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## SUBSTITUTION OF DOMESTIC FOR IMPORTED CLAYS IN WHITEWARE BODIES

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### ABSTRACT

Domestic kaolins and ball clays were substituted for imported clays in white-ware bodies of the more important types. The substitutions were based on compositions in terms of RO, RO<sub>2</sub>, and R<sub>2</sub>O<sub>3</sub>, of the bodies and raw materials, and on physical properties of the raw materials and those required of the bodies. Laboratory tests of dried and heat-treated specimens indicated that the properties of imported-clay bodies could be duplicated by domestic-clay bodies and factory tests showed that in most cases this would involve only minor changes in plant procedure. The vitrification temperatures of white-ware bodies were correlated with their RO contents. The plasticities and the strengths of the dry specimens depended chiefly on the ball clay contents of the bodies. The RO and ball clay contents can be varied widely with little effect on the physical properties of white-ware bodies heated to the same degree of vitrification.

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### I. INTRODUCTION

Numerous investigations of white-ware bodies have proved that the preparation and properties of each raw material employed, as well as the method of preparing the body and forming the ware, all have their effects upon the properties of the product. These factors should be borne in mind whenever one raw material is substituted for another.

In previous attempts to substitute domestic for imported clays the experimental work was largely of an empirical nature. The cost entailed by such procedure was so great that investigations have since been made by various workers to obtain fundamental data which would make possible such substitutions by scientific methods.

The present paper follows reports of two investigations dealing with china clays and kaolins.<sup>1</sup> The first<sup>2</sup> covered the essential

<sup>1</sup> In this paper the choice of the terms "kaolin" and "china clay" is based on commonly accepted usage. *J. Am. Ceram. Soc.* **16**, 269 (1933).

properties of English china clays since they constituted the largest volume of imported clays. The second<sup>3</sup> report dealt with representative American kaolins. It suggested a method of modifying the kaolins to make them simulate the properties of the china clays by adding such materials as were necessary to bring the mixtures containing the domestic clays to the same fluxing content as that of the imported clays. That investigation showed that a mere substitution of a kaolin or a combination of kaolins for china clay would be apt to change considerably many of the body's properties.

The present investigation aims to establish a less empirical method of arriving at body formulas by specifying not only the clay content but also, to a certain extent, the chemical formulas.

The method of attacking the problem of substitutions is presented in this report with supporting data obtained by attempting to duplicate the commercial bodies containing imported clays, in whole or in part, with bodies prepared from domestic materials.

## II. MATERIALS AND METHODS

Three kaolins were chosen for this work as representative of their types. The imported china clay and ball clay and the American ball clays, feldspars, and flint were materials on hand, the chemical compositions of which were known. The chemical compositions of these materials and their compositions in terms of RO, RO<sub>2</sub>, and R<sub>2</sub>O<sub>3</sub>, which serve as the basis for batch calculations, are given in table 1.

TABLE 1.—*Compositions of raw materials*

Material	Ignition loss	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	RO	RO <sub>2</sub>	R <sub>2</sub> O <sub>3</sub>
	%	%	%	%	%	%	%	%	%	%	%	%
English ball clay.....	15.1	46.4	35.5	0.8	0.8	0.2	0.4	1.0	0.1	1.7	47.2	36.3
English china clay.....	12.4	47.0	37.7	.9	.2	.2	.2	1.6	.2	2.2	47.2	38.6
Kentucky ball clay 4.....	14.7	49.9	31.4	.6	1.5	.2	.3	1.2	.2	1.9	51.4	32.0
Tennessee ball clay 5.....	13.6	50.3	31.5	.6	1.3	.2	.3	2.0	.3	2.8	51.6	32.1
Florida (ball) kaolin.....	13.7	46.3	37.7	.8	.5	.5	(*)	0.2	.0	0.7	46.8	38.5
Georgia kaolin.....	13.7	45.7	38.7	.3	1.4	.2	(*)	.0	(*)	.2	47.1	39.0
North Carolina kaolin.....	13.2	47.9	37.4	.4	.0	.1	(*)	1.0	.1	1.2	47.9	37.8
Maine feldspar.....	0.3	72.7	15.1	.1	.1	.3	(*)	8.3	3.1	11.7	72.8	15.2
Buckingham feldspar.....	.3	66.5	18.2	.1	.0	.2	.1	12.4	2.0	14.7	66.5	18.3
Flint.....		100									100	

\* Tracc.

