A STUDY OF ENAMEL FILM STRENGTH AS AFFECTED BY THE PROPERTIES OF THE ENAMEL BEFORE, DURING AND AFTER DRYING

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THESIS

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Melbourne Kenneth Blanchard ENTITLED "A Study of Enamel Film Strength as Affected by the Properties of the Enamel Before, During and After Drying" BE ACCEPTED* AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF Doctor of Philosophy in Engineering

In Charge of Thesis

Head of Department

Recommendation concurred in†

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A STUDY OF [illegible] MILL LIQUORS, BEFORE, DURING, AND AFTER DRYING

1. INTRODUCTION

The importance of the influence of soluble salts in porcelain enamel mill liquors has long been realized, and several investigations(1-7) have been made to develop a better understanding of fired enamel properties as affected by the soluble constituents in the slip. This phase of enamel research was stimulated most by recognition of the role of soluble salts in determining the property of enamel "film strength"; with particular regard for the defect "tearing". Most of the work in this field has been concerned with the analysis and correction of certain shop problems.

Table 1, showing a few of the myriad of chemical reactions possible in an enamel mill liquor, makes clear one of the reasons for the lack of data concerning anything more than a specific problem. The ionization behavior, the solubilities and natures of crystallization, and the pyrochemical properties of these salts must also be considered in an investigation of their effects when present in the frit, clay, and water system of a porcelain enamel. The complexity of a fundamental study is apparent, and the data obtained would be useful only if it contained minute detail of every possible case over the broad field of variables.

However, recent advances in methods of study have brought forward new techniques that allow the elimination of some of the above complexities. Methods of grouping of variables have been developed for more careful control, and the utilization of

Table 1. Possible Chemical Reactions Between Soluble Salts Present in Enamel Mill Liquors

$\underline{BaCl_2}$

$BaCl_2 + H_2SiF_4 = 2HCl + BaSiF_6$

$BaCl_2 + MgSO_4 = BaSO_4 + MgCl_2$

$BaCl_2 + (NH_4)_2CO_3 = BaCO_3 + 2NH_4Cl$

$BaCl_2 + (NH_4)_2SO_4 = BaSO_4 + 2NH_4Cl$

$3BaCl_2 + 2(NH_4)_3PO_4 = Ba_3(PO_4)_2 + 6NH_4Cl$

$BaCl_2 + 2NaOH = Ba(OH)_2 + 2NaCl$

$BaCl_2 + Na_2B_4O_7 + 3H_2O = 2NaCl + 2H_3BO_3 + Ba(BO_2)_2$

$BaCl_2 + Na_2CO_3 = BaCO_3 + 2NaCl$

$BaCl_2 + Na_2SiO_3 = BaSiO_3 + 2NaCl$

$BaCl_2 + Na_2SO_4 = BaSO_4 + 2NaCl$

$\underline{H_3BO_3}$

$H_3BO_3 = HBO_2 + H_2O$

$2H_3BO_3 = B_2O_3 + 3H_2O$

$H_3BO_3 + 3HF = 3H_2O + BF_3$

$4H_3BO_3 + 2NaOH = Na_2B_4O_7 + 7H_2O$

$4H_3BO_3 = 5H_2O + H_2B_4O_7$

$H_3BO_3 + NaOH = NaBO_2 + 2H_2O$

$H_3BO_3 + NaOH = NaH_2BO_3 + H_2O$

$4H_3BO_3 + Na_2CO_3 = Na_2B_4O_7 + 6H_2O + CO_2$

$\underline{HBO_2}$

$2HBO_2 = B_2O_3 \cdot H_2O$

$HBO_2 + NaOH = NaBO_2 + H_2O$

B_2O_3

$2B_2O_3 + 2H_2O = 4HBO_2$

$2B_2O_3 + H_2O = H_2B_4O_7$

$2B_2O_3 + 6H_2O = 4H_3BO_3$

$B_2O_3 + 2NaBO_2 = Na_2B_4O_7$

$B_2O_3 + NaOH = 2NaBO_2 + H_2O$

$B_2O_3 + Na_2CO_3 = Na_2B_4O_7 + CO_2$

$B_2O_3 + 3Na_2SO_4 = 3SO_3 + 2Na_3PO_3$

$2B_2O_3 + 6HF = H_3PO_3 + 3H_2O + 3HBF$

$CaCl_2$

$CaCl_2 + BaSO_4 = CaSO_4 + BaCl_2$

$3CaCl_2 + H_2SiF_6 + 6NaOH = 3CaF_2 + 6NaCl + Si(OH)_4 + 2H_2O$

$CaCl_2 + 2NaF = CaF_2 + 2NaCl$

$CaCl_2 + 2NaOH = Ca(OH)_2 + 2NaCl$

$CaCl_2 + 2NaAlO_2 = 2NaCl + Ca(AlO_2)_2$

$CaCl_2 + Na_2SiO_3 = CaSiO_3 + 2NaCl$

$CaCl_2 + Na_2SO_4 = 2NaCl + CaSO_4$

H_2SiO_3

$H_2SiO_3 = H_2Si_4O_9 + 3K_2O$

$H_2SiO_3 + 2NaOH = Na_2SiO_3 + 2H_2O$

$H_2SiO_3 + Na_2CO_3 = Na_2SiO_3 + H_2CO_3$

$H_2SiO_3 + BaCl_2 = BaSiO_3 + 2HCl$

$H_2SiO_3 + CaCl_2 = CaSiO_3 + 2HCl$

$H_2SiO_3 + Na_2SO_4 = Na_2SiO_3 + H_2SO_4$

$Na_2B_4O_7$

$Na_2B_4O_7 + BaCl_2 + 3H_2O = 2NaCl + 2H_3BO_3 + Ba(BO_2)_2$

$Na_2B_4O_7 + 3H_2O = 2H_3BO_3 + 2NaBO_2$

$Na_2B_4O_7 + 7H_2O = 2NaOH + 4H_3BO_3$

$Na_2B_4O_7 + Na_2CO_3 = 2Na_2B_2O_4 + CO_2$

Na_2CO_3

$Na_2CO_3 + BaCl_2 = BaCO_3 + 2NaCl$

$Na_2CO_3 + BaSO_4 = Na_2SO_4 + BaCO_3$

$Na_2CO_3 + CaCl_2 = CaCO_3 + 2NaCl$

$Na_2CO_3 + 2H_2O = 2NaOH + H_2CO_3$

$Na_2CO_3 + MgCl_2 = MgCO_3 + Na_2SO_4$

$Na_2CO_3 + MgSO_4 = MgCO_3 + Na_2SO_4$

$Na_2CO_3 + Na_2SiF_6 + H_2O = 6NaF + H_2SiO_3 + 2CO_2 =$

$HF + Na_2SiO_3 + H_2O$

NaOH

$2NaOH + MgSO_4 = Na_2SO_4 + Mg(OH)_2$

$4NaOH + Na_2SiF_6 = 6NaF + Si(OH)_4$

$2NaOH + BaCl_2 = BaOH + 2NaCl$

$2NaOH + 4H_3BO_3 = Na_2B_4O_7 + 7H\ O$

$NaOH + HBO_2 = NaBO_2 + H_2O$

$NaOH + H_3BO_3 = NaBO_2 + 2H_2O$

Na_2SiF_6

$Na_2SiF_6 + 4NaOH = 6NaF + Si(OH)_4$

$Na_2SiF_6 + 2Na_2CO_3 + H_2O = 6NaF + H_2SiO_3 + 2CO_2$

Na_2SiO_3

$$Na_2SiO_3 + CaCl_2 = CaSiO_3 + 2NaCl$$

$$Na_2SiO_3 + 6HF = 2NaF + SiF_4 + 3H_2O$$

$$Na_2SiO_3 + 6HF = Na_2SiF_6 + 3H_2O$$

$$Na_2SiO_3 + H_2O = 2NaOH + H_2SiO_3$$

Na_2SO_4

$$Na_2SO_4 + BaCO_3 = BaSO_4 + Na_2CO_3$$

$$Na_2SO_4 + BaCl_2 = 2NaCl + BaSO_4$$

$$Na_2SO_4 + CaCl_2 = CaSO_4 + 2NaCl$$

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further branches of ceramic technology has made possible a more general application of the data of specific cases. The trend of study is definitely toward the more detailed type of investigation, but obviously, the most valuable type of data that could be contained in a preliminary study of this sort would be a simple, workable concept, applicable to a whole field of related cases.

Object of the Study

With full consideration for the above, this investigation was started. Specifically, the problem dealt with enamel film strength; with particular regard to the defect tearing. The object of the investigation was to further clarify the mechanism of tearing as affected by enamel film properties. As would be expected, the specific problem necessarily involves the more general object of furthering the knowledge concerning the effects of soluble salts in porcelain enamel mill liquors.

II. STUDY OF MECHANICAL TEARING AS DIFFERENTIATED FROM "THERMAL" TEARING

General Statement

The experimental work of preceding investigators has been concerned only with the type of tearing known as "thermal" tearing or that type which results from the effects of soluble salts in the mill liquors of porcelain enamels. Another type which is recognized by industry is the mechanical tearing which arises from bending the dry, white cover enamel to such a degree that rupture of the coat occurs resulting in tear cracks which appear after fusion of the enamel. This type of tearing is often very troublesome to producers of porcelain enameled signs or any other enameled ware subjected to bending during processing. Since this type of rupture is recognized as tearing in its simpler form, it was felt that a portion of this study should be given over to an investigation of mechanical tearing.

Procedure 1--Cross Bending of Dry Enamels

The study of mechanical tearing was begun by cross bending dry cover-coat enameled pieces in a simple fulcrum-lever bending device, firing the pieces, and then observing the resultant coating. The specimens were covered by spraying ground coat enameled stock with 45 grams per square foot of cover coat enamel. Five specimens for each enamel were cross flexed on a five-inch span, the degree of flexing increasing in increments of 0.05 inch from the first sample at 0 flexure to the fifth sample at 0.25 inch flexure. The six enamels used were standard white cover coats characteristic of the different types of white enamels used commercially at present. These enamels for the preliminary survey were prepared by wet

grinding of each frit with the standard mill additions. In addition to the above specimens, a number of samples were applied with enamels prepared from the same frits as above, but having in this case mill added agents reputed to be effective in increasing the resistance of dry enamels to mechanical tearing. These agents, $MgCO_3$, arabic and tragacanth gums, bentonite, and ammonium alginate, were added as 0.5 percent of the mill batch. In order to obtain the relative effectiveness of the added agents, these enamels were treated in the same manner as those above.

Results

The results of this series of experiments showed principally that both mechanical and thermal tearing have the same appearance in the fused enamel, the mechanical tearing being easily distinguished by its directional nature. That is, the mechanical tears are always distributed in such a manner that the applied strain is relieved.

