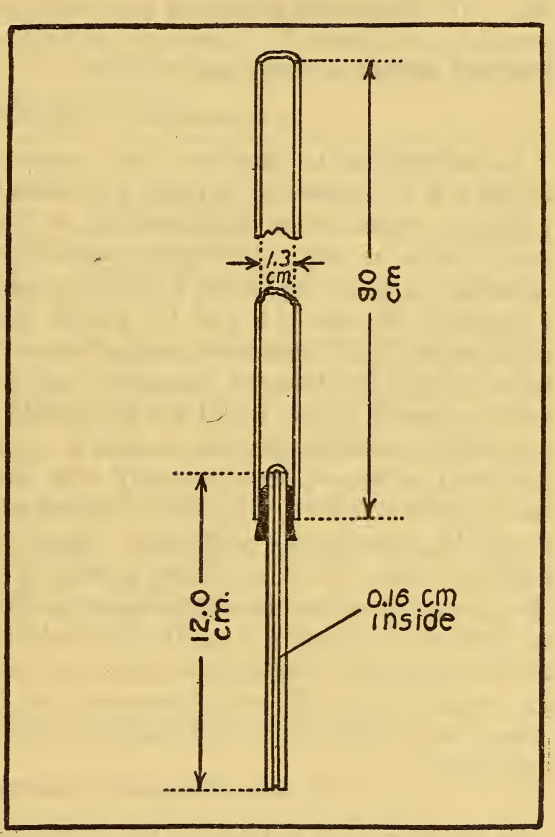


Fig. 7.—*Cross section of apparatus used in factory work for measuring consistency of enamel slips*

(*d*) METHOD OF USING APPARATUS

There were 10 available intervals on the feed tube for which the average rate of flow corresponding to the average height of enamel slip could be determined. For regular plant work good results can be obtained by taking observations at three to five of these intervals. The upper part of the feed tube is more suitable for making observations on the slower running slips, due to the curvature of the lower part of the graph, which is discussed in footnote 15. The lower part of the feed tube is more suitable for making observations on the faster running slips, because an excessive rate of flow is liable to lead to turbulence, which upsets the régime of flow and vitiates the results.

In fact, it was only by using different parts of the tube that the one apparatus could be used successfully for enamel slips of the two extremes of consistency. For many intermediate slips, however, the whole tube could be used if desired. It is advisable to take a reading at the highest and at the lowest interval which is practicable with any particular class of slips, and to include one to three intermediate readings, depending on the distance between the two extreme readings. (In the results published here more readings were taken than would be necessary for plant-control work, because the additional readings served as confirmatory data.)

(*e*) DUPLICATION OF APPARATUS

In attempting to duplicate the apparatus described above, it would not be necessary to enter into minute measurements. The variations which occur in dimensions of glass tubes and capillaries would make an exact duplication of the specified dimensions very difficult. A feed tube having a diameter between 1.2 and 1.5 cm and a capillary between 1.5 and 1.8 mm in diameter would meet the requirements for dimensions specified above. Results obtained with tubes of slightly different diameters, and plotted on the empirical basis suggested below, would not be entirely comparable, and in any one shop it would be desirable to hold in reserve an apparatus which had been compared experimentally with the one in use, so that, if the latter were broken, the results obtained with the reserve apparatus would be immediately applicable. Since it is not difficult to get capillary tubing which is uniform enough so that different sections of the same tube are practically the same for this purpose, there need be no significant difference in results obtained with the reserve apparatus. In the absence of comparative tests upon the same slips two sets of apparatus having different dimensions can be compared by regular calculation of yield value and mobility in the manner which has been described.

(*f*) SIMPLIFICATION OF CALCULATIONS

In the process of simplifying the calculation of results every step was eliminated which could possibly be disposed of without changing the nature of the resulting diagrams. To this end rate of flow was simply plotted against the arithmetic average head, without even multiplying the latter by specific gravity to obtain hydrostatic pressure. The extreme range of specific gravities encountered in two typical factories was from 1.6 to 1.95. An example of the results obtained by this method may be seen in Figure 8.

These results are only relative, and whenever publication is contemplated, the regular scientific method of expression should be used, in order that the results may be comparable with other published data. Results obtained by the simplified method will be expressed

in this paper in terms of *relative mobility* and *relative yield value*, while the regularly calculated results will be expressed as *yield value* and *mobility*.

In this work the relative mobility is defined as the rate of flow of the slip, in cubic centimeters per second, under a head 50 centimeters greater than the relative yield value. Thus curve No. 6, Figure 8, shows a relative yield value of 20 and a relative mobility of 0.21.

2. OTHER TESTS USED IN FACTORY WORK

The following tests were made on the slips in addition to determinations of mobility and yield value.

(a) SPECIFIC GRAVITY DETERMINATIONS

The specific gravities were determined by weighing the slips in a copper bottle [23] holding one liter.