Having chosen the approximate percentages of certain of the raw materials in the body<sup>4</sup> and knowing the compositions of the raw materials and of the heated body being formulated, the calculation of the batch formula becomes comparatively simple. In the simulation of a body it is possible to use as a starting point either the chemical composition of the heated body or the batch formula. Both of these were tried in this study. As a simplification most of the bodies were formulated by using only one kaolin or china clay, one feldspar, and no auxiliary flux.

<sup>3</sup> J. Am. Ceram. Soc. 18, 163 (1935).

<sup>4</sup> Certain assumptions must be made. The ball clay content must be assumed, for experience has shown that batch formulas calculated from chemical compositions will not necessarily give satisfactory results unless various physical properties are taken into consideration. It is also necessary to decide if more than 1 kaolin or more than 1 feldspar is to be used and, if so, the approximate proportions of the two like materials.

*Method of calculation.*—By chemical analysis of a sample of heated electrical porcelain it is found that its percentage composition can be expressed as:

$$\begin{aligned} \text{RO} &= 5.30 \\ \text{RO}_2 &= 70.70 \\ \text{R}_2\text{O}_3 &= 24.00 \end{aligned}$$

A body of this type requires a ball clay content of approximately 25 percent to give it the desired properties prior to heat treatment, and the use of more than one type of ball clay is desirable. With the above information and the RO, RO<sub>2</sub>, and R<sub>2</sub>O<sub>3</sub> contents of the raw materials known (table 1), the percentage of each raw material in the batch formula is calculated as follows:

Heated body L5			Raw materials	
RO	RO <sub>2</sub>	R <sub>2</sub> O <sub>3</sub>	Parts <sup>a</sup>	Percent <sup>d</sup>
<i>%</i> 5.30	<i>%</i> 70.70	<i>%</i> 24.00		
0.24	6.43	4.00	<sup>b</sup> 0.125 Kentucky ball clay	11.67
5.06	64.27	20.00		
0.35	6.45	4.01	.125 Tennessee ball clay	11.67
4.71	57.82	15.99		
4.66	28.97	6.05	<sup>c</sup> .398 Maine feldspar	37.16
0.05	28.85	9.94		
0.05	12.01	9.94	<sup>c</sup> .255 Georgian kaolin	23.81
0.00	16.84	0.00		
	16.80		.168 Flint	15.69
	0.04		1.071	100.00

<sup>a</sup> Total exceeds 1.000 because the analyzed body had been heated, while raw materials contain water, organic matter, etc.

<sup>b</sup> 0.125 represents one-half of the empirically chosen ball clay content and multiplied by the RO, RO<sub>2</sub>, and R<sub>2</sub>O<sub>3</sub> contents, respectively, of Kentucky ball clay, table 1, yields 0.24 percent of RO, 6.43 percent of RO<sub>2</sub>, and 4.00 percent of R<sub>2</sub>O<sub>3</sub>.

<sup>c</sup> Arrived at as follows: Since the feldspar and kaolin must furnish the remainder of RO and R<sub>2</sub>O<sub>3</sub>, let  $x$  = parts of feldspar required and  $y$  = parts of Georgia kaolin required.

Then:  
 $11.7x + 0.2y = 4.71$  (the feldspar contains 11.7 percent of RO and the kaolin 0.2 percent.)  
 $15.2x + 39.0y = 15.99$  (the feldspar contains 15.2 percent of R<sub>2</sub>O<sub>3</sub> and the kaolin 39.0 percent.)  
 Solving,  $x = 0.398$  part feldspar.  
 $y = 0.255$  part kaolin.

<sup>d</sup> Parts/1.071 × 100 = percent.

All bodies were made in slip form, using about 30 percent of water, with sodium silicate as the deflocculant, and cast in plaster molds. The test specimens were about 7 by 1 by 1 cm.