The different frits, when incorporated in the standard enamels, showed marked differences in their capacities to resist the mechanical stresses. This series is shown in Figure 1. The characteristic of one frit being able to resist mechanical tearing better than another is either due to its capacity for resisting the applied mechanical stress or to its capacity for healing the cracks more completely during fusion. If the former is true, the differences between the enamels are only due to different quantities and kinds of soluble salts present which have been leached from the frit. If the latter supposition is true, the healing capacities of the enamels may be dependent upon either the type and quantity of soluble salts present or upon the temperature-viscosity relations

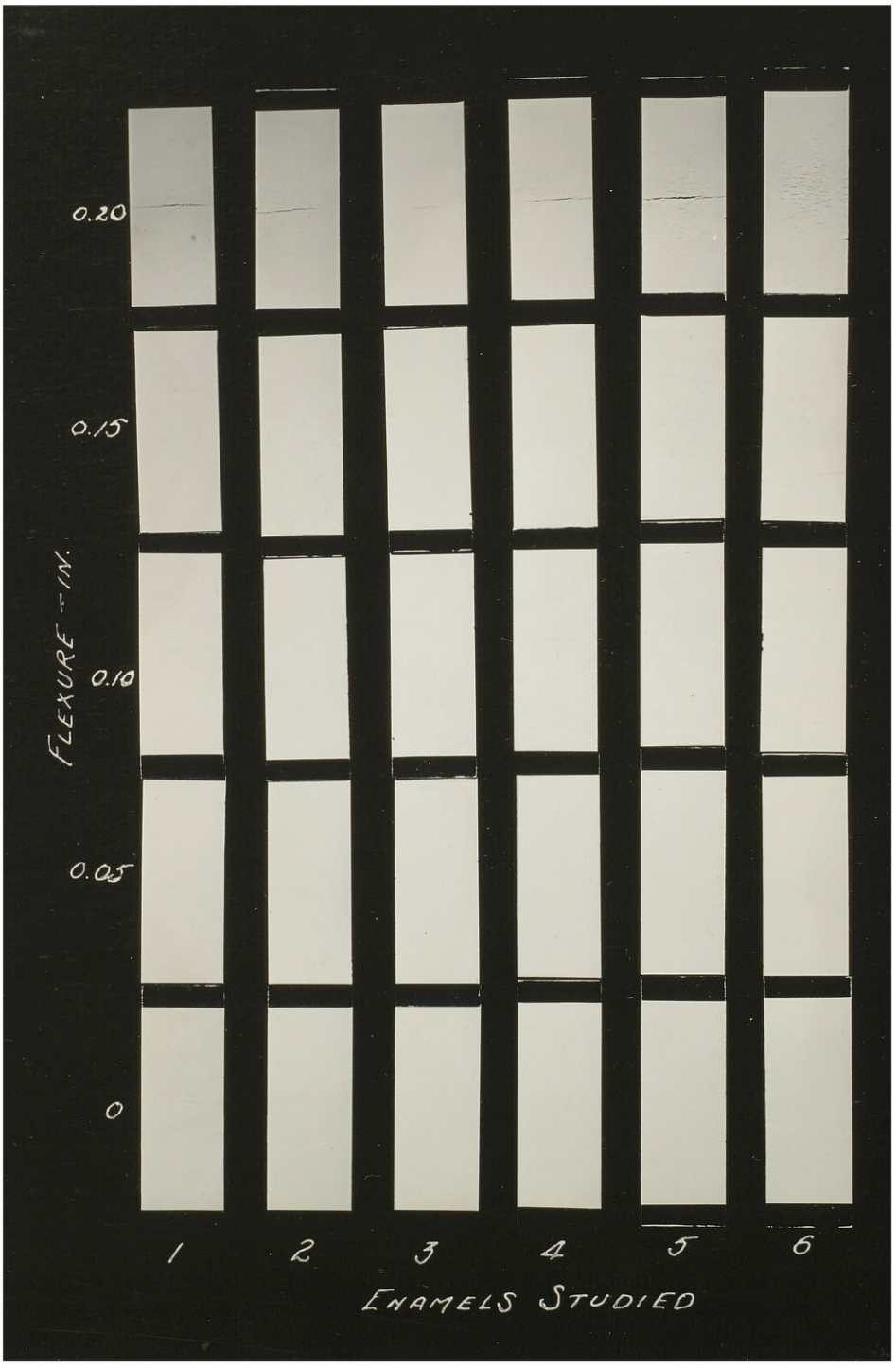


Figure 1. Photograph showing flexed samples of six different enamels.

of the enamel.

The cross flexed samples of the enamels which contained the mill added reagents gave the following results: $MgCO_3$ increased markedly the resistance to mechanical tearing, bentonite increased resistance slightly, and gums had little or no effect on resistance to this type of mechanical tearing.

The action of $MgCO_3$ in increasing the resistance of an enamel to mechanical tearing is probably due to a softening or weakening of the enamel. That is, the $MgCO_3$ gives the enamel coating a fluffy and soft texture in which the strains applied may be better absorbed than in an enamel film having a brittle nature. On the other hand, the bentonite probably exerted a strengthening action on the enamel giving it actually more strength and possibly more elasticity with which to resist a bending stress. The increase in resistance to mechanical tearing was not as marked in enamels containing bentonite as it was with those containing $MgCO_3$.

The differences in the resistances to mechanical tearing of the first series of enamels investigated led to several new branches of experimentation. As has been said before, the superior qualities of one enamel over another are due either to the character of the dry enamel as regards its resistance to mechanical flexing or to the capacity of the enamel for healing more completely during fusion. The latter supposition would be dependent upon the viscosity-temperature characteristics of each frit as well as upon the same characteristics of the soluble salts present. Although the soluble salts present in an enamel seldom exceed a total of 0.4% of the dry weight of frit employed, their effect must not be neglected.

Procedure 2--Study of the Effect of Soluble Salts on Mechanical Tearing

In order to eliminate the viscosity factor introduced by the different frits, one frit was chosen and from it were prepared a series of enamels containing varying proportions of H_3BO_3 and $NaNO_2$, the soluble salts previously found to be effective in cause or prevention of thermal tearing. The proportions of each salt used in each enamel were as shown in Table 2.

Salts were added to give 1 gram total $NaNO_2$ + H_3BO_3 per 100 grams of frit.

Table 2. Soluble Salt Compositions

Enamel	% Na_2O	Gms. $NaNO_2$	% B_2O_3	Gms. H_3BO_3
1	70.6	1.57	29.4	0.523
2	64.0	1.425	36.0	0.64
3	59.0	1.313	41.0	0.728
4	57.5	1.28	42.5	0.755
5	47.0	1.045	53.0	0.942
6	45.5	1.012	54.5	0.97
7	41.5	0.924	58.5	1.04
8	27.5	0.612	72.5	1.288
9	25.0	0.556	75.0	1.331
10	13.5	0.302	86.5	1.535
11	8.0	0.178	92.0	1.634

These additions to a dry-milled, single type, frit gave a series of enamels which differed only in the quantity of soluble salt. The enamels were prepared by rapidly mixing the previously

dry milled frit with water, clay, and electrolyte. This treatment minimized solution of the frit. Samples were sprayed as before to 45 grams dry enamel per square foot; dried thoroughly, and five specimens of each enamel were cross flexed over a range from 0 to 0.10 inch, each sample being flexed 0.025 inch more than the preceding one. These samples were fired for three minutes at 1450°F, the normal maturing temperature for this enamel.

Results

This series of enamels, photographed in Figure 2, showed very clearly the two separate and distinct types of tearing. In the region of medium $NaKO_2$, the tear cracks were of the pure mechanical type, while the enamels high in H_3BO_3 showed severe thermal tearing. The unflexed samples high in H_3BO_3 were thermally torn but the five or six unstressed enamels grouped around the region of $Na_2O \cdot B_2O_3$ were from all standpoints good enamels. The stressed samples around this metaborate region, however, gave marked evidence of the differences in resistance to mechanical tearing of these normally good enamels. That is, the samples at or very near to the sodium metaborate line showed the maximum resistance to the mechanically made defect, the tear lines becoming worse for each constant flexure with an increase of either soluble salt. Those stressed samples containing a large proportion of H_3BO_3 as a soluble salt showed the effects of both mechanical and thermal tearing. Considering only those enamels of this series which were ordinarily good before stressing, it may be said that the differences in their resistances to mechanical tearing were due only to the differences in the quantity of the soluble salts present.

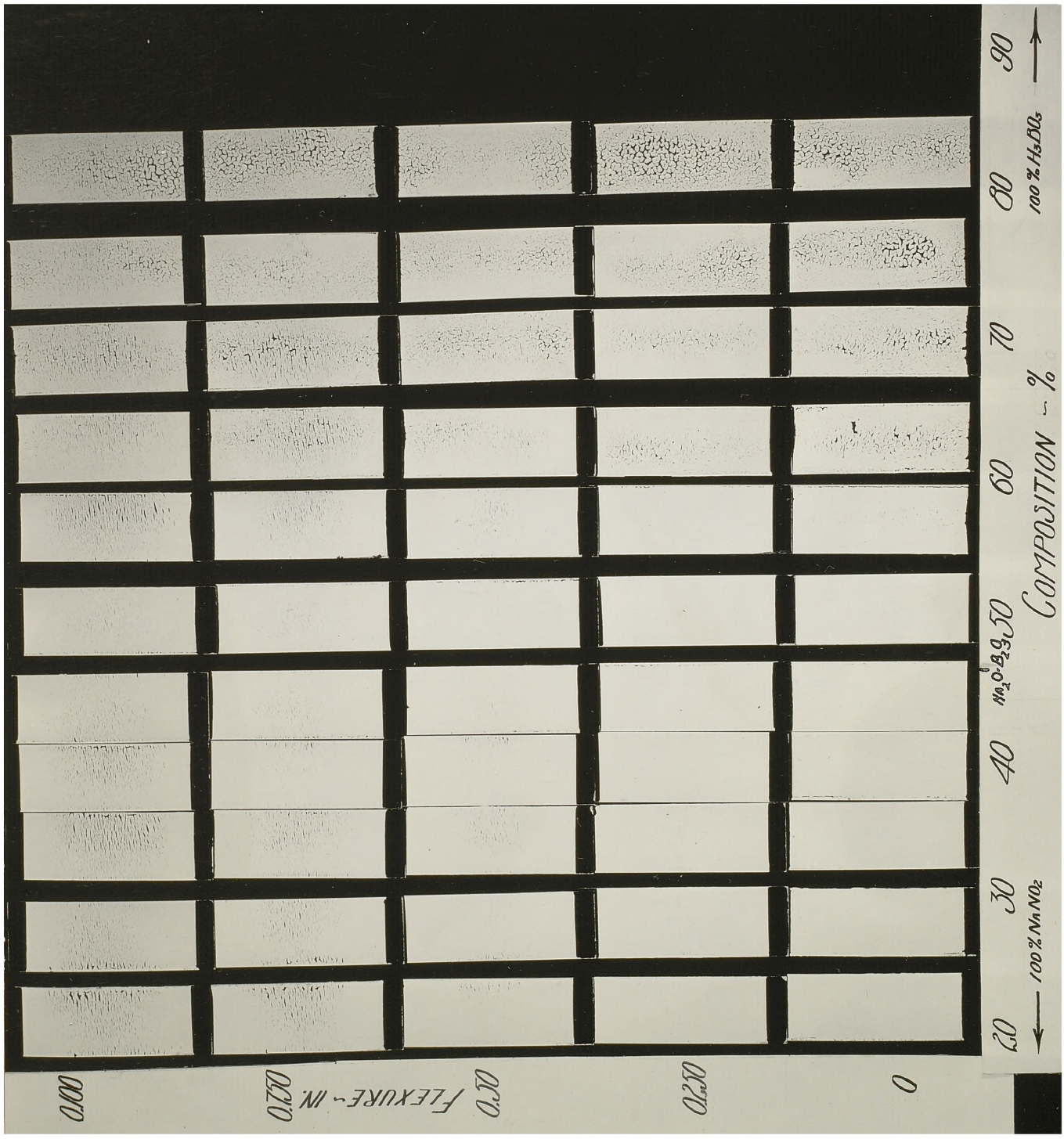


Figure 2. Photograph of fired enamels containing mixtures of $NaNO_2$ and H_3BO_3.

Whether the proportions of these salts in those enamels gave them more actual mechanical resistance or whether they allowed better healing during fusion, the effective minimization of mechanical tearing was due solely to the soluble salts present.

Procedure 3 and Results--Study of the Effect of Soluble Salts on Fusion of Torn Enamels

The next step was to attempt to determine whether the stressed enamels containing the proper porportions of soluble salts healed better on fusion, or whether they actually cracked to a lesser degree during flexing. It was thought that the investigation could be carried out by choosing three enamels from the series of Figure 2, close enough to the sodium metaborate composition so that all three would be, while unflexed, among the good enamels. A number of samples of these enamels were then flexed to a degree that caused rupture in all three series; then they were fired at the normal firing temperature for varying lengths of time so that the progress of widening or healing of the cracks could be followed. In theory, the method should allow the visual determination of whether one enamel had more cracks than another at the beginning, or whether the second enamel fused the cracks over to a greater degree than the first. After completion of this experiment, it was found that the above suppositions were not entirely true. It was impossible to determine the relative degrees of cracking during the first stages of firing as the enamels showed no visible signs of cracking until incipient fusion began. In addition to this, the enamels drawn from the furnace before fusion tended to flake from the metal during cooling so that whole sheets of the cover coat could be lifted away from the ground coat.

It appeared, in those remaining samples which were fused, that the enamel which contained the soluble salts in the ratio of the metaborate had less actual cracking than did either of the other two series of samples. The cracks in the enamels containing high H_3BO_3 seemed to be spread more during the first stages of fusion than did the cracks in the other two series of enamels, leading to the belief that this enamel was being subjected to the effects of thermal as well as mechanical tearing. This last is the principal difficulty in a study of mechanical tearing as affected by soluble salts. If the range of quantity of soluble salts is wide enough to give visible differences in the final enamels, the phenomenon of thermal tearing is introduced giving uncertainty to the results.