(b) DETERMINATIONS OF WATER CONTENT

Some of the moisture contents were determined by the wet and dry weight method. Others were calculated from the formula

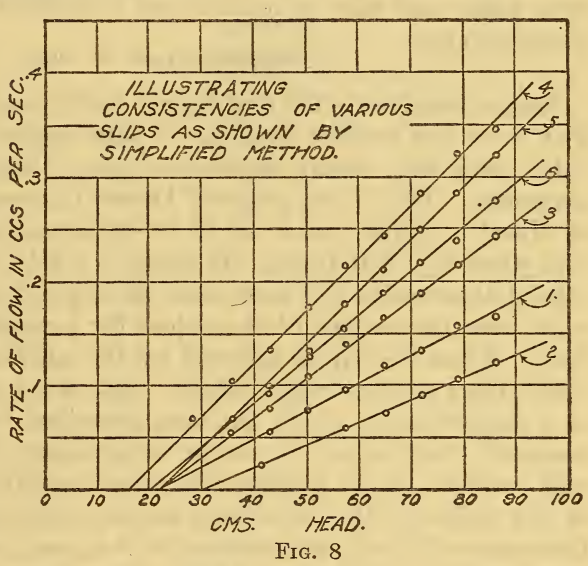


FIG. 8

$$\text{Per cent water} = \frac{A - D}{(A - 1)\,D} \times 100$$

where D is the specific gravity of the slip, and A is the true specific gravity of the dry solids, which is determined by solving for A in a case in which both D and per cent water are known. Once A has been determined, this is a time-saving method for slips which differ only in water content.

(c) WEIGHT PER UNIT AREA TESTS

The slips were also tested to determine the weight per unit area which would adhere to a metal base under definite conditions. This test has recently gained considerable favor in the industry for some

[23] The use of a copper bottle for this purpose has found some favor in the industry because of the ease of calibration and relatively small chance of being broken, as compared to glass.

types of work. The test was conducted as follows: A flat sheet of iron, 12 by 12 inches and of known weight was dipped into the slip and withdrawn vertically. The top edge was immediately turned to the bottom and the piece held stationary until the draining was complete. As soon as the slip at the lower edge of the piece became stationary, that edge was gently brought in contact with a flat surface to remove the excess slip, and then the piece was weighed. From these data the weight per unit area is easily calculated. In one factory, however, it had been found more expedient for plant-control purposes to use the total weight of the coated piece to express the adjustment of the slip, a fact which is indicative of the point of view which was kept in mind in the simplification of test methods described above.

(*d*) DETERMINATION OF "SET"

Results obtained in the first factory work which was done indicated that there was another property of slips besides mobility and yield value, and not wholly dependent upon them, which should be measured. This is the property known to enamelers as "set." If an object is dipped into a slip of low-yield value and poor "set," the slip, when it is withdrawn, will drain to a relatively thin layer, and careful observation will show that the slip continues to drain downward over the surface of the object for a relatively long period of time. When the slip is adjusted by the addition of a "setting-up" agent, there are two visible effects. One is the adherence of the slip in a thicker layer, which has been described before and is due to increased yield value. A careful observation of the surface of the well "set-up" slip as it drains will show in addition that at any point on the surface of the metal base the slip moves for a short time and then stops with such abruptness that it appears to seize some support and remains stationary. As the piece drains, the slip becomes stationary first near the upper edge, the border of the stationary part advancing toward the bottom of the piece. When the slip becomes motionless at the bottom of the piece, the draining is complete.

(1) DEFINITION OF TERMS.—A slip which drains quickly is said to be *well set*, or to have a *good set*, or a *short draining period*. If the draining period increases on standing, the slip is said to lose its set. One which takes a relatively long time to completely drain is said to be *poorly set*, or to have a *poor set*, or a *long draining period*.

(2) METHOD OF MEASURING.—By dipping a flat sheet of a definite size, setting it to drain at a given angle, and measuring the time necessary for the draining to become complete, a quantitative measure of the set of a slip can be obtained in arbitrary units. For these tests a flat enameled piece 5 by 8 inches was used. It was dipped, drawn out rapidly in a vertical position, and immediately

placed on a rack with the end which was last to emerge from the slip on top. The lower edge was offset 1 inch from the vertical plane passing through the upper edge. By means of a stop watch the time was noted just as the piece was placed on the rack, and again just when the enamel became motionless at the lower edge of the piece. The draining period of slips tested in the laboratory varied from 8 to 45 seconds. The movement of the slip can be easily detected when the observer is in the proper position relative to the source of light, and readings can be checked within 10 per cent with a little practice.

3. RESULTS OF PLANT WORK

(a) GENERAL DESCRIPTION

Work was done in two plants doing different types of work. The output of the first includes a great deal of flat ware, such as signs and stove parts. The enamels are applied by "draining" and spraying. None of the ware requires shaking to secure an even coating. The product of the second plant includes shaped ware, such as cooking utensils, and calls for an enamel of higher yield value. These shaped pieces require shaking to secure an even coating of enamel.

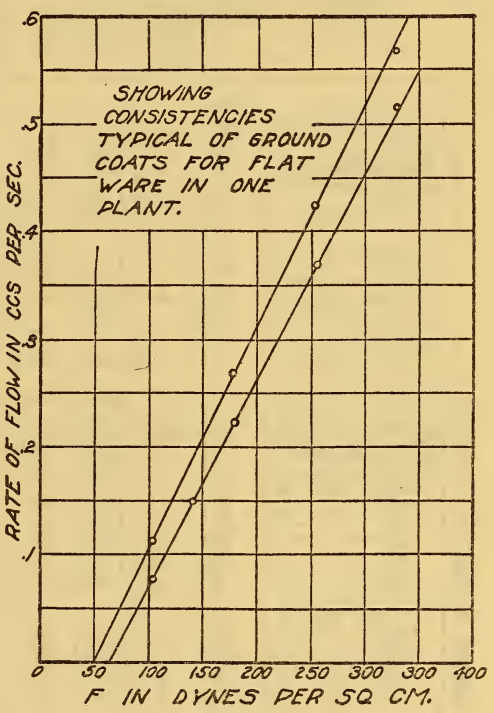


Fig. 9

In the first plant data were obtained to show that enamels used for different purposes have considerably different mobilities and yield values. The data are of especial interest in that they show the range of mobilities and yield values in which ground coats used in that type of work fall. Figure 9 shows some typical graphs obtained with ground coats fror draining. The results indicated the desirability of making additional tests, including the set of each slip, and can not be considered as complete without them. The complete series of tests was made in the second plant.