Test specimens were heated in an electric furnace, the schedule being 6 hours to reach the desired temperature, which was held 1 hour, after which the furnace was allowed to cool overnight. Accuracy of temperature control was found to be important. A difference of as little as 5 to 10° C in maximum temperature of the heat treatment resulted in a measurable difference in the properties of some bodies, especially in the case of apparent porosity. The temperature of heat treatment

desired was, in most cases, the minimum required for vitrification and, as a result, most of the specimens had not attained maximum bulk specific gravity. The properties of the test specimens were determined by standard methods.

### III. LABORATORY TESTS

In the preliminary work kaolin was substituted for china clay in vitreous and semivitreous tableware, electrical porcelain, and sanitary ware. Batch formulas were based on bodies recommended to the Bureau by the industry at one time or another. Using the data in table 1, chemical formulas (formulas in terms of  $RO-RO_2-R_2O_3$  percentages) of the reference bodies, and batch formulas of the bodies containing substitutions, were calculated. These batch and chemical formulas are given in table 2. Body V9 differs from V8 only in the brand of feldspar used and the flint content. The proportions of North Carolina and Florida kaolins used in substituting a mixture of these two clays for china clay are based on their exchange capacities, shrinkages, particle sizes, and strengths.

Data collected are given in table 2.

It was difficult to distinguish the china clay bodies from the kaolin bodies in appearance when both received the minimum heat treatment productive of maximum bulk specific gravity. In the semivitreous condition the presence of appreciable amounts of  $TiO_2$  in the Georgia and South Carolina kaolins caused a cream-white color.

Following these preliminary tests, samples of commercial bodies were solicited from a number of whiteware producers. Of the samples received, two electrical porcelains, two sanitary-ware bodies, one vitreous-china body, one wall-tile body, and one vitreous floor-tile body were analyzed and their compositions calculated in terms of  $RO$ ,  $RO_2$ , and  $R_2O_3$ . The  $RO$ ,  $RO_2$ , and  $R_2O_3$  contents of the feldspars used by the producers were also calculated from chemical compositions furnished by them. These data and the reported heat treatments used in the plants, together with the bulk specific gravities and apparent porosities of the heated specimens, determined on the samples furnished the laboratory, are presented in table 3. Samples *P1*, *P5*, and *P6* were formed by casting, samples *P2* and *P8* by dry-pressing, and samples *P3*, *P4*, and *P7* by plastic processing. The following information was furnished by the producers: The floor- and wall-tile bodies (*P8* and *P2*) and the semivitreous-china body (*P7*) contained all domestic clays; the china clay in one insulator body (*P5*) and both the ball and china clays in the other (*P3*) had been imported; and the clay used in the vitreous-china and the two sanitary-ware bodies (*P4*, *P1*, and *P6*) was nearly all imported.



TABLE 2.—Preliminary bodies involving substitution of American for English clays in whiteware bodies