III. CONSIDERATION OF THE MECHANISM OF MECHANICAL AND THERMAL TEARING

General Statement--Part one

The work on mechanical tearing led directly to this second phase of study, as several of the results deserved further attention. The flexed enamels which were calcined could easily be lifted away from the ground coated sample after cooling. After removal of these enamels, it was noted that there were left on the ground coat, adhering white ridges of cover enamel which followed the contours of the cracks in the sheet of cover enamel which had been lifted away. These ridges, under each mechanically made crack, resembled very closely the "delta" formations characteristic of the more severe types of thermal tearing. It had been thought previously that these deltas were characteristic only of enamels high in boric acid and that they were primarily responsible for thermal tearing. However, their appearance in good enamels, mechanically torn, gave a common characteristic to thermally and mechanically torn enamels.

Procedure 1--Visual Observations of Tearing Enamels During Heating

Since it was difficult to obtain a continuous picture of the progress of the tearing process by drawing samples from a furnace at definite intervals, another method of observation was sought. A small furnace was prepared in which samples could be observed throughout the process of firing. The furnace was equipped with a quartz window through which observations were made with a low power binocular microscope. Small ground coated samples about an inch square were covered with enamels prepared from the frits previously mentioned. From each frit, two series of enamels were

prepared, one containing $NaNO_2$ and H_3BO_3 in the correct ratio for $Na_2OB_2O_3$, the other containing 0.5% H_3BO_3 as the added electrolyte. These enamels were prepared as before by quickly mixing water, clay, and electrolyte to the previously dry-ground frits. These enamels were sprayed on the ground coated samples at about 50-55 grams per square foot. It was later found advantageous to apply some of the enamels by pouring them directly on the piece which was gently tapped to smooth the enamel surface. After drying, the enamels containing the two soluble salts in the proper ratio for $Na_2OB_2O_3$ were mechanically flexed and their behaviors on firing were noted. Later, those samples containing high H_3BO_3 were also examined.

Results

The process of tearing during heating appeared to be the same for both series of samples. The first action noticeable was the formation of a series of hair line cracks in the surface of the enamel. The mechanically flexed enamels showed cracks parallel to the direction of flexing, while the high H_3BO_3 enamels showed a type of rupture sometimes described as "mud cracking." See Figure 3.

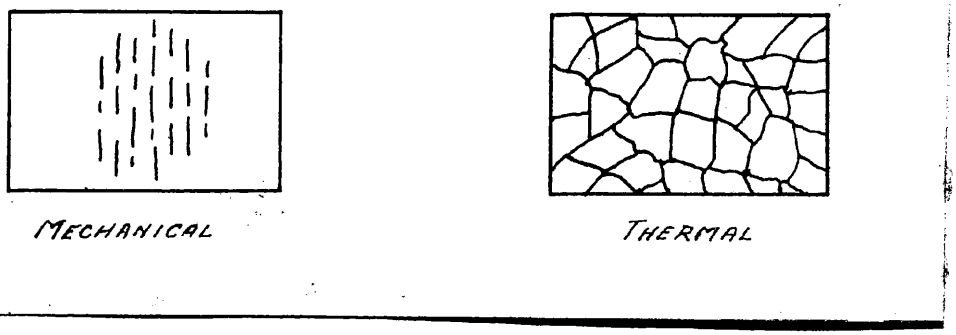


Figure 3. Diagrams of two types of tearing.

On continued heating, these hair line cracks were widened by the drawing back of the separate patches of cover enamel leaving the ground coat exposed. This second process appeared to be an action arising from shrinkage of the heated layer. The third noticeable behavior was that of lifting in the enamel layer away from the ground coat at the edges of the cracks. Lastly, the lifted edges were flattened out, and the edges of the cracks in the enamels began to round off and a partial closing was noticeable. The completion of this action in the mechanically torn enamels was dependent upon the degree of cross bending to which the dry enamel had been subjected. Complete healing of tear cracks, without showing the blue ground coat, was noted in samples not too severely flexed. Rounding of the edges of the patches of white enamel was followed by their fusion into the exposed ground coat and later by their smoothing out and carrying to the surface, lines of blue enamel. The various steps are diagrammed in Figure 4.

General Considerations of the Mechanism of Enamel Film Rupture

When a dry coat of cover enamel is flexed, the ordinary result is a tension crack. The nature of this crack is dependent upon the degree of flexure, thickness of the coating, and the physical nature of the enamel layer, brittleness, friability, and surface character. Ordinarily, a normal enamel coating, if flexed below the elastic limit of the ground coated steel, shows one of two types of cracks--the most common being the crack following a single straight line perpendicular to and penetrating the whole enamel layer to the ground coat. In Figure 5 is shown an exaggerated cross section of this type of cracking. This type of crack merely separates the enamel into two separate sheets. The second

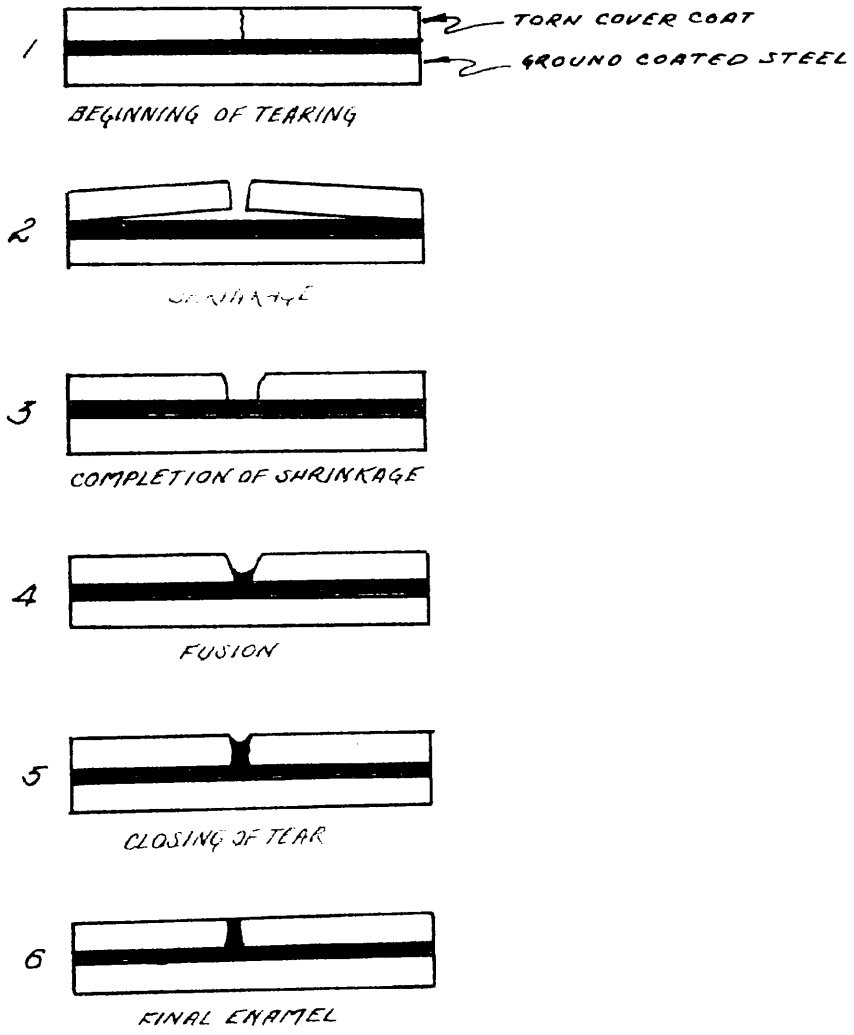


FIGURE 4 PROCEDURE OF TEARING DURING FIRING

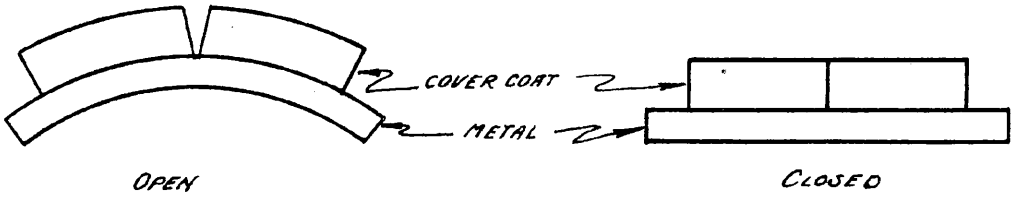


Figure 5. Diagram of "V" type of mechanical cracking.

type noted is that which starts at the top surface of the enamel layer as a single crack and branches as an inverted Y to the lower surface. Figure 6 shows an exaggerated cross section of this type of break. Between the legs of the inverted Y is left a ridge of enamel which is split from the layer during cracking. As has been

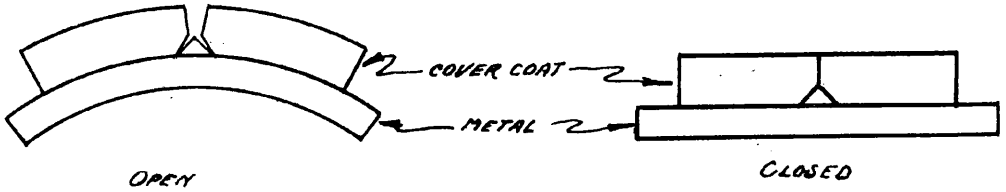


Figure 6. Diagram of "inverted Y" type of mechanical cracking.

pointed out previously, this ridge in mechanically flexed enamels is not apparent until the enamel has been calcined and lifted from the ground coated piece. In many materials, particularly brittle ones, this ridge formation is characteristic when the material is broken in tension.

It is obviously the tendency in either type of fracture

for the enamel to split away from the ground coat. That is, in addition to the relief of strain by cracking, the enamel will also relieve strain by freeing itself from the ground coat. Exaggerated, the condition is shown in Figure 7. This tendency will be

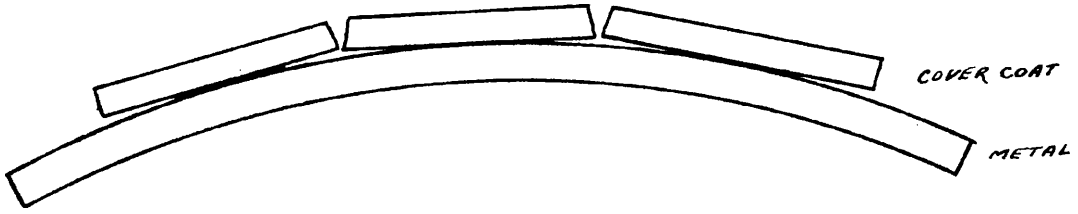


Figure 7. Diagram showing relief of strain in flexed enamel.

dependent upon the physical character of the enamel. If the binding force is stronger between the particles in the dry enamel itself than between the enamel and the ground coat, the tendency will be more toward loosening of the enamel from the ground coat. If, however, the reverse is true, the strain will be absorbed more in cracking than in lifting from the ground coat. In either case, it is probable that the mechanical working weakens the dry bond between the cover enamel and the ground coat so that the layer of cover enamel has less resistance to the forces of shrinkage set up during fusion. The above observations were clearly borne out by the calcined enamels that had been mechanically flexed. The portions around the center of the sample, where bending was most severe, were easily removed from the ground coat by lifting with a knife blade; while the enamel on the ends of the piece adhered in

many cases very firmly.

During the first stages of heating, the forces of shrinkage tend to draw the enamel away from the previously formed cracks, with little or no resistance from the forces holding the enamel layer to the ground coat. This same shrinkage, in a normal, unruptured, enamel may possibly be taken up by a myriad of small separations between the grains of material present, rather than in ten or twenty much larger separations at points of rupture and poor adherence.

General Statement--Part Two

The similarity of the two types of tearing as observed in this series of experiments led to a reconsideration of the mechanism of thermal tearing. It had been noted in preparation of the large samples for the above experiments that often those enamels high in H_3BO_3 tended to break during drying, particularly those which had been applied heavily. It was also noted that the same enamels applied heavily on the small pieces often tended to come loose very easily and fall from the ground coat. The observations led to the belief that the shrinkage on drying was possibly responsible for these behaviors of high H_3BO_3 enamels.