The tests made at the second plant, producing shaped ware, included all types of enamels being used there, from those of lowest

to those of highest mobility and yield value. Tests on each slip included determinations of set, weight per unit area, yield value and mobility, specific gravity, water content, and room temperature. The results of these tests are given in Table 3.

TABLE 3.—*Tests made at plant producing shaped ware*

Test No.	Kind of enamel and condition	Set, or draining period	Weight per unit area		Yield value		Mobility		Specific gravity	Water	Room temperature	
			Ounces per square foot	Grams per square meter [1]	Relative units	Standardized units	Relative units	Standardized units			°F.	°C.
		Seconds								*Per cent*		
1	White, ready for delivery	20	6.4	1,950	21.5	130	0.133	0.113	1.918	24.0	81	27.2
2	White, heavy	34	7.5	2,290	30.0	181	.108	.090	1.921	23.8	83	28.3
3	Same, water added	20	6.4	1,950	21.6	135	.188	.164	1.892	25.2	82	27.8
4	Same, more water added	21	4.0	1,220	16.0	85	.253	.206	1.872	26.0	82	27.8
5	Same, salts added	18	6.0	1,830	22.0	133	.251	.216	1.872	26.0	82	27.8
6	Same, stood overnight	21	5.2	1,590	20.0	117	.211	.179	1.880	25.4	77	25.0
7	White, from dipping table	24	8.5	2,590	27.7	172	.107	.085	1.942	23.0	76	24.5
8	Same, water and salts added	20	7.2	2,200	26.0	155	.186	.158	1.892	25.2	76	24.5
9	Same, more water and salts added	16	7.7	2,350	27.0	165	.272	.234	1.858	26.7	76	24.5
10	Same, stood two hours	16	7.0	2,140	24.3	146	.247	.213	1.858	26.7	78	25.6
11	Ground coat, heavy	11	5.2	1,590	18.8	100	.584	.579	1.636	36.5	79	26.2
12	Same, water added	13	3.3	1,010	14.0	70	.708	.707	1.610	38.1	78	25.6
13	Same, salts added	9	4.6	1,400	17.3	93	.718	.733	1,610	38.1	78	25.6
14	Ground coat, heavy	12	4.2	1,280	15.5	83	.592	.594	1.643	36.1	78	25.6
15	Ground coat, as used	10	4.8	1,460	18.2	96	.661	.669	1.621	37.3	82	27.8
16	do	10	4.2	1,280	17.3	93	.650	.660	1.631	36.7	82	27.8
17	do	10	4.3	1,310	16.9	88	.775	.790	1.600	38.7	81	27.2
18	do	10	4.2	1,280	17.7	92	.708	.722	1.621	37.3	80	26.7
19	do	10	4.6	1,400	17.7	96	.708	.722	1.630	36.8	80	26.7
20	do	9	4.6	1,400	18.1	97	.636	.638	1.650	35.6	80	26.7
21	One coat gray, as used	11	7.7	2,350	26.3	151	.438	.403	1.767	28.9	74	23.3
22	do	11	7.7	2,350	23.3	137	.387	.366	1.773	28.6	74	23.3
23	do	13	7.9	2,410	31.6	173	.282	.235	1.807	26.8	75	23.9
24	do	10	8.0	2,440	27.6	168	.397	.379	1.773	28.6	76	24.5
25	do	13	6.7	2,040	24.0	142	.273	.240	1.835	25.4	80	26.7
26	do	10	7.7	2,350	25.2	147	.361	.341	1.775	28.4	76	24.5
27	do	10	10.4	3,170	39.0	224	.268	.240	1.794	27.4	76	24.5
28	do	12	7.6	2,320	27.2	157	.273	.240	1.818	26.2	77	25.0
29	do	13	7.2	2,200	24.7	144	.332	.297	1.799	27.2	77	25.0
30	do	12	6.6	2,010	25.6	143	.343	.303	1.796	27.3	78	25.6

[1] Figured to nearest 10 g even.

(*b*) COMPARISON OF RESULTS OBTAINED BY SIMPLIFIED METHOD WITH REGULARLY CALCULATED RESULTS

(1) COMPARISON OF APPEARANCE OF THE TWO TYPES OF GRAPHS.—Results on the same group of enamel slips is represented by the six curves in Figure 8 and Figure 10. Those in Figure 10 were obtained by the calculations and corrections used in the laboratory work, and those in Figure 8 by the simplified method which has been described. A comparison of these two figures indicates that the difference in consistency of slips is shown by the simplified method with an accuracy which is adequate for plant needs.