Body	English (Devon) ball clay	English china clay	Tennessee 5 ball clay	Florida (ball) kaolin	North Carolina kaolin	Georgia kaolin	Maine feldspar	Flint	Bulk sp gr of dried bars	Transverse strength of dried bars	Heated 1 hr at	RO	RO <sub>2</sub>	R <sub>2</sub> O <sub>3</sub>	Bulk sp gr of heated bars	Transverse strength of heated bars	Volume shrinkage during heating	Apparent porosity
	%	%	%	%	%	%	%	%		lb/in. <sup>2</sup>	°C	%	%	%		lb/in. <sup>2</sup>	%	%
SV1.....	13.0	24.5	-----	6.0	9.0	-----	12.5	35.0	1.79	-----	1,265	2.5	74.3	23.2	2.23	6,300	25.6	7.2
SV1.....	13.0	24.5	-----	6.0	9.0	-----	12.5	35.0	1.79	-----	1,225	2.5	74.3	23.2	2.13	-----	22.2	11.5
SV4.....	13.0	-----	-----	13.5	24.5	-----	15.5	33.5	1.77	-----	1,225	2.5	74.3	23.2	2.04	4,800	19.7	16.1
SV6.....	13.0	-----	-----	6.0	9.0	22.0	17.0	33.0	1.88	-----	1,225	2.5	74.3	23.2	2.14	5,500	18.4	11.6
HT1.....	25.0	20.0	-----	-----	-----	-----	32.0	23.0	1.93	-----	1,245	4.9	73.0	22.1	2.34	6,900	23.1	.5
HT4.....	25.0	-----	-----	6.0	12.5	-----	34.0	22.5	1.90	-----	1,245	4.9	73.0	22.1	2.30	6,200	23.3	2.6
HT5.....	25.0	-----	-----	-----	-----	18.0	35.5	21.5	1.93	-----	1,245	4.9	73.0	22.1	2.32	6,200	22.3	1.3
S1.....	17.5	32.5	-----	-----	-----	-----	25.0	25.0	1.89	350	1,260	4.2	72.4	23.4	2.36	7,100	25.5	2.2
S4.....	17.5	-----	-----	10.0	20.5	-----	28.5	23.5	1.83	385	1,260	4.2	72.4	23.4	2.28	6,400	25.4	3.4
S5.....	17.5	-----	-----	-----	-----	29.0	31.0	22.5	1.92	400	1,260	4.2	72.4	23.4	2.34	6,900	23.4	2.4
S8.....	-----	-----	12.0	8.0	8.0	18.5	30.0	23.5	1.85	305	1,260	4.2	73.0	22.8	2.36	6,600	25.7	2.2
V7.....	8.0	33.0	-----	6.0	-----	-----	19.0	34.0	1.85	290	1,285	3.3	75.2	21.5	2.31	6,200	25.4	.9
V5.....	8.0	-----	-----	16.5	20.5	-----	22.5	32.5	1.81	-----	1,295	3.3	75.2	21.5	2.26	6,500	25.1	1.2
V6.....	8.0	-----	-----	6.0	-----	29.5	25.0	31.5	1.89	-----	1,285	3.3	75.2	21.5	2.32	6,700	23.5	2.4
V7.....	-----	-----	10.0	5.0	-----	31.0	24.0	30.0	1.87	-----	1,290	3.3	74.7	22.0	2.33	6,990	24.9	1.2
V8.....	-----	-----	8.0	8.0	8.0	24.5	23.5	28.0	1.85	320	1,290	3.3	73.7	23.0	2.32	7,000	25.5	2.0
V9.....	-----	-----	8.0	8.0	8.0	24.5	(*)	33.3	1.85	325	1,290	3.3	73.7	23.0	2.31	7,100	25.5	1.4

\* 18.2 percent of Buckingham feldspar.

TABLE 3.—*Commercial whiteware bodies*

Body <sup>a</sup>	Type of ware	Plant heat treatment	Bulk sp gr of heated pieces	Appar-ent porosity	Body composition <sup>b</sup>			Feldspar composition			
					RO	RO <sub>2</sub>	R <sub>2</sub> O <sub>3</sub>	RO	RO <sub>2</sub>	R <sub>2</sub> O <sub>3</sub>	K/Na
<i>P1</i> -----	Sanitary-----	Cone 10-----	2.38	% 0.3	% 4.6	% 70.4	% 25.0	% 14.6	% 65.7	% 19.5	3.5
<i>P2</i> -----	Wall tile-----	Cone 8 to 9---	1.92	24.1	2.2	74.3	23.5	12.7	69.3	17.6	2.5
<i>P3</i> -----	Electrical porcelain.	Cone 10-----	2.41	0.0	6.3	69.7	24.0	15.0	65.8	18.6	6.2
<i>P4</i> -----	Vitreous china	1,235° C-----	2.38	.0	4.9	73.1	22.0	14.9	65.8	19.2	4.1
<i>P5</i> -----	Electrical porcelain.	Cone 10-----	2.39	.1	5.3	70.7	24.0	13.4	68.3	17.9	2.3
<i>P6</i> -----	Sanitary-----	Cone 11-----	2.35	1.0	4.8	72.2	23.0	13.8	68.5	17.4	3.6
<i>P7</i> -----	Semivitreous---	Cone 8 (?)-----	2.07	16.5	2.7	76.7	20.6	13.8	68.2	17.8	5.3
<i>P8</i> -----	Floor tile-----	Cone 11 to 12.	2.37	0.0	8.1	67.1	24.8	12.5	69.2	17.9	2.1

<sup>a</sup> The digits indicate bodies of corresponding chemical formulas (in terms of percentage RO, RO<sub>2</sub>, and R<sub>2</sub>O<sub>3</sub>) and numbers in table 4.