Procedure 1 and Results--Observation of Cracked Enamel Films

The first series of experiments were designed to verify these previous observations. Enamels containing a high percentage of H_3BO_3 were prepared and applied at varying thicknesses on ground coated pieces and after drying, they were inspected for cracking. Of the various dyes and indicators tried, the most successful was a suspension of lampblack in kerosene, a mixture which outlined any cracks instantaneously. In general, the cracking was always

present in heavily applied enamels, but in some of the thinner applications, tearing was not evident until calcination of the sample. The thicker the sample, ordinarily, the more severe the cracking.

In addition to the above tests, the same enamels were applied to glass plates through which the process of drying could be watched with the aid of a microscope. Observations of this nature gave no information as the cracks forming on drying were absolutely undetectable, even at higher magnifications. In most cases, even when the cracks were outlined by the employed stain, visible evidence of depth or width of the crack was not observable. However, in some cases, as has been pointed out, the heavily applied enamel on a small sample has broken into two or three pieces during drying.

Procedure 2 and Results--Linear Drying Shrinkage Measurements

It was next thought desirable to measure, if possible, the linear drying shrinkage of an enamel high in H_3BO_3 and compare it with the shrinkage of an enamel containing $Na_2OB_2O_3$ as the soluble component. Enamels were prepared as previously from several of the available frits and these slips were poured, in measured amounts, into steel briquet molds resting on a greased glass plate. After complete drying, the briquet molds were removed and the shrinkages were measured. For its purpose, this experiment failed as the tendency of the samples to curl prevented any accurate measurement of the small order of linear shrinkage observed. This curling did, however, lead to further experiments. It was noted that those samples high in H_3BO_3 curled more in every case than did those containing $Na_2OB_2O_3$. The ends of the specimens lifted up and away from

the glass plate, leaving a bow in the enamels, in some cases, of as much as 1/2 inch from center to end. Characteristic samples are shown in Figure 8. This behavior showed that either the shrinkage of the surface layer was greater than that of the under layer, or that the surface layer was rigid enough, after shrinkage, to prevent movement of the lower layer.

Procedure 3 and Results--Study of Stresses in Dried Enamel Films

In further experimental work concerning the drying stresses set up in enamel layers, various slips were applied on other non-rigid bases. Enamels prepared as previously described, containing the soluble salts in the proper ratio for $Na_2OB_2O_3$, were sprayed in varying thicknesses on thin celluloid and their drying behaviors were compared with enamels having a high content of H_3BO_3 which had been applied at the same thicknesses on like celluloid strips. Although the behaviors were not always predictable, the thin coatings (30-40 grams per square foot) tended to bend up at the corners and edges while the heavier coatings bent the opposite direction in a manner similar to that previously described. In either case, the enamels containing a high percentage of H_3BO_3 as a soluble component showed more severe bending than the slips having the salts in the proper ratio for sodium metaborate.

In addition to the above, similar enamels were applied on waxed paper, tin foil, and on various thicknesses of shim stock. In all cases the results were the same as those given in procedure 2, the degrees of bend in the various materials being dependent upon their relative resistances to bending. This visual result was supplemented by measurements of the relative strains set up in split rings of shim stock during the drying of enamel coatings.

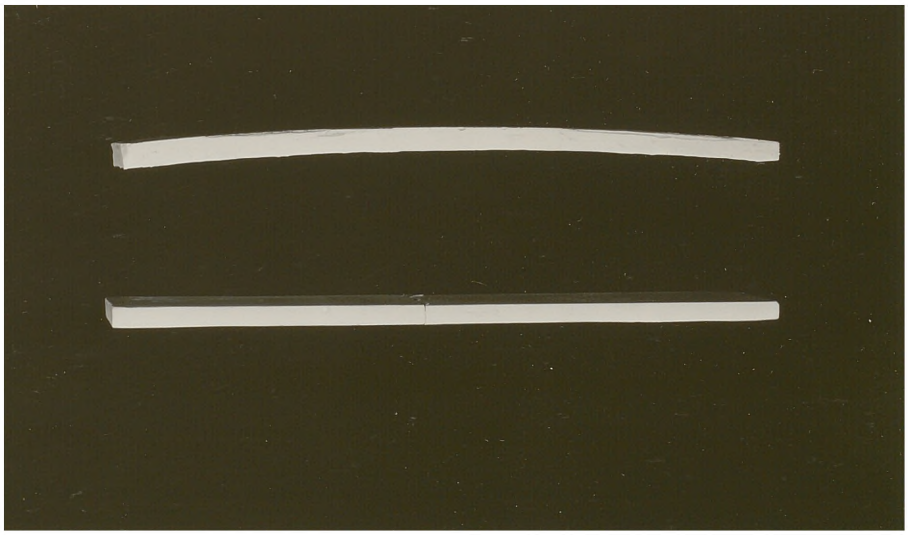


Figure 8. Photograph of dried enamel samples, one tearing, one non-tearing. Note curvature of tearing enamel.

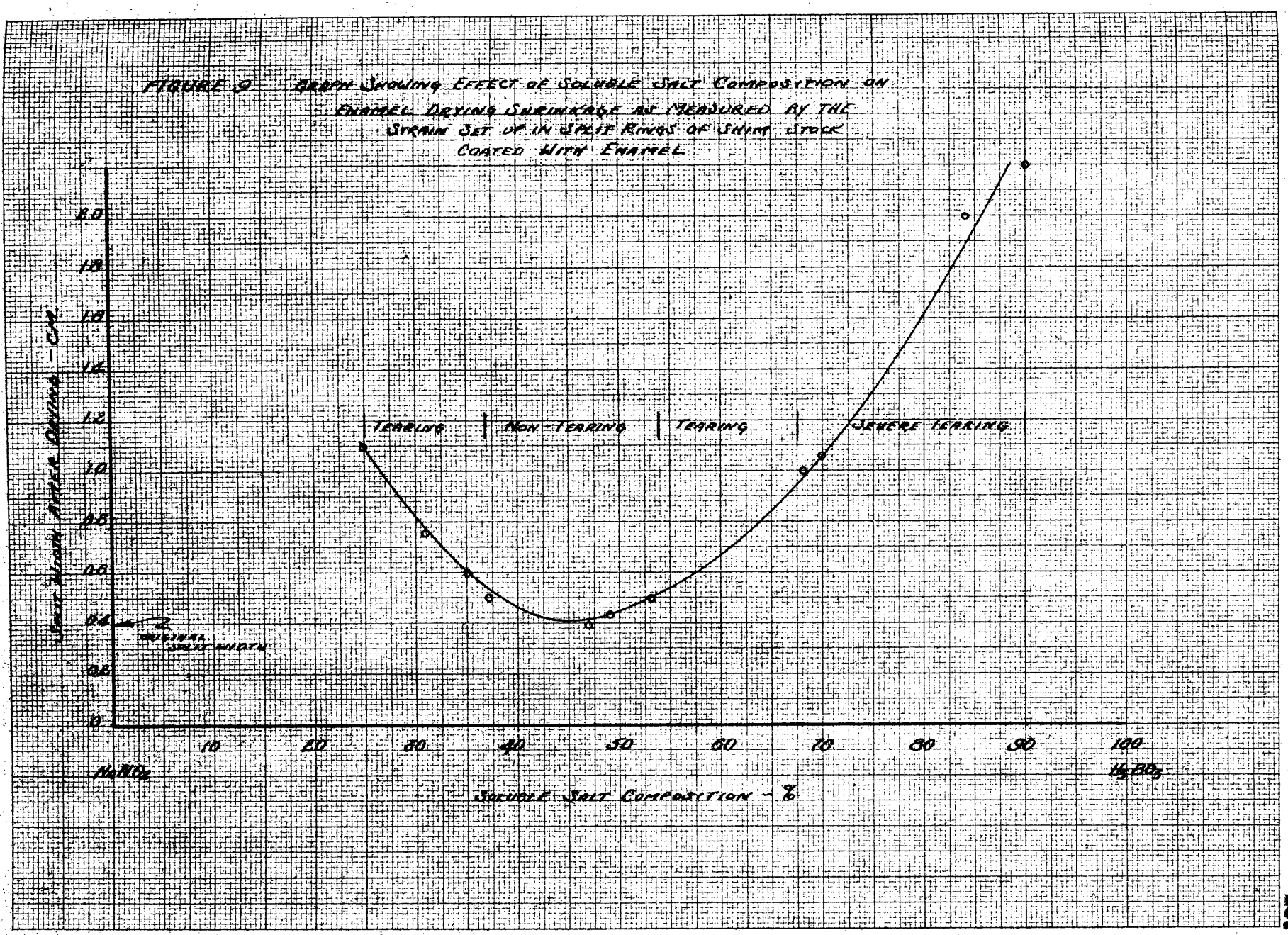
Enamels containing $NaNO_2$ and H_3BO_3 in the combinations given in Figure 9 were sprayed to a thickness of 45 grams per square foot on two inch diameter split rings of 0.01 inch shim stock which were one inch wide and had an original split width of 0.4 cm. The enamels were prepared by wet milling, and 1 per cent total electrolyte was added to each slip. After drying, the increases in split widths were measured as a criterion of tensile strain set up in the enamel during drying. To check these measurements against the tearing character of the enamels, the same slips were sprayed and fired on ground coated pieces. The results of these experiments are shown in Figure 9. Wet milled enamels were found to have the same characteristics when total quantities of H_3BO_3 and $NaNO_2$ as low as 0.2 per cent were added to the slips.

These experiments served to show clearly the behaviors of good and bad enamels during drying on surfaces in which the strains of shrinkage were relieved by warping and bending. If these enamels are applied on rigid surfaces to which they adhere, the release of strain in the tearing enamels is brought about by the cracking which is fundamentally responsible for tearing. The observed strains are either affected by a difference in total drying shrinkage between good and poor enamels, or there is a shrinkage gradient in the poor enamel. A shrinkage gradient may exist in an enamel coating if the surface shrinks and becomes hard before the remainder of the enamel is dry.

Procedure & and Results--Measurements of Volume Drying Shrinkages of Enamels

To determine whether any differences existed between the total drying shrinkages of tearing and non-tearing enamels, the

FIGURE 9 — GRAPH SHOWING EFFECT OF SOLUBLE SALT COMPOSITION ON ENAMEL DRYING SHRINKAGE AS MEASURED BY THE STRAIN SET UP IN SPLIT RINGS OF SHIM STOCK COATED WITH ENAMEL



following measurements were made. Duplicate samples of two enamels were prepared by rapidly mixing the previously dry milled frit, clay, and electrolyte, and carefully measured quantities of each enamel were placed in glass weighing bottles and allowed to dry. After drying, the dry volumes were determined by the standard method of weighing the enamels dry, saturated, and suspended in kerosene. The weighings were made on an analytical balance and the calculated results were considered to be precise to at least four significant figures. Although a total bulk volume shrinkage of over 35 per cent was measured, the accuracy of the data was uncertain as the thick layers of enamel in the bottles were intersected by numerous cracks which introduced possible errors in the determinations of saturated weights. The enamels were saturated in kerosene in an evacuated chamber to insure complete filling of the pore spaces and cracks but the subsequent blotting of kerosene from the enamel surfaces before the saturated weight determinations did not guarantee that some of the kerosene from the cracks was not removed.

In making a second attempt to measure the drying shrinkage of an enamel, it was thought that a thinner layer of enamel in the weighing bottle would be less conducive to the troublesome cracking. Therefore, a second group of enamel slips were prepared and poured in thinner layers into larger weighing bottles. The layers, however, were still relatively thick (3/8 to 1/4 inches) in comparison with a layer of enamel as it is applied to ground coated steel. This group of enamels was allowed to dry thoroughly and the determinations of dry volumes were made as before. This time, however, the cracks occurring in the layers were known to be completely full of kerosene before the saturated weighings were made.

This determination of the apparent bulk dry volume contained a summation of three volumes: (1) the true volume of the solids, (2) the volume of pores, and (3) the volume of cracks. Since the volumes of the cracks were included, no significance could be attached to a change in apparent bulk volume. Therefore, further determinations were made so that the volumes of the cracks could be eliminated and a true measurement of bulk volume could be obtained. These determinations consisted of measurements of the true porosity of uncracked enamel samples taken from the layers in the bottles. After measuring the true porosity, the figures obtained were added to the true dry volume of solids so that the resulting figure was the true bulk volume of the dry enamel. These figures are given in Table 7.