(2) Relation Between Mobility and Relative Mobility.—In Figure 11 all the mobility values of the slips given in Table 3 are

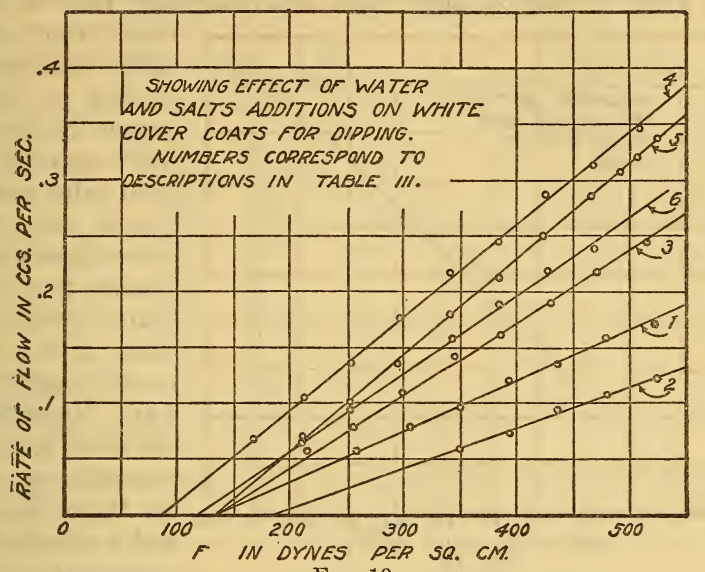


Fig. 10

plotted against their relative mobilities. It is apparent from this figure that the relation is amply good so that the relative units will suffice to make the distinctions necessary for plant-control work.

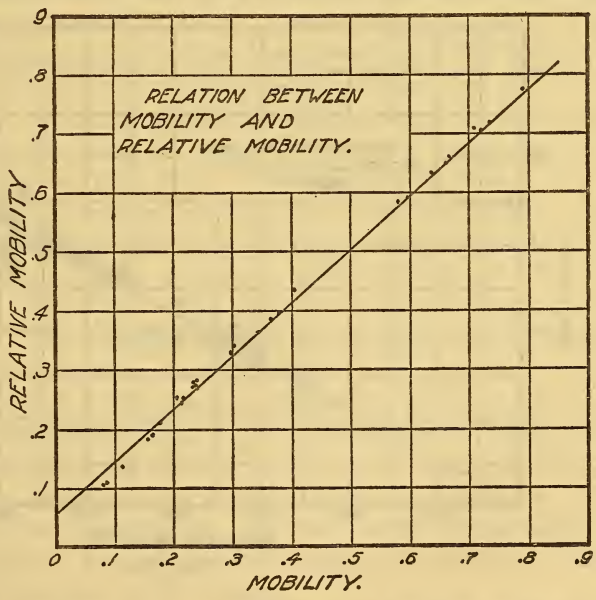


Fig. 11

(3) Relation Between Yield Value and Relative Yield Value.—Figure 12 shows the relation between the yield values and relative yield values recorded in Table 3. Here, too, the relationship is approximately linear, and shows that the relative yield-values are practically all within one unit of the straight line on which they might be expected to fall if they had been corrected for specific gravity and other factors considered in obtaining the yield values.

(c) RELATION BETWEEN YIELD VALUE AND WEIGHT PER UNIT AREA

The weight-per-unit-area tests and determinations of set are much better fitted for use on slips which drain smoothly than on those which must be shaken to obtain an even coating, as, for instance, the gray and white coats of high yield value used for shaped ware. For, unless these slips are shaken, they do not drain smoothly, but slide off the metal in an irregular manner. Nevertheless, the tests under discussion were made on these slips too, and a correlation of results shows the existence of remarkably consistent relationships.

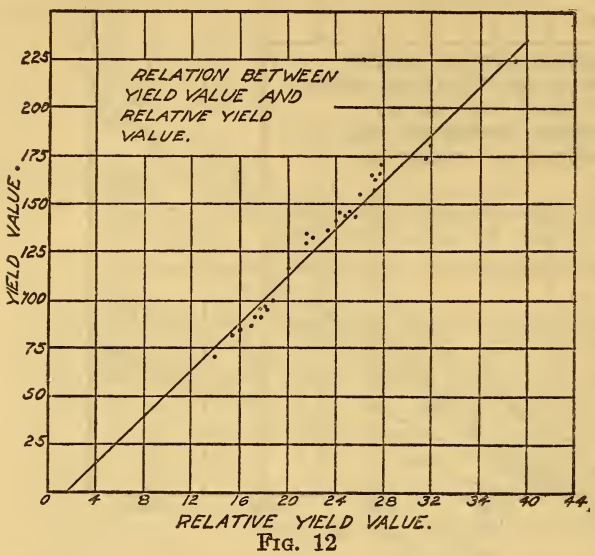


FIG. 12

(1) GRAPHICAL REPRESENTATION OF RELATIONSHIPS.—Figure 13 shows the relation between yield value and weight per unit area for