<sup>b</sup> Calculated from chemical analyses.

From the body compositions (table 3) and the chemical formulas of the raw materials (table 1) body formulas were calculated, using equal parts of Kentucky and Tennessee ball clays, a combination of kaolins found to give satisfactory results in the preliminary work, Maine feldspar and Pennsylvania flint. The RO content of *L8* (table 4) was so great that it was necessary to substitute some of the purer Buckingham feldspar for that from Maine in this body. The temperature of heat treatment was derived in some cases from an approximate correlation between RO content and vitrification temperature of whiteware mixtures already studied and, in others, from data furnished by the manufacturers. In this paper vitrification is defined as that condition obtained by the minimum temperature or heat treatment producing maximum bulk specific gravity. This criterion was used because it was found in preliminary work that some specimens reach maximum bulk specific gravity before minimum apparent porosity and that, after passing the former point, their physical properties were affected adversely.

All of the test bodies (table 4) cast well and after heat treatment appeared to be quite satisfactory. Some specimens of bodies *L3* and *L5* were heated to semivitrification and some to vitrification.

TABLE 4.—Laboratory bodies simulating commercial bodies

Body *	Ken- tucky 4 ball clay	Ten- nessee 5 ball clay	Flor- ida (ball) kaolin	North Caro- lina kaolin	Georgia kaolin	Maine feld- spar	Flint	Total clay	Bulk sp gr of dried bars	Trans- verse strength of dried bars	Heated 1 hr at	RO	RO <sub>2</sub>	R <sub>2</sub> O <sub>3</sub>	Bulk sp gr of heat- ed bars	Trans- verse strength of heated bars	Volume shrinkage during heating	Appar- ent po- rosity
	%	%	%	%	%	%	%	%		lb/in. <sup>2</sup>	°C	%	%	%		lb/in. <sup>2</sup>	%	%
L1-----	7.0	7.0	4.7	4.7	26.3	32.6	17.7	49.7	1.89	455	1,255	4.6	70.4	25.0	2.37	8,300	25.5	0.3
L2-----	9.3	9.3	-----	-----	35.4	13.1	32.9	54.0	1.89	410	1,235	2.2	74.3	23.5	2.16	6,300	19.0	12.0
L3-----	11.7	11.7	-----	-----	20.7	45.4	10.5	44.1	1.90	505	1,165	6.3	69.7	24.0	2.30	6,000	22.1	3.0
L3-----	11.7	11.7	-----	-----	20.7	45.4	10.5	44.1	1.90	505	1,235	6.3	69.7	24.0	2.38	9,200	24.6	.0
L4-----	4.7	4.7	4.7	4.7	22.1	36.3	22.8	40.9	1.90	340	1,245	4.9	73.1	22.0	2.38	6,800	24.7	.4
L5-----	11.7	11.7	-----	-----	23.8	37.2	15.6	47.2	1.90	415	1,165	5.3	70.7	24.0	2.25	5,400	20.7	6.4
L6-----	11.7	11.7	-----	-----	23.8	37.2	15.6	47.2	1.90	415	1,245	5.3	70.7	24.0	2.38	8,700	24.9	.0
L6-----	7.0	7.0	4.7	4.7	21.1	34.5	21.0	44.5	1.89	325	1,255	4.8	72.2	23.0	2.39	8,000	25.4	.1
L7-----	7.0	7.0	4.7	4.7	21.4	17.7	37.5	44.8	1.89	325	1,210	2.7	76.7	20.6	2.14	5,200	16.7	13.0
L8-----	7.1	7.1	-----	-----	24.3	<sup>b</sup> 59.1	-----	38.5	1.89	305	1,230	8.1	67.1	24.8	2.39	8,300	24.9	1.0

\* The digits denote the chemical formulas to be those of correspondingly numbered bodies in table 3.