Table 7. Volume Drying Shrinkages of Tearing and Non-tearing Enamels

Enamel Number	Original Bulk Volume	Final Apparent Bulk Volume	Final True Bulk Volume	% Volume Drying Shrinkages
*5	9.432	7.194	7.063	33.41
5	9.570	7.138	7.060	33.75
11	9.695	7.356	7.219	34.30
11	9.677	7.262	7.110	35.10

Considering the extremes of the values given, it is obvious that the difference between them (almost 2%) is not enough to account for the formation of tear cracks in an enamel. This difference would be less than 1% if expressed as linear shrinkage, and this is not sufficient to effect the degrees of bending that have been noted.

* These numbers refer to soluble salt compositions given previously in Table 2.

Summary

When enamels are applied heavily on a surface to which they do not adhere, the sole difference in the character of tearing and non-tearing enamels is resultant from the manner in which the drying shrinkage takes place. In the poor enamel, the drying is such that the shrinkage takes place in steps, with surface layer curling and cracking due to completion of surface shrinkage before internal shrinkage has progressed to the same degree. The good enamel has practically the same shrinkage, but the drying character is such that the shrinkage takes place evenly throughout the whole layer. When the same enamels are applied on rigid surfaces to which they adhere, the differential surface drying stresses in the poor enamels are absorbed by surface cracking; followed by internal cracking along the same ruptures, so that the surface crack penetrates to the base on which the enamel is applied. The enamel that does not tear has no strain gradient to be absorbed, and the shrinkage is uniform throughout. However, the total shrinkage is high in the non-tearing enamel, and it is obvious that the overall strain must be relieved by other means.

IV. EXAMINATION OF TEXTURAL PROPERTIES OF ENAMEL FILMS

General Statement

The work of Part III has shown that there are several fundamental differences in the physical behaviors of tearing and non-tearing enamels. Principally, the tearing enamels have a drying shrinkage gradient, and the dryed enamel surface is hard and brittle; while the non-tearing enamel has a uniform drying shrinkage, with a soft dried surface. These differences in dried surface character suggested the approach to this step of the investigation, which was aimed toward examination of enamel textural characteristics. The particular question of interest was one regarding the nature of enamel texture and its mechanism in causing or preventing tearing.

Procedure 1 and Results--Study of Thin Sections of Dry Enamels

The method of study was simply one in which thin sections were cut in various directions from dried samples of tearing and non-tearing enamels. The enamels were prepared by wet milling of frit, clay, and water to a fineness of 2 grams. The milled enamel was divided into two parts, to one of which was added 0.2% $NaNO_2$, and to the other, 0.5% H_3BO_3. Enamels were applied by spraying on ground coated pieces, and by pouring in iron molds on glass plates. Before grinding, the dry enamels were saturated with Canada balsam to prevent slaking, and the grinding was carried out in the ordinary manner. To more nearly insure equal thicknesses of two compared specimens, both were cemented on the same slide, as close together as possible. Photomicrographs of several samples were taken and they are presented in Figures 10 to 15.

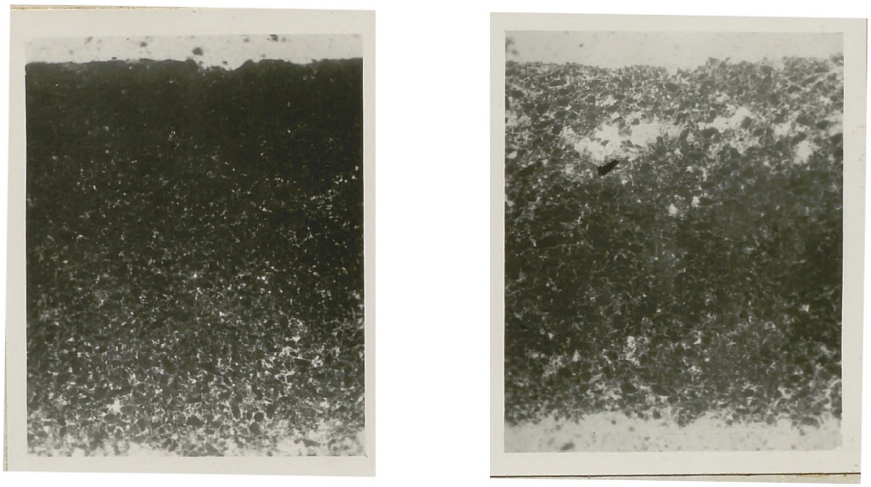
Exposure times for both negatives and prints for each set of samples were maintained constant to insure comparative results.

Result

Figure 10 shows magnified sections cut perpendicular to the surfaces of a tearing and a non-tearing enamel which had been applied to a thickness of approximately 50 grams per square foot on a surface to which the enamel adhered. These cross sections show clearly the textural differences in a tearing and a non-tearing enamel. The good enamel is loosely packed, and has an open network of pores. The poor enamel shows a gradation of denseness from the top surface down, with no loose structure near the top, and a more porous texture near the bottom. The differences in surface texture are more clearly shown in Figure 11, which are representative sections of samples cut parallel and close to the top surfaces of the same enamels that were used for Figure 10. Note the striking difference in pore structure.

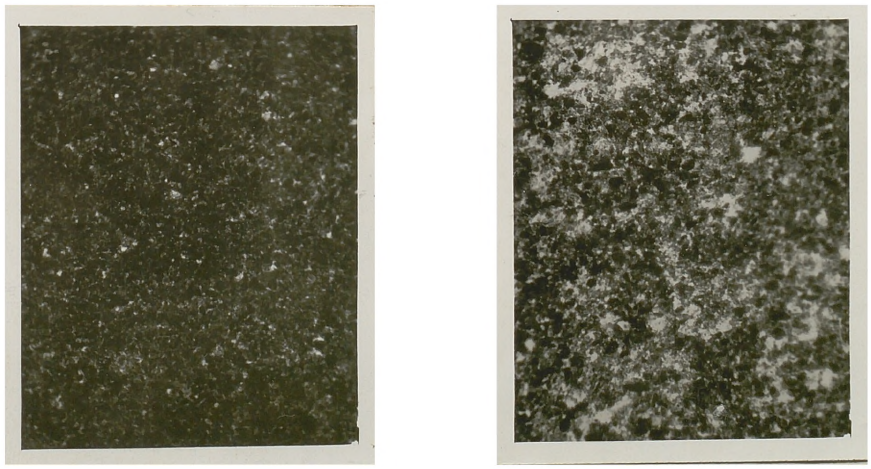
Figure 12 shows the textural differences in cross sections of another pair of enamels, one good and one poor. Figure 13 shows samples cut parallel to and close to the surface of the same enamels used for Figure 12. Here again, the textural differences are obvious.

To make the conditions as extreme as possible, several samples were prepared by drying extra-thick samples on a glass plate. The method was simply one in which the enamel slip was poured into an iron briquet mold on a glass plate. Samples for Figure 8 were prepared in this manner. Figure 14 shows sections cut perpendicular to the surfaces of two of these thick sections,



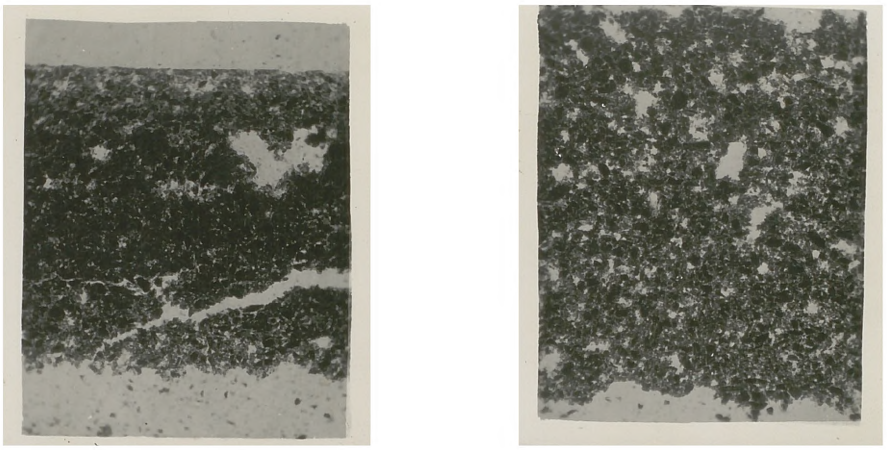
Tearing Non-Tearing

Figure 10. Photomicrographs of thin sections cut perpendicular to dry surfaces of a tearing and a non-tearing enamel, both applied at 50 grams per square foot.



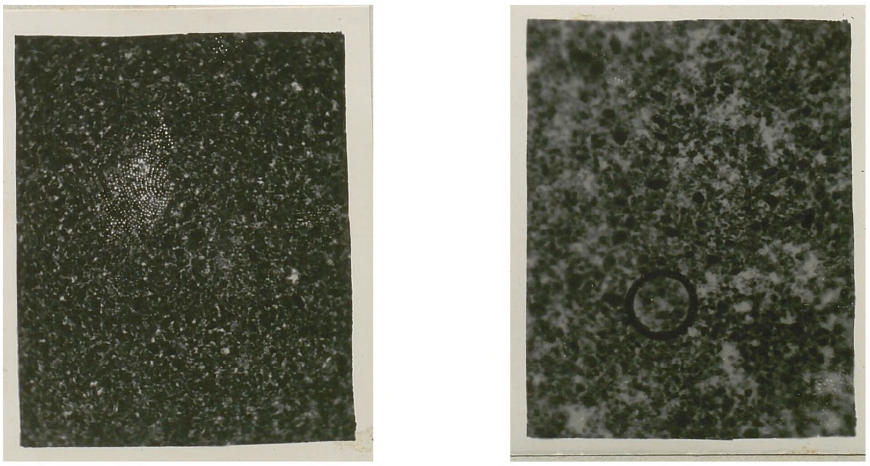
Tearing Non-Tearing

Figure 11. Photomicrographs of thin sections of enamels, cut parallel to surfaces of enamels used in sections shown in Figure 10.



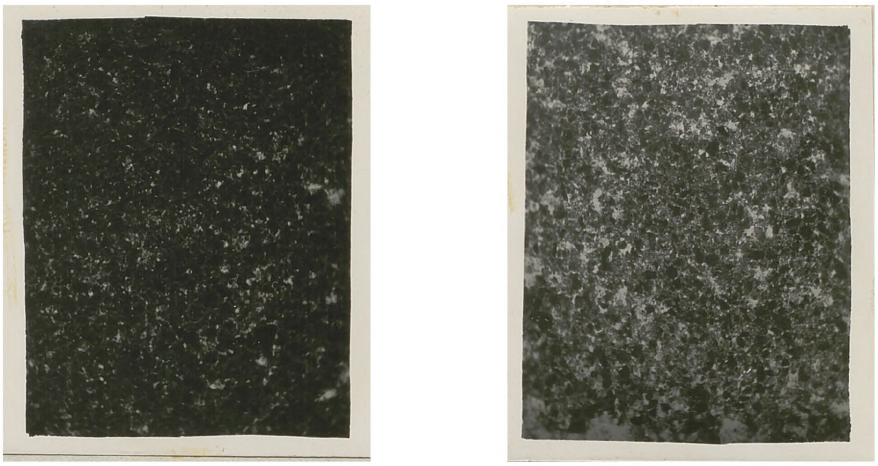
Tearing Non-Tearing

Figure 12. Photomicrographs of thin sections cut perpendicular to dry surfaces of a normally applied tearing and non-tearing enamel.



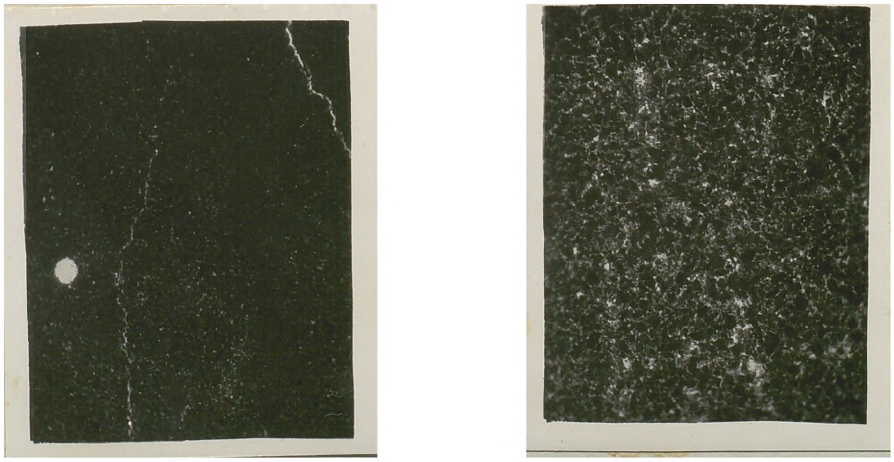
Tearing Non-Tearing

Figure 13. Photomicrographs of thin sections cut parallel to surfaces of enamels used in sections shown in Figure 12.