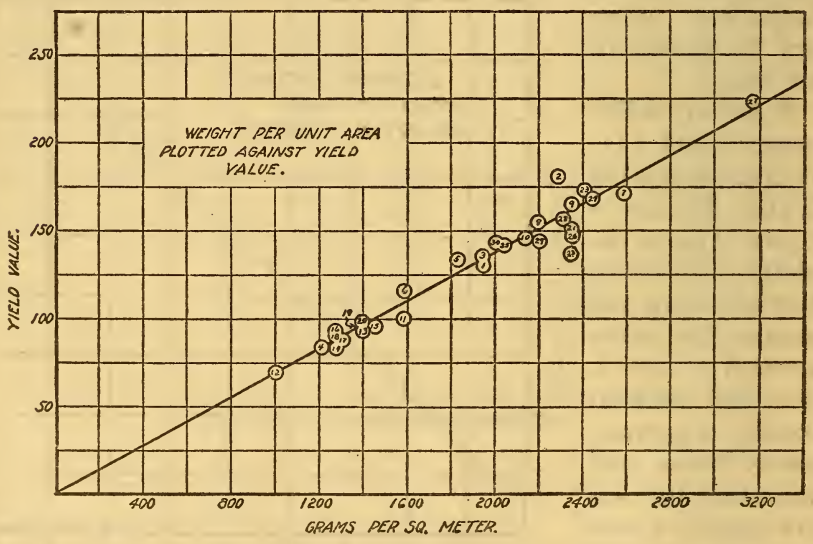


FIG. 13

the slips referred to in Table 3. It is apparent that, in general, an increased yield value will produce an increased weight per unit area. However, a few fairly wide variations occur in some of the slips.

TABLE 4.—*Effect of "set" on relation between yield value and weight per unit area*

Relatively short draining period (highly set slip)				Relatively long draining period (poorly set slip)			
Test No.	Draining period	Excess weight [1]	Weight deficiency [1]	Test No.	Draining period	Excess weight [1]	Weight deficiency [1]
	Seconds	*g*	*g*		*Seconds*	*g*	*g*
11	11	140		1	20	60	
13	9	40		2	34		340
15	10	60		3	20		10
16	10		80	4	21	0	0
17	10	20		6	21		100
18	10		40	7	24	90	
19	10		20	8	20		60
20	9		20				
21	11	160		Total		150	510
22	11	360					
24	10	0	0				
26	10	210					
27	10		70				
Total		990	230				

[1] Terms "Excess weight" and "Weight deficiency" explained in text under part V, 3, (c), (2). "Effect of set" on "Relation between yield value and weight per unit area."

(2) EFFECT OF SET.—It is not surprising that the relationship between yield value and weight per unit area should be imperfect in the slips that did not drain evenly, but it seemed logical to look to set as the probable source of other irregularities. The data in Table 3 show that it is possible for two slips of equal yield value, or two of equal mobility, to have different sets. In Table 4 the influence of set is shown in the following way: The slips having a relatively high set, or short draining period (9 to 11 seconds) were placed in one group, and those having a poor set, or long draining period (20 to 24 seconds and one of 34 seconds) were placed in another group. Then the weight per unit area which each slip gave in excess of (or less than) that value which would bring the point for that slip exactly on the line was determined from Figure 13. Thus slip No. 11 had a draining period of 11 seconds and gave a weight of 1,590 g/m^2, which was 140 g in excess of the weight which would have placed the point exactly on the line. Slip No. 11 was, therefore, credited with an "excess-weight" of 140 g. Slip No. 6 was given a "weight-deficiency" of 100 g, and so on. The averages of the excess weight and weight deficiency columns show that, in the highly set slips, the average excess was 430 per cent of the weight deficiency, while in those of relatively poor set the excess weight was only 29 per cent of the weight deficiency. While there are a number of exceptions, the observations indicate that a very highly set slip will tend to give a weight per unit area in excess of that indicated by the yield value alone, while a poorly set slip will tend to give a smaller weight per unit area than that indicated by the yield value alone.

(*d*) RELATION BETWEEN MOBILITY AND SET

It has been mentioned that it is possible for two slips of the same mobility to have different sets. Yet there is a broad relationship

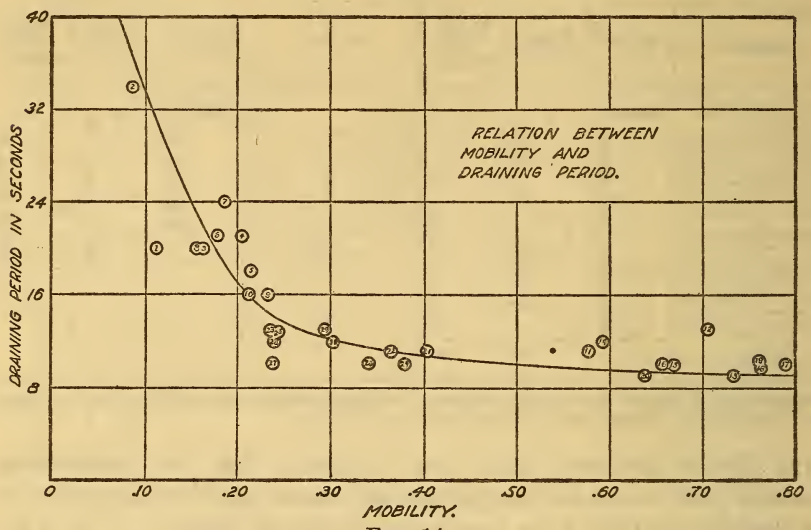


FIG. 14

between the two which indicates that they are by no means wholly independent. In Figure 14 mobility is plotted against set, or draining