<sup>b</sup> And in addition 2.4 percent of Buckingham feldspar.

The composition in terms of  $RO$ ,  $RO_2$ , and  $R_2O_3$  of each body tested is plotted on the triaxial diagram in figure 1. The  $M$  series of bodies (table 5) located along the straight line  $xy$  in this diagram was tested in order to establish more closely the relation between  $RO$  content and vitrification temperature. These bodies were resorted to in an attempt to minimize the effect of variations in clay,  $RO_2$  and  $R_2O_3$  contents. The line was drawn so that the clay contents of the bodies would be approximately 45 percent, which was about the average of those of the commercial samples, as calculated from the chemical

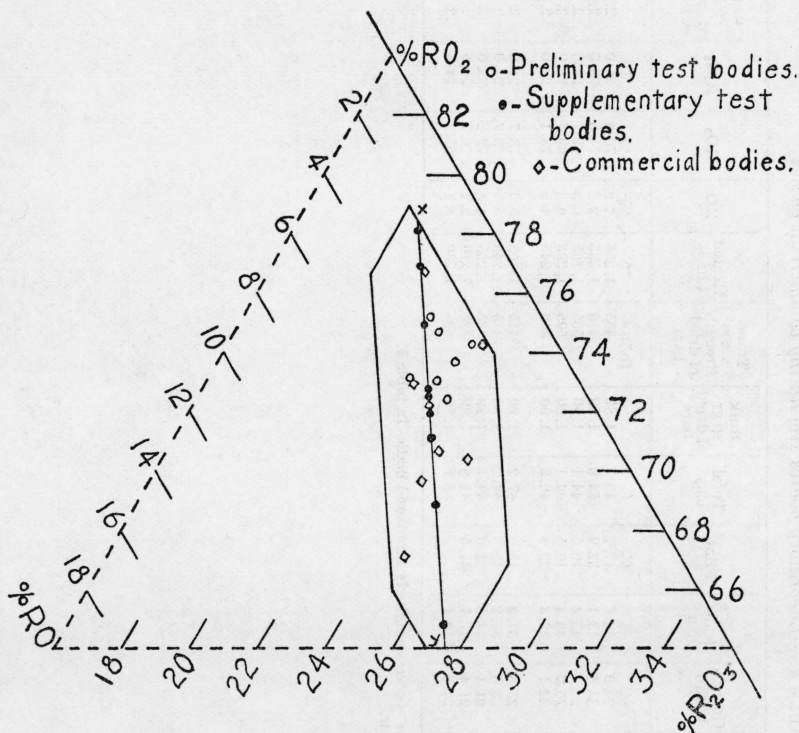


FIGURE 1.—A portion of the  $RO-RO_2-R_2O_3$  system showing the location of the body compositions studied.

formulas. This clay content is high enough to assure sufficient plasticity, strength, and vitrification range, and also low enough to avoid excessive shrinkage and poor glaze fit. The  $RO$  contents of the bodies in the  $M$  series were the same as those of the commercial bodies (table 3). No attempt was made to vitrify the wall-tile body, but the normally semivitreous-china body was heated to vitrification, and body  $M9$  was added to fill the gap between 2.7 and 4.6 percent of  $RO$ . The relation between temperature of heat treatment and  $RO$  content is



shown by the curve in figure 2. This curve is described by the equations:

$$T=1398-30R, \text{ from } R=2.5 \text{ to } 4.8, \text{ and}$$

$$T=\frac{R-6.5}{0.3-0.08R}+1234, \text{ from } R=4.8 \text{ to } 8.5,$$

where:

$T$  = temperature ( $^{\circ}\text{C}$ ) to which the specimen was subjected for 1 hour

$R$  = the percentage of RO in the ignited body.