Tearing Non-Tearing

Figure 14. Photomicrographs of thin sections cut perpendicular to dry surfaces of a very thick tearing and non-tearing enamel.



Tearing Non-Tearing

Figure 15. Photomicrographs of thin sections of enamels, cut parallel to surfaces of enamels used in sections shown in Figure 14.

one containing $NaNO_2$; the other containing H_3BO_3. Again the textural differences are apparent, with the non-tearing enamel having an open, loose structure, and the tearing enamel having a comparatively high density near the surface. Figure 15 shows sections cut parallel to the surfaces used in cross section for Figure 14. The differences are again clear.

Analysis

These enamels, prepared from different frits, are characteristic of a number of sections examined microscopically. The result was the same in every case, and shows conclusively the differences in the texture and packing character of tearing and non-tearing enamels in the dry state. In the case of the tearing enamels, the density of surface and near surface packing shows clearly why the drying behavior is as it was observed. The capacity for denser packing, and the finer pore structure hinders drying so that the previously mentioned shrinkage gradient is effective in setting up the tearing stresses. The good enamels, on the other hand, have the open structure essential for even drying and even shrinkage. In addition, the good enamels are capable of absorbing any shrinkage stresses, even or uneven, because of their networks of large open pores. In effect, the "film strength" of the non-tearing enamel appears to actually be "film weakness", in that the cracking that would free the stress in a dense enamel occurs as a single tear, while the same stress could be absorbed by a hundred cracks in the loosely packed enamel. This last is clearly illustrated in Figure 17, a case in which the densely packed enamel was "too strong", and the separate particles were bound together

tenaciously enough so that fracture in one large crack finally resulted.

Procedure 2--Determinations of Drying Behaviors

The packing character of these enamels should theoretically have an important role in determining their drying behaviors, and it was thought advisable to examine the drying character from the standpoint of water loss vs. time. The determinations were made by weighing samples of tearing and non-tearing enamels which were suspended from an analytical balance in a drying chamber. In this manner, the samples, having a constant area, could be accurately weighed at regular, continuous, intervals during the drying. Samples of good and poor enamels were sprayed and dipped on ground coated pieces, and their weight losses during drying were determined at 25°C., 75°C., 95°C., and 105°C.; the relative humidity being constant for each pair of samples.

Results and Analysis

The data from these determinations showed clearly one effect of the packing character of the enamels. In every case, the non-tearing enamel was completely dry before the tearing enamel; the differences in time being an inverse function of the temperature. This result is one that would normally be predicted. It would also be expected that a difference in rates of loss should exist between tearing and non-tearing enamels, but none were measurable. The thinness of the coatings, and the cracking in the poor enamels may account for this. Figure 16 shows a typical water loss versus time graph for two enamels dried at constant temperature and relative humidity.

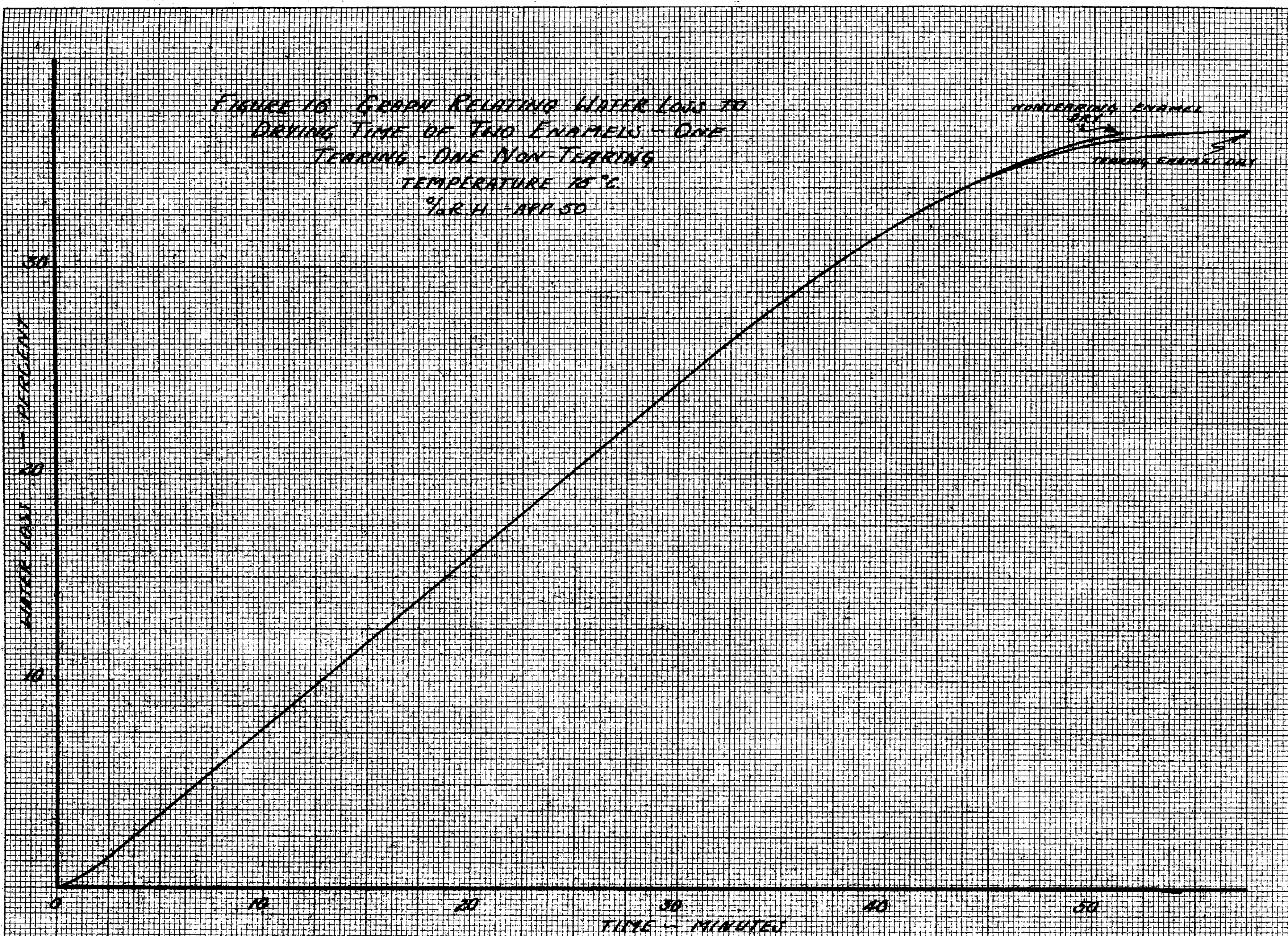


FIGURE 16 GRAPH RELATING WATER LOSS TO DRYING TIME OF TWO ENAMELS – ONE TEARING – ONE NON-TEARING
TEMPERATURE 75 °C
% R.H. – APP 50

Procedure I and Results--Study of the Effect of Drying Rate on Tearing Resistance

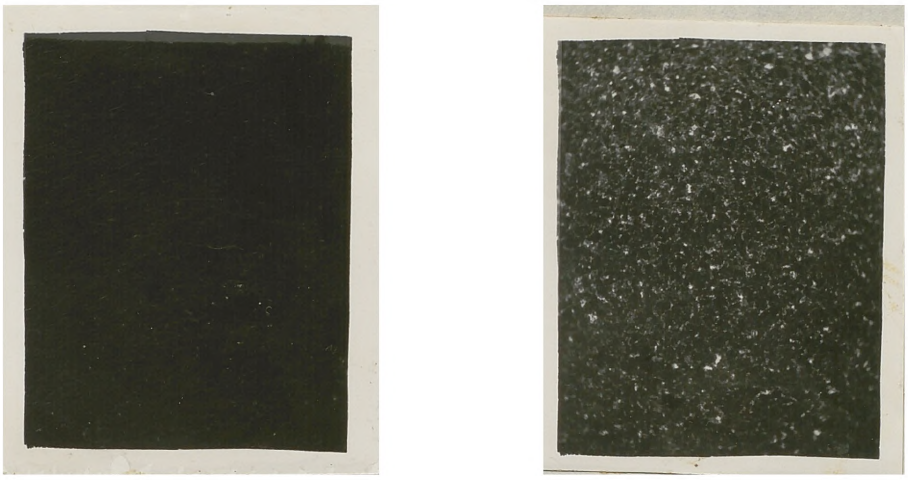
In conjunction with these drying experiments, the more practical aspects of the problem of drying behavior were also examined. Ground coated pieces were sprayed with 50 grams per square foot of an enamel that was known to tear, and these samples were dried at various temperatures and relative humidities. Some were dried at room temperature, both at room humidity and at elevated humidities under damp cloths, and some were dried in a drying chamber at various temperatures between 25°C. and 110°C., with normal and elevated humidities. Samples were also dried in infra-red radiation and over gas flames and electric hot plates. The pieces were inspected for tearing, and little differences were noted--regardless of the drying conditions. This result is what would be expected, when viewed from the standpoint of what has been said of the packing character of tearing enamels. As long as the shrinkage takes place with dense packing, the net result will be the same with any normal drying procedure. If drying was carried out so that the time was infinitely long, and no moisture gradient existed during removal of water, there is a possibility that the tearing tendency during drying could be eliminated. One other possibility of preventing tearing during drying is worthy of mention: the removal of water instantaneously, or flash drying. This last was approached by spraying wet enamel on a hot test piece, and the tearing was seen to be minimized, but continuous flash drying is not possible after a thin coat of enamel has been applied on the test piece.

Procedure 4 and Result--Study of Thin Sections of Calcined Enamels

It had been noted, in the microscopic studies of enamels during firing, (Procedure 1, Part III) that the action occurring in a tearing enamel during heating appeared to be simply a manifestation of shrinkage away from cracks previously started. It would appear logical that such action would be shown by textural characteristics in the enamel as studied in thin section. Using the same technique as before, thin sections were prepared from samples of tearing and non-tearing enamels which had been calcined to 1000° F. for 10 minutes. The calcined samples were made from thick samples of dried enamel which had been prepared by casting enamel slip in briquet molds resting on a glass plate.

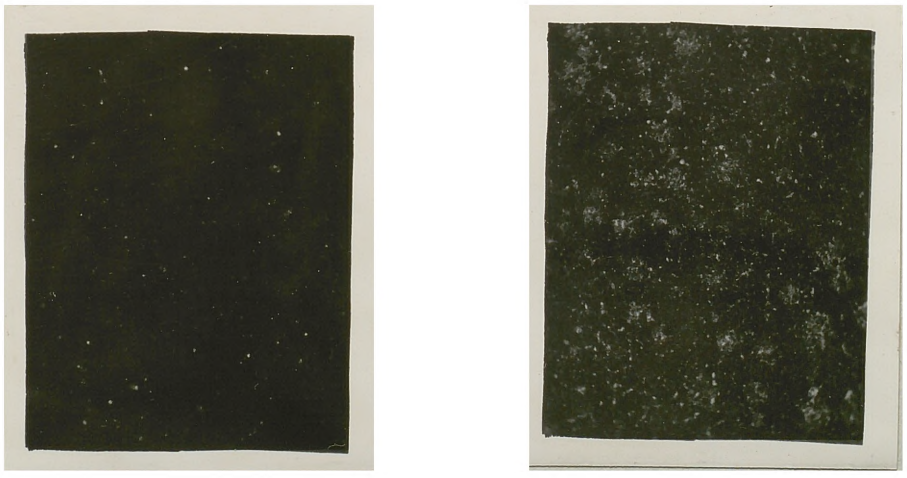
Result

Photomicrographs of thin sections cut perpendicular and parallel to surfaces of calcined tearing and non-tearing enamels are shown in Figures 17 and 18. The characteristics of these sections are not distinctly different from the characteristics of the dry enamels discussed under Procedure 1 of this section. The tearing enamels in all cases have become packed more densely, while the non-tearing enamels have maintained their open structure. The relative behaviors during heating at calcining temperatures are shown also in the photograph, Figure 19, a picture of calcined, thick samples of enamel. The curled sample is a typical tearing enamel, while the flat one is of a non-tearing variety. Shrinkage has progressed both samples, but the surface and near surface shrinkage of the poor enamel is made obvious in comparison to the good enamel. The surface of the tearing enamel was very hard, and it appeared that sintering had taken place to at least half the



Tearing Non-Tearing

Figure 17. Photomicrographs of thin sections cut perpendicular to surfaces of a calcined tearing and a non-tearing enamel.