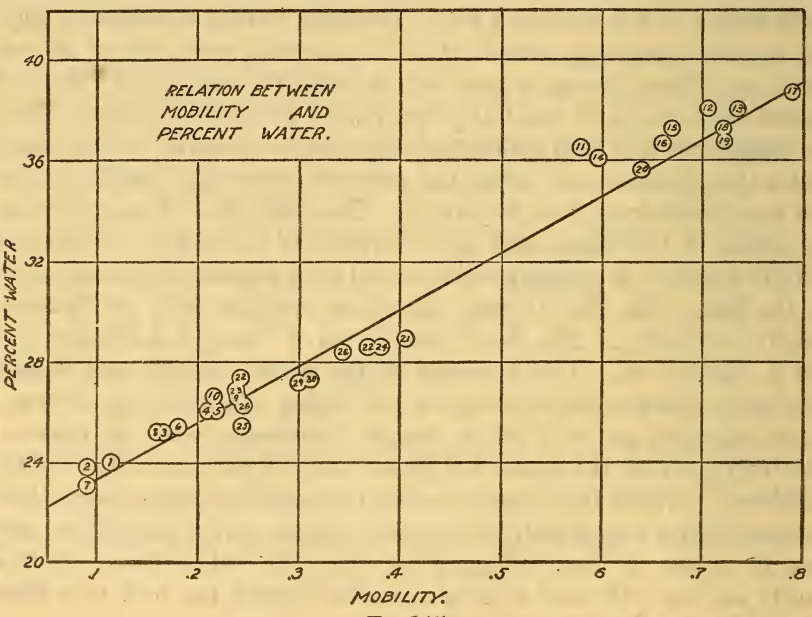


FIG. 15

period. From this figure it appears that as mobility approaches zero, the draining period increases indefinitely and, as mobility in-

creases, the draining period approaches some small value as a limit. In more commonplace language, a slip of high mobility drains quickly, and one of low mobility drains slowly.

(e) RELATION BETWEEN MOBILITY AND PERCENTAGE OF WATER

Although other things besides total water content affect mobility that factor is so powerful that by means of it mobility can be controlled. This fact is clearly demonstrated in Figure 15, which shows that, disregarding the differences in the various types of slips, an increase in the water content from 23 to 39 per cent of the whole caused an eightfold increase in mobility.

(f) RELATIVE EFFECT OF WATER AND SALTS ADDITION ON CONSISTENCY

The changes in consistency caused by additions of water and a setting-up agent, as shown in Figure 10, are worthy of study because they show just what takes place when an enamel is set up for use by these additions. Slip No. 2 (fig. 10) represents a white enamel of high yield value, low mobility, and a water content of 23.8 per cent. Raising the water content to 25.2 per cent (slip No. 3) caused an increase in mobility from 0.090 to 0.164, and lowered the yield value from 181 to 135. Increasing the water content to 26.0 per cent (slip No. 4) caused the mobility to increase to 0.206 and the yield value to drop to 85. The addition of salts to slip No. 4 caused an increase in yield value to approximately that of slip No. 3, with only an insignificant change in mobility. Thus, in the adjustment from No. 4 to No. 5, the yield value was changed without affecting mobility, and in the adjustment from No. 3 to No. 5 the mobility was altered with no change in the resulting yield value. The change from No. 5 to No. 6 shows the alteration in consistency which was brought about by standing overnight.

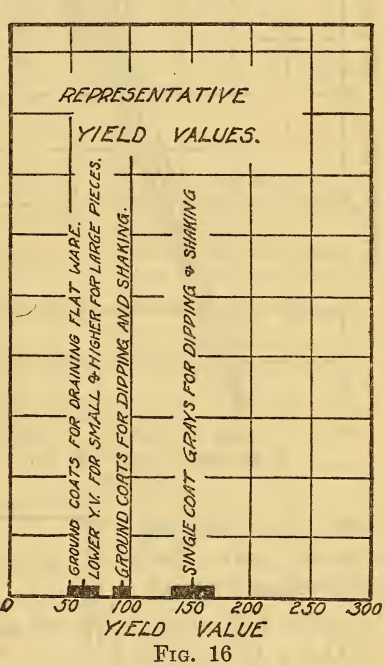


FIG. 16

(g) CLASSIFICATION OF ENAMEL SLIPS

Since the consistency which is most desirable depends upon the size and shape of the piece to be coated, and the manner of application, it would be difficult to lay down any hard and fast rules stating the proper consistency for given types of slips. The consistency

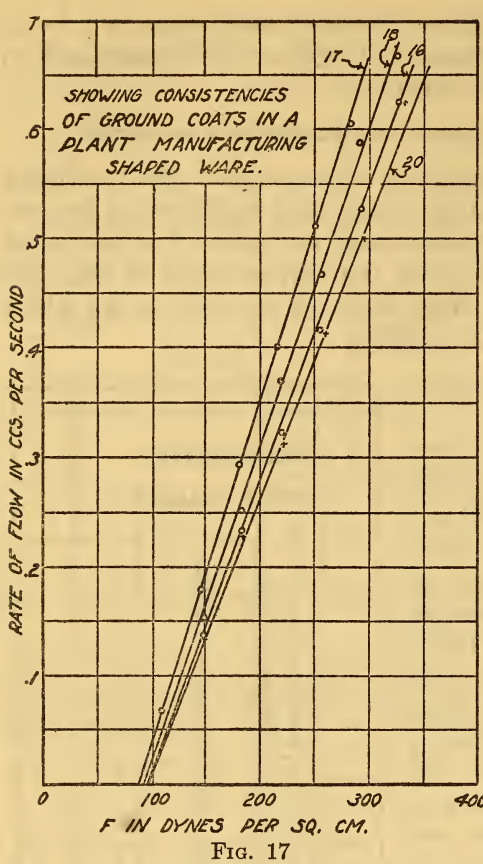


FIG. 17

which is most suitable for any given shape should be ascertained by trial, and can be reproduced by aid of the factory tests for consistency. The data shown in Figure 16, however, suggest the differences in yield value between slips used for different purposes and the limits between which the majority of individual slips of the respective types fell in the factory tests made in this investigation.