Additional data on these bodies are given in table 5. Bodies  $M6$  and  $M7$  are identical with  $L6$  and  $L7$ , respectively, table 4. Included in table 5 are data on bodies  $M2$ ,  $M3$ ,  $M5$ , and  $M7$  heated to less than their vitrification temperatures and bodies  $MG$ ,  $EC$ , and  $MM$ , which

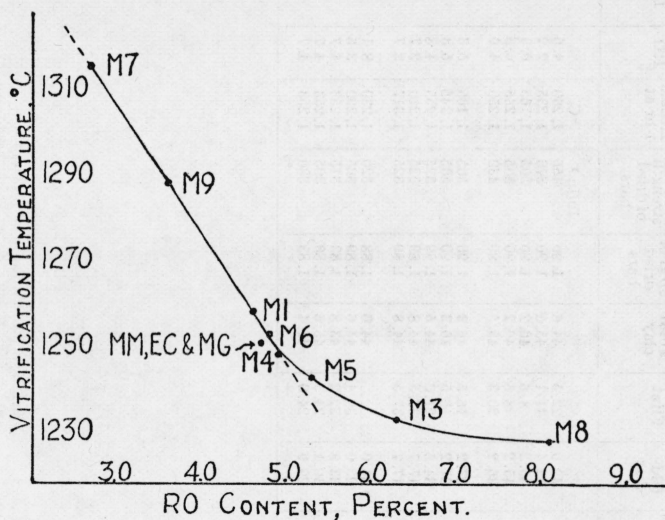


FIGURE 2.—Relation between minimum vitrification temperature and RO content of the bodies studied when heated according to the schedule described on page 67.

were tested to determine the comparative effects, especially on vitrification temperature, of incorporating magnesium carbonate,<sup>5</sup> china clay, and muscovite mica, respectively. The comparatively low bulk specific gravity of the dry specimens and the great shrinkages during heat treatment of these bodies were caused by accidental addition of excess deflocculant to the casting slips.

<sup>5</sup> The addition of dry magnesium carbonate directly to the body mixture was tried during the preliminary work of this investigation, but the bodies developed tiny blisters. In the present test the salt was mixed with the water before addition of the raw materials, with consequent elimination of the blistering.

TABLE 5.—Bodies used to determine relation between RO content and vitrification temperature

Body	Kentucky 4 ball clay	Tennessee 5 ball clay	Florida (ball) kaolin	North Carolina kaolin	Georgia kaolin	Maine feldspar	Flint	Total clay	Bulk sp gr of dried bars	Transverse strength of dried bars	Heated 1 hr at	RO	RO <sub>2</sub>	R <sub>2</sub> O <sub>3</sub>	Bulk sp gr of heated bars	Transverse strength of heated bars	Volume shrinkage during heating	Apparent porosity
	%	%	%	%	%	%	%	%		lb/in. <sup>2</sup>	°C	%	%	%		lb/in. <sup>2</sup>	%	%
M1-----	7.0	7.0	4.7	4.7	21.2	32.9	22.5	44.6	1.90	455	1,260	4.6	72.6	22.8	2.39	8,400	25.3	0.1
M2-----	9.4	9.4			26.7	13.4	41.1	45.5	1.90	370	1,235	2.2	78.1	19.7	2.18	5,900	17.8	10.2
M3-----	11.7	11.7			22.8	45.2	8.6	46.2	1.90	505	1,165	6.3	68.8	24.9	2.31	6,100	22.6	3.0
M3-----	11.7	11.7			22.8	45.2	8.6	46.2	1.90	506	1,235	6.3	68.8	24.9	2.39	8,700	25.2	0.0
M4-----	4.7	4.7	4.7	4.7	24.7	36.2	20.3	43.5	1.89	430	1,250	4.9	72.0	23.1	2.39	7,100	25.5	.0
M5-----	11.7	11.7			22.9	37.2	16.5	46.3	1.90	505	1,165	5.3	71.1	23.6	2.25	5,700	20.7	6.3
M5-----	11.7	11.7			22.9	37.2	16.5	46.3	1.90	505	1,245	5.3	71.1	23.6	2.38	9,100	24.9	0.0
M6-----	7.0	7.0	4.7	4.7	21.1	34.5	21.0	44.5	1.89	325	1,255	4.8	72.2	23.0	2.39	8,000	25.4	.1
M7-----	7.0	7.0	4.7	4.7	21.4	17.7	37.5	44.8	1.89	325	1,210	2.7	76.9	20.4	2.14	5,200	16.8	12.6
M7-----	7.0	7.0	4.7	4.7	21.4	17.7	37.5	44.8	1.89	325	1,317	2.7	76.9	20.4	2.38	7,800	25.2	0.3
M8-----	7.0	7.0			30.0	34.0		44.0	1.88	320	1,230	8.1	64.8	27.1	2.40	8,700	26.6	.0
M9-----	7.0	7.0	4.7	4.7	21.2	25.0	30.4	44.6	1.89	325	1,290	3.6	74.9	21.5	2.39	7,600	25.5	.2
M9 <sup>b</sup> -----	4.7	4.7	4.7	4.7	21.2	33.8	22.2	43.8	1.83	315	1,253	4.7	72.4	22.9	2.40	9,500	28.7	.1
EC <sup>c</sup> -----	4.7	4.7	4.7	4.7	22.6	30.1	24.3	45.6	1.83	305	1,253	4.7	72.4	22.9	2.41	9,400	28.7	.1
MM <sup>d</sup> -----	4.7	4.7	4.7	4.7	22.6	29.9	24.0	41.4	1.83	330	1,253	4.7	72.4	22.9	2.39	9,200	27.9	.1