Tearing Non-Tearing

Figure 18. Photomicrographs of thin sections of calcined enamels, cut parallel to surfaces of enamels used in sections shown in Figure 17.

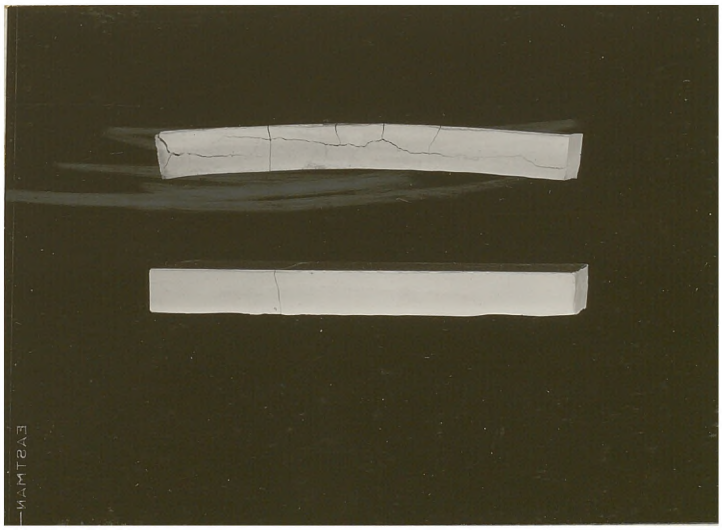


Figure 19. Photograph of calcined enamel samples, one tearing, one non-tearing. Note the curvature of the tearing enamel.

depth of the sample. On the other hand, the non-tearing sample was comparatively soft and was homogeneous throughout.

Summary

Here again the effect of shrinkage is clearly demonstrated, and the difference in packing characteristics is further emphasized. The calcining treatment appears to be simply an agency for further promoting the same physical features that were observed in the studies of dry enamels. The more tightly packed enamel simply becomes denser; the surface shrinkage being enhanced more than the interior shrinkage by a quantity equivalent to the difference that existed after drying. The non-tearing enamel undergoes uniform shrinkage; with the maintenance of an open structure. It is clear what would have resulted if these enamels had been fastened so that linear shrinkage could not be relieved by movement. The dense surfaced sample would have undergone stress release during the widening of a few surface cracks while the loosely packed enamel would have absorbed the same shrinkage in hundreds of smaller cracks.

V. CONSIDERATION OF CHEMICAL AND PHYSICO-CHEMICAL EFFECTS RESPONSIBLE FOR THE PACKING CHARACTERISTICS OF TEARING AND NON-TEARING ENAMELS

General Statement

The study has shown that the behavior during shrinkage, coupled with the textural characteristics of the enamel, are responsible for low film resistance to the tearing tendency. Both characteristics have been shown to be manifestations of the packing density of the dried enamel film. Since the only variables allowed to enter were the soluble salts and their concentrations, the packing character must be determined by them. It was the purpose of this part of the investigation to study the mechanism of packing.

In a system in which clay is in contact with water, the first effect of any added soluble salt is dependent upon the kind and amount of ions that are furnished to the system. The kind and amount of ions in the solution govern the degree of dispersion or coagulation of the clay portion of that system, and, other things being equal, fix the suspending power of the clay. This is effected by fixing the states of aggregation of the clay fraction in the system. For a given water content in which a coagulated clay makes a "thick" slip, a "thin" slip would be the result if the same clay were dispersed, with the thicker of the two having the better suspending power for an added non-plastic.

The physico-chemical property of a clay that is responsible for its ability to assume varying degrees of aggregation is based on its characteristic capacity to adsorb ions. The clay particle has at or near its surface a negative charge which attracts positively charged ions (cations) and holds them with a

tenacity which is a function of the electrical field strengths and concentration of the cations in solution. One cation may be exchanged for another on the clay particle by exchanging the type of ion in the surrounding solution. For example, a Na+ clay may be made into a H+ clay by simply leaching the clay with an acid. In general, small amounts of cations with high field strengths will coagulate clay-water suspensions. Such ions are H+, Fe+++, Mg++, and Ba++. Small additions of cations with low field strengths, such as Na+, K+, and Li+, tend to disperse clay slips or make them thin and fluid. If larger quantities of these low field strength ions are added to clay slips, the action is to coagulate them again after the first cycle of dispersion. Curve 1 of Figure 20 shows this effect on the viscosity of a slip of clay, quartz, and water, to which has been added various quantities of NaOH.

Procedure 1 and Results--Study of Ionized Salts in Clay Slips

An enamel slip is essentially a slip in which frit is suspended in clay and water. The ordinary water content is such that the system is very mobile or "thin" when the clay fraction is dispersed. If the clay is coagulated properly the slip is said to be "set-up." The preponderant ion in enamel mill liquors is the Na+ ion resulting from frit solution, and the action of this sodium is to bring about in an enamel slip the second cycle coagulation that was described above. The curve 2 in Figure 20 is a relationship of viscosity to salt concentration for a clay, quartz, and water slip to which concentrated mill liquor from a non-tearing frit had been added. Note the similarity between the two curves, one slip containing NaOH and the other, the actual mill liquor. The first few portions of NaOH disperse the slip, allowing the flint

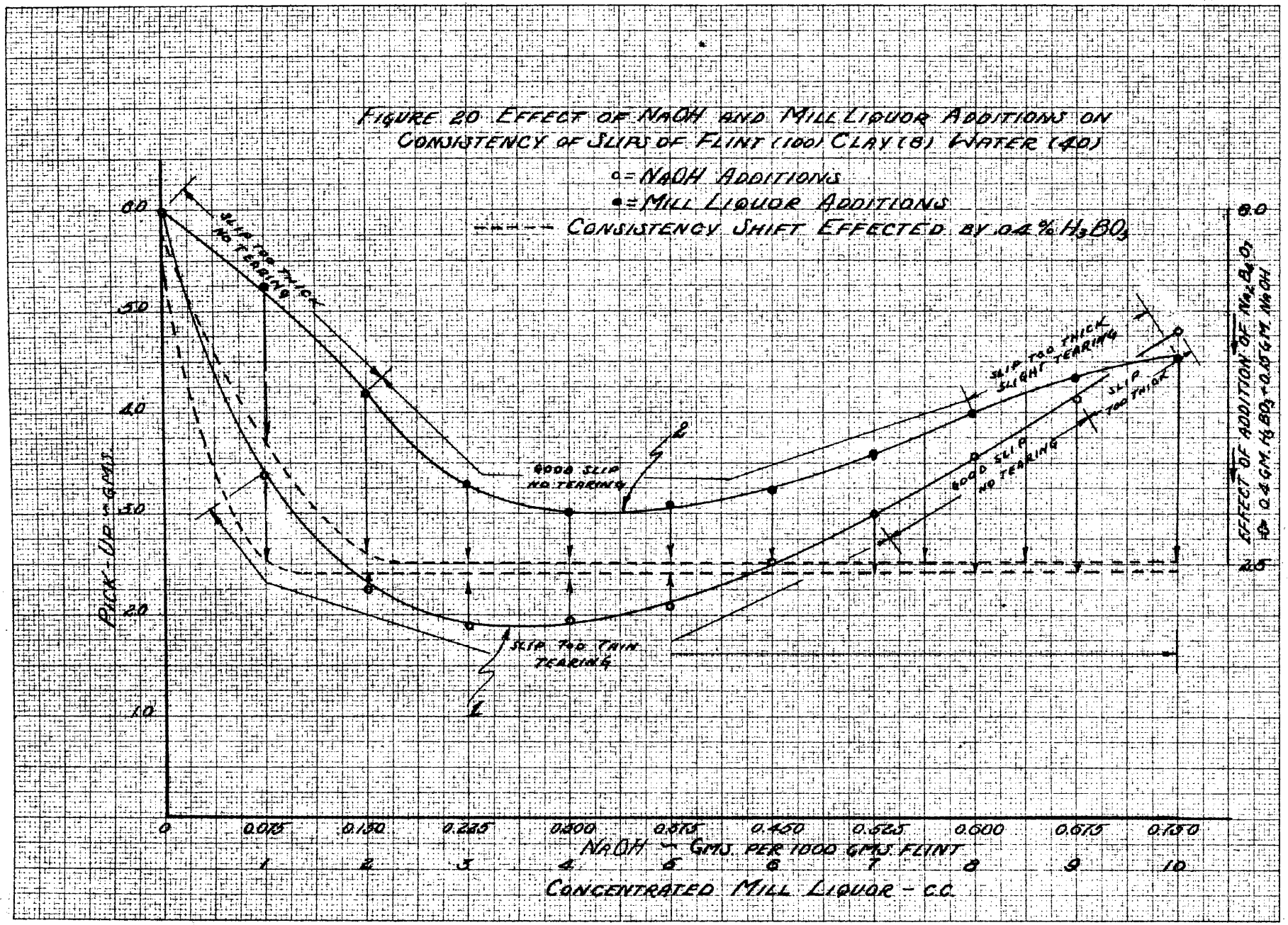


FIGURE 20 EFFECT OF NAOH AND MILL LIQUOR ADDITIONS ON CONSISTENCY OF SLIPS OF FLINT (100) CLAY (8) WATER (40)
o = NAOH ADDITIONS
• = MILL LIQUOR ADDITIONS
---- CONSISTENCY SHIFT EFFECTED BY .04% H_3BO_3
PICK-UP - GMS.
60
50
40
30
20
10
SLIP TOO THICK NO TEARING
GOOD SLIP NO TEARING
SLIP TOO THICK SLIGHT TEARING
SLIP TOO THICK
GOOD SLIP NO TEARING
SLIP TOO THIN TEARING
EFFECT OF ADDITION OF $Na_2B_4O_7$ @ 0.2 GM. H_3BO_3 + 0.05 GM. NaOH
6.0
4.0
2.0
0
0.075
0.150
0.225
0.300
0.375
0.450
0.525
0.600
0.675
0.750
NAOH - GMS. PER 1000 GMS. FLINT
1
2
3
4
5
6
7
8
9
10
CONCENTRATED MILL LIQUOR - C.C.

to settle out and making it useless as a suspension, further addition giving the slip the normal, good set, and further additions thickening it to such a degree that it is no longer usable. The addition of concentrated mill liquor (0.64 grams solid/c.c. mill liquor) from a non-tearing enamel gave the slip the same characteristics as the NaOH, but not to the same degree. As indicated on the curves, the region of best set is in the trough of the mill liquor curve, while the NaOH additions at the trough give an exceedingly thin slip. The slip containing the mill liquor is, in the region of good set, not coagulated completely in comparison to the ends of the curve. However, in comparison with the NaOH slip at the trough, the mill liquor slip is coagulated. The differences in trough depths of the curves are due to sodium salts in the mill liquor which buffer the action of Na^+ at a higher level, preventing the primary dispersion resulting from addition of a single base such as NaOH. Most important among these salts are NaF, $Na_2B_4O_7 \cdot 10H_2O$, Na_2SO_4, $Na_2O \cdot B_2O_3$, Na_2CO_3 and $Na_2O \cdot SiO_2$.

It may be well to make clear that the conditions of dispersion and coagulation as used here are entirely relative and can exist in different degrees. The data of Figure 20 can be used to clarify this. The slip containing mill liquor, if considered by itself, has three separate regions: two of relative coagulation and one of relative dispersion. The NaOH slip has the same three regions, but the action of the single, highly ionized base is such that the degree of dispersion at the trough is high enough to render the slip too thin. The salts contained in the mill liquor are ionized in such a balance that the degree of dispersion at the trough is actually a degree of coagulation when compared to the

NaOH slip. In other words, the trough values are simply relative points between two extreme end members, one being closer to a condition of complete coagulation than the other. The good set of an enamel slip cannot be correctly termed as an absolute state of coagulation, but simply as a high degree of coagulation. Hereafter in this paper, the two words should be understood to connote the degree of the condition rather than the absolute state itself.