(1) GROUND COATS FOR DRAINING, GROUND COATS FOR DIPPING, AND SINGLE COAT GRAY ENAMELS.—Ground coats for draining flatware had yield values falling between the limits 50 and 75, ground coats for dipping shaped ware had yield values between 88 and 100, and single-coat gray-enamel slips for dipping shaped ware had yield values between 135 and 170. Mobility and yield values for the ground coats for draining are shown in Figure 9, the ground coats for dipping in Figure 17, and the gray-enamel slips in Figure 18.

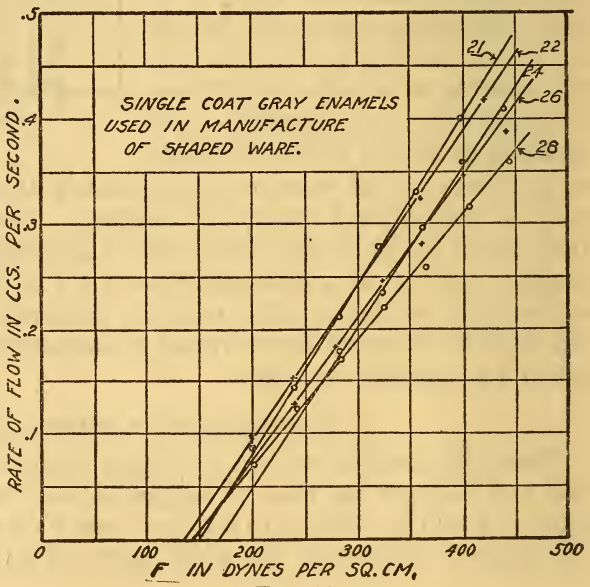


FIG. 18

(2) ADJUSTMENT OF IRREGULARITIES IN CONSISTENCY.—The fact that some of the gray-enamel

slips which were tested fell outside the limits indicated in Figure 18 is shown in Figure 19. The yield values of slips 25 and 28 (fig. 19) fall within the limits indicated in Figure 18, but their mobility is somewhat less. Nos. 23 and 27 are of approximately the same mobility as Nos. 25 and 28, but are of considerably greater yield value. These variations show the irregularities which are liable to occur in the consistencies of slips when they are not controlled by consistency tests. If it had been desired to adjust the consistency of these slips before using, to conform to those shown in Figure 18, it could have been easily done by the methods discussed under "Relative effect of water and salt solutions on consistency." For instance, the mere addition of the proper amount of water no doubt would cause the consistency of No. 23 to practically coincide with that of No. 26.

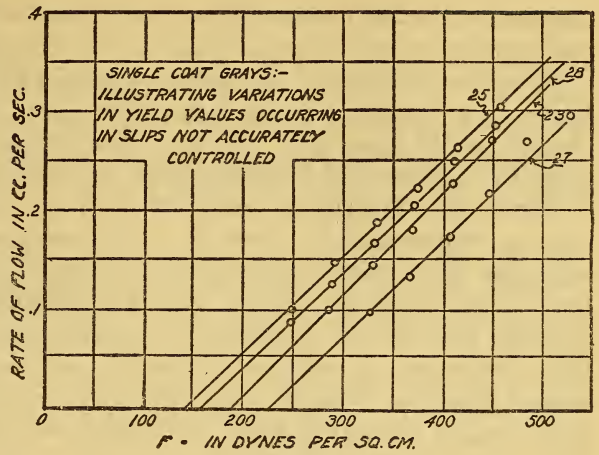


Fig. 19

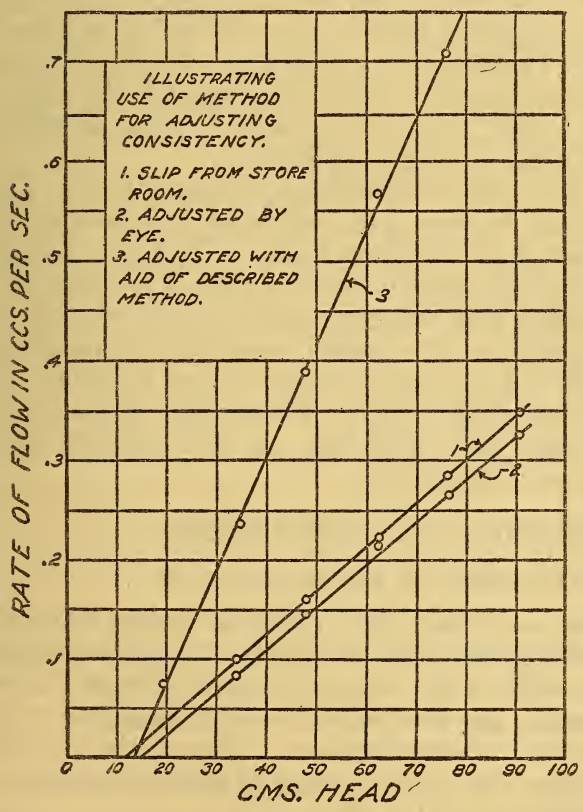


Fig. 20

As an illustration of the usefulness of the simple factory method for determin-

ing consistency and locating the nature of a defect in consistency without resorting to laborious calculations, the following instance is cited.