The difference between a dispersed slip and a coagulated slip, insofar as the finer fraction is concerned, is due to the state of aggregation of the clay particles. A coagulated slip is one in which, for example, a hundred clay particles are bound together in a porous, soft, water containing, cluster; while the dispersed system is such that the hundred clay particles remain as separate entities, each surrounded by a water film, and each free to move without hinderance from the other members of the system. With this simple picture, it is clear how the two states of aggregation affect the packing character of drying slips. The coagulated system, made up for example, of ten clusters of a hundred particles each, will pack during drying so that the ten clusters touch and have between them large pore spaces and relatively few points of contact between clusters. The same slip, if dispersed, will consist of a thousand separate particles, free to pack with a much finer system of pores. The fine pore size of the dispersed slip makes the drying more difficult, with the consequent strain incurred with the existence of a moisture gradient. The same packing character, with the numerous contact points and consequent high strength, makes the absorption of this strain more difficult in that the separate particles can not easily be pulled apart,

large cracks resulting only when the concentrated strain over an area becomes strong enough to break the forces between particles. On the other hand, the loosely packed system dries with no moisture gradient and the forces between clusters of frit and clay are weak enough to permit easy release of overall drying strain. The conditions of the slips with the resultant effects on the tearing tendency are shown in Figure 20. The tearing tendency was determined by the inspection of dried and calcined samples of each enamel. The results as marked out along the two curves are those that could be accurately predicted from the above concept of slip aggregation and packing, with the exception of the one detail in regard to the tearing tendency of the slip that is highly coagulated by the 10 c.c. of mill liquor.

Consideration of the Effect of Crystalline Salts in Enamel Films

The preceding discussion has covered only the features of the tearing tendency that are the effects of the ionized soluble salts. The behavior of the salts during crystallization must also be considered. If borates in an enamel mill liquor are present in excessive quantities, their deposition at the enamel surface can mechanically influence the packing so that tearing results. An example of this extreme case was furnished by the slip of Figure 20 which had been coagulated by a 10 c.c. addition of mill liquor from a non-tearing enamel. This addition, however, furnished two and one half times the quantity of salts ordinarily found in the mill liquor from which the concentrated additions used above were prepared.

Consideration of the Effects of Specific Salts on the Tearing Tendency

Boric acid has long been considered to be the principal

cause of tearing, and the addition of H_3BO_3 to an enamel slip invariably results in a reduction in resistance to rupture. When this weak acid was added to the slips used for the data of Figure 20, it had a characteristic effect on the properties of the slips that gave ample ground for a discussion of the effect of H_3BO_3 when added to porcelain enamels.

The dotted lines of Figure 20 show the effect of a 0.04% H_3BO_3 addition on consistency and tearing resistance of the NaOH and mill liquor slips. With NaOH or mill liquor there is a very slight reduction of viscosity, but with small additions of NaOH or mill liquor, the reduction of viscosity is rapid and the slips are thin, remaining so over the rest of the field, as shown. Tearing occurs as indicated over almost the entire range. The slip containing mill liquor has been dispersed to a greater degree over its total length, and the NaOH slip has been dispersed in two regions and relatively coagulated in the trough region. The explanation for this action may logically be assumed to be a result of chemical reaction with the materials already present in solution in the slips. The resultant chemical compound shows all of the attributes of a buffering salt in that further addition of NaOH or mill liquor has no effect over the range studied. The ionization of Na^+ from the buffering compound is such that the amount of ions free to fix the slip consistency are constant.

The minimum value of consistency is achieved at approximately 0.15 grams of NaOH, and this amount is that theoretically necessary to form $Na_2B_4O_7 \cdot 10H_2O$ upon reaction with H_3BO_3. As a check, the amount of borax (.61 grams) that would be formed in this reaction was added to a slip containing no soluble salt and the

effect on consistency is shown on the right in Figure 20. This experimental reasoning does not prove that the buffering salt is borax, but the evidence makes it clear that the compound is a borate which fixes the Na+ ion concentration at a level that disperses this type of slip to give it the packing characteristics that result in tearing.

The action is probably the same in enamel slips. If the composition of the frit is such that the resultant soluble salt approaches the borax composition, tearing will result. If H_3BO_3 is added to a normal enamel, the equilibrium between Na+, and OH^-, $CO_3^=$, $SO_4^=$, F^-, Borate$^-$, or other anions present will be shifted so that the dispersion reaches the degree where tearing begins. The normal enamel mill liquor is buffered with an effective Na+ ion concentration that is higher than the concentration allowed when the H_3BO_3 is added, so that not enough are available for maintaining the proper degree of slip coagulation. To reestablish this proper equilibrium, the Na+ ion concentration can be raised by adding enough of an ionizable sodium salt to completely repress the buffer and have sufficient excess remaining for proper slip coagulation. The buffer action may be nullified in this manner by the addition of any of several sodium salts. Those found to be effective are: $NaNO_2$, NaOH, Na_2CO_3, $NaNO_3$, $NaBO_2$, and NaCN. As would be expected, some other sodium salts of lower solubility and lower ionizability, are found to reduce the tearing tendency. Among these are sodium oxalate, sodium citrate, sodium molybdate, and sodium fluoride. Some of these salts, of course, are undesirable because of their blistering tendency during firing, caused

by the decomposition during heating of the objectionable anion or anion radical. The quantities of these salts necessary to establish the proper equilibrium are dependent upon their solubility and ionization. Thus less NaOH is required than $NaNO_2$ or NaCN, and less Na_2CO_3 is required than sodium citrate or sodium oxalate.

Other salts that react favorably in increasing the effective Na^+ ion concentration and in giving final compounds with the proper solubility are those that have a character similar to sodium. Among these are $ZnBO_2$, $Zn(NO_3)_2$, $LiNO_3$ and $Pb(NO_3)_2$. Here again are compounds effective in reduction of the tearing tendency but are not used because of unfavorable behavior during decomposition. They are merely cited to illustrate that salts other than sodium are effective in stopping tearing. The sodium salts are not at all unique in their behaviors, and if the composition of enamel frits gave something other as a soluble product than the sodium borates, the same conditions of tearing could be produced and remedied entirely without them. Salts of boron have long been considered to be alone in their capacity to produce tearing, but this is only because enamel frits are compounded of soluble borates. A boron free enamel has been prepared by the authors, and has been found to tear as badly as any normal enamel to which H_3BO_3 has been added.

Consideration of the Effect of Firing on the Packing Character of Enamel Films

As has been pointed out, the firing treatment seems to have only the effect of enhancing any film defect that exists after drying is complete. If the packing nature of the dry enamel is such that drying strain has been introduced, with or without release, the firing treatment and consequent shrinkage appear to enhance

these to the degree that would be expected. It is probably in this capacity that the mode and nature of crystallization of the various soluble salts is most important. Hurst and Andrews[6] have discussed the melted viscosities of the various salts during fusion, and they report the effects to be such that the tearing tendency is enhanced by heating, the separate patches of torn enamel being drawn away from the previously formed ruptures.

VI. SUMMARY

The results of this investigation can probably best be summarized in a flow sheet in which the various properties and conditions governing these properties are related to the characteristics studied. Figure 21 is such a flow sheet, listing each variable in the sequence considered logical in this study.

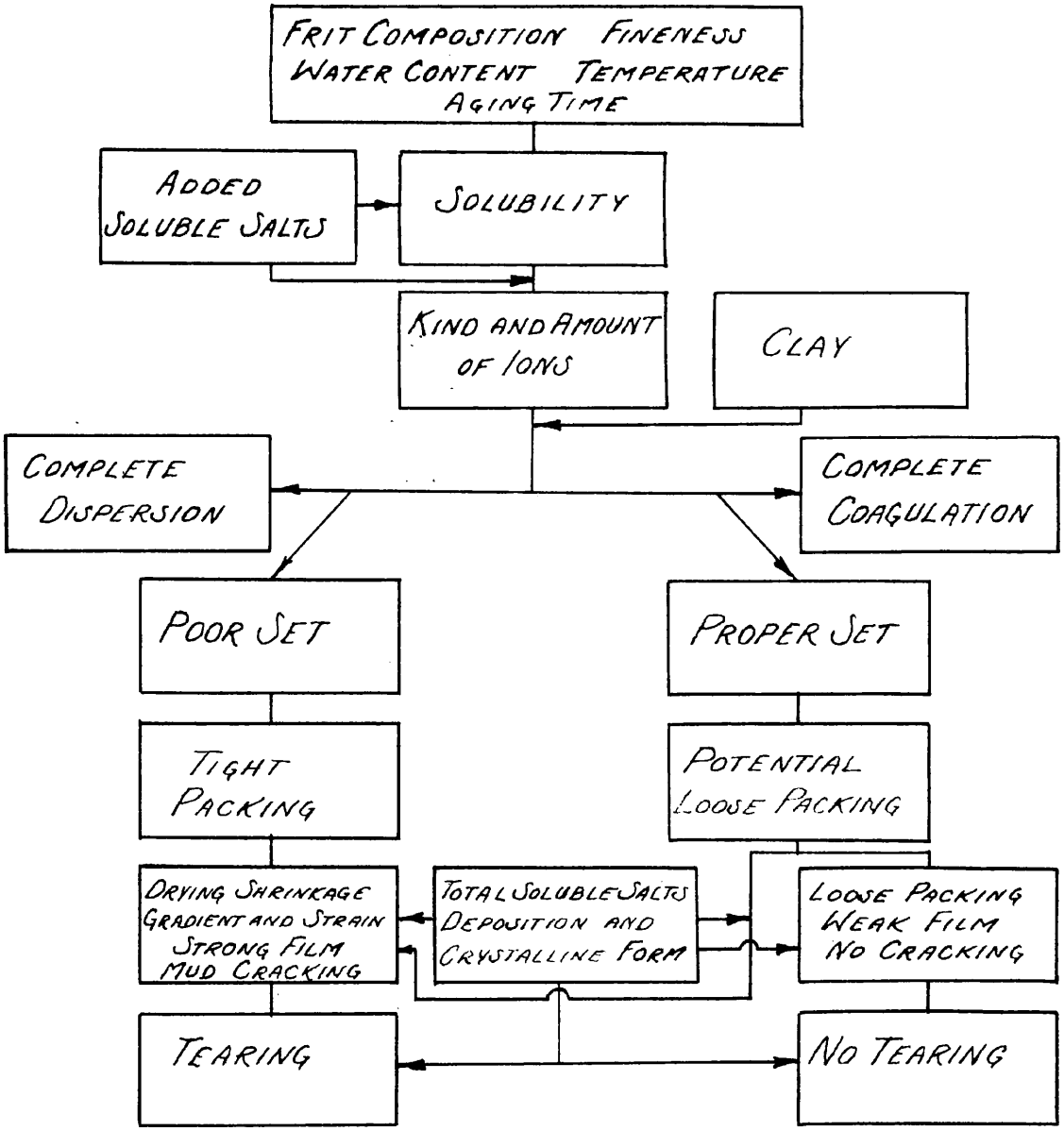


FIGURE 21 RELATIONSHIP OF VARIABLES DETERMINING TEARING TENDENCY

VII. CONCLUSIONS

Observations of the results of this study offer the following conclusions:

1. Enamel tearing is a defect resulting from the shrinkage stresses set up in an enamel film during drying and very early firing combined with the inability of the film to properly absorb these stresses.

2. The capacity of a non-tearing enamel to resist tearing is due to the absence of a strain gradient during drying coupled with a loose, weak, texture.

3. The characteristic shrinkage and resultant strain gradient in tearing enamel is due to the packing character of the enamel during drying.

4. The packing character of an enamel is determined primarily by the state of aggregation of the enamel slip as determined by the kind and quantity of adsorbed ions present. The ion most effective in enamel slips is the Na^+ ion freed upon solution of frit glass. The final state of aggregation of a dry enamel is influenced in extreme cases by the total quantity, disposition, and crystalline characteristics of the soluble salts present. In most cases, however, the film strength depends upon the physical structure of the dried enamel as fixed by the behavior of ionized salts in the slip.

5. Boric acid, when added to an enamel slip, causes tearing by forming a buffer salt (borax probably) that disperses the slip, allowing it to pack so that strain and tearing result. Sodium nitrite, and a number of other salts, prevent tearing by properly repressing the buffer and balancing the Na^+ ion concentration to give the enamel the proper packing characteristics.

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