In regular commercial production a certain spraying enamel had a tendency to present a wavy appearance when applied and to cause clogging of the spray gun. Several observations of consistency were made by the described factory method, the results of which are shown in Figure 20. The slip as brought from the storeroom had a consistency as represented by curve 1. The practical man in charge of adjusting the consistencies of spraying enamels set up the slip for use by his usual methods, adding salts and judging the results by eye. The slip then had a consistency as represented by curve 2. With this consistency it behaved about in its usual manner. These graphs, however, showed that the yield value and mobility were both low, as compared with other slips used in the same work. This condition was not surprising when it was considered that a very small clay addition had been made at the mill and that the water content was relatively low. Since the nature of the defect in consistency suggested that the low mobility might be responsible, additions of water and salts were made, which raised the mobility considerably without materially affecting the yield value, as shown by curve 3 (fig. 20). The slip thus adjusted was described by the practical man who was responsible for the consistency of the spraying slips as "lighter" and "easier to work with." Also, the wavy effect after application was no longer apparent.

This result could have been accomplished in several ways. For instance, more clay could be used in the mill batch and more water then added without introducing additional salts. The point which is here emphasized is that this method of testing showed just how this slip differed in consistency from the others and indicated what steps could be taken to improve it. The method eliminated the necessity of working in the dark and permitted a graphic record of changes in consistency which were brought about. Furthermore, the method embodies adequate means for reproducing the most desirable consistency once it has been determined.

VI. SUMMARY AND CONCLUSIONS

1. CONSTITUTION OF AN ENAMEL SLIP

An enamel slip has two or more solid phases in various states of subdivision. The solid particles can be roughly classified according to size into those particles which are large enough to require some support to retard settling, and those which are small enough to be of assistance in suspending the larger particles. There is also a liquid phase made up of water with different kinds of matter in solution, which affect the consistency of the slip.

2. FUNDAMENTAL FACTORS GOVERNING CONSISTENCY

The fundamental factors which control the consistency of an enamel slip may be summarized briefly. They are (*a*) the kind and quantity of colloidal matter present, (*b*) the degree of flocculation of this matter, (*c*) the percentage of water in the slip, and (*d*) the size of the particles which have to be suspended by means of the colloidal structure.

The kinds of colloidal matter in a slip are (*a*) the colloidal particles of enamel frit, (*b*) the colloidal portion of the clay added at the mill, and (*c*) the colloidal portion of opacifying (or other) material added at the mill. The quantity of colloidal matter present depends upon (*a*) the amounts and character of the mill additions, and (*b*) the grinding, which produces more colloidal matter from each of these sources as it continues. Grinding is retarded by the presence of borax in the mill.

The degree of flocculation of the colloidal matter is controlled by (*a*) the character and concentration of the materials dissolved from the frit and mill additions, (*b*) the age of the slip, and (*c*) salts added for control purposes.

The percentage of water is, of course, controlled by the operator.

The size of the particles which have to be suspended by the colloidal structure is dependent upon the fineness of grinding.

The above-mentioned group of factors governs consistency in the following way. A higher colloidal content makes a slip more susceptible to control of consistency. Thus, given a slip of certain colloidal content, in a definite state of flocculation, a change in state of flocculation will produce a definite effect. With another slip, identical in every respect except that its colloidal content is higher, an equal change in the state of flocculation will produce a greater change in consistency. Flocculation may reach a maximum in a slip and yet the yield value of that slip may be lower than that of another not as highly flocculated but with greater colloidal content. The water content is a powerful factor. Even though a slip has a relatively high colloidal content, flocculated to a high degree, it is possible to add so much water that the structure is destroyed and is no longer able to suspend the coarser particles. Regarding the effect of the size of the coarser particles, it is easy to see that, of two slips having equal colloidal content but differing in the size of the coarser particles, the one with the coarser particles would have more tendency to lose its uniform consistency through settling.

3. MEASUREMENT OF PROPERTIES WHICH DESCRIBE CONSISTENCY

The effects of variations in the above-mentioned factors can be expressed in terms of mobility, yield value and set, measured with simple apparatus; and the values determined by simple calculation.

Measurement of weight per unit area also offers a valuable means of standardization of slips of medium and low yield value. The apparatus required consists of a graduated tube with a capillary outlet for measuring mobility and yield value and a flat metal shape with a wooden rack for measuring set and weight per unit area. A stop watch is required for the first three of these tests and a scale weighing to tenths of an ounce or grams is needed for the last. No calculation more difficult than simple division is necessary.

4. OBTAINING SLIPS OF THE DESIRED CONSISTENCY

Mobility is lowered by reducing the water content and raised by increasing it. For any given type of enamel the water content can be satisfactorily calculated from the specific gravity.

Yield value can be lowered by omitting some of the clay addition at the mill, introducing less salt, decreasing the grinding, or by aging. It can be raised by increasing the clay addition, using clay of higher colloidal content, grinding finer, or using more salts.

Set is partially dependent upon yield value and mobility, but in any given slip can be controlled by adding salts to increase it or allowing it to stand for the reverse effect.

It is desirable to prepare the slip as near to the desired consistency as possible, leaving a minimum of adjustment to be made at the time of its use.

WASHINGTON, December 14, 1926.