<sup>a</sup> And in addition 22.0 percent of Buckingham feldspar.

<sup>b</sup> Contains 0.2 percent of MgCO<sub>3</sub>.

<sup>c</sup> Contains 26.8 percent of English china clay.

<sup>d</sup> Contains 4.7 percent of muscovite mica.

## IV. FACTORY TESTS

After making the foregoing tests in the laboratory, body formulas were calculated from the data in tables 1, 3, and 5 and sent to the cooperating manufacturers for testing under commercial conditions. The batch and chemical formulas of these bodies are given in table 6. The following notes were appended to the formulas furnished the manufacturers in case they wished to make minor changes in the ball clay or flux content:

1. 4.7 percent of Kentucky ball clay approximates 5.0 percent of Tennessee ball clay, minus 0.3 percent of feldspar.

2. 1.0 percent of Tennessee ball clay approximates 0.78 percent of Georgia kaolin, plus 0.16 percent of feldspar, plus 0.06 percent of flint.

3. 4.7 percent of North Carolina kaolin approximates 4.7 percent of Georgia kaolin, plus 0.3 percent of feldspar.

4. 1.0 percent of  $\text{CaCO}_3$  approximates 3.8 percent of feldspar, minus 1.9 percent of Georgia kaolin, minus 1.6 percent of flint.

5. In the laboratory good slip and casting properties were obtained by using 0.2 percent, dry basis, of sodium silicate as the deflocculant. (Subsequent experiments with deflocculants have shown 0.12 to 0.13 percent, dry basis, of sodium gallate, prepared according to the formula of Schramm and Hall<sup>6</sup> to give better results with these bodies.)

TABLE 6.—Factory test bodies

Body <sup>a</sup>	Ken- tucky 4 ball clay	Ten- nessee 5 ball clay	Florida (ball) kaolin	North Carolina kaolin	Georgia kaolin	Feld- spar <sup>b</sup>	Flint	Total clay	Ignited basis		
									RO	RO <sub>2</sub>	R <sub>2</sub> O <sub>3</sub>
	%	%	%	%	%	%	%	%	%	%	%
<i>TM11</i> -----	7.0	7.0	4.7	4.7	26.0	26.1	24.5	49.4	4.6	70.4	25.0
<i>TM61</i> -----	7.0	7.0	4.7	4.7	20.8	27.7	28.1	44.2	4.8	72.2	23.0
<i>TM22</i> -----	9.4	9.4	-----	-----	26.4	12.3	42.5	45.2	2.2	78.1	19.7
<i>TM3</i> -----	11.7	11.7	-----	-----	21.5	35.3	19.8	44.9	6.3	69.7	24.0
<i>TM53</i> -----	11.7	11.7	-----	-----	23.5	29.0	24.1	46.9	5.3	71.1	23.6
<i>TM44</i> -----	4.7	4.7	4.7	4.7	24.8	28.5	27.9	43.6	4.9	72.0	23.1
<i>TM55</i> -----	11.7	11.7	-----	-----	22.5	32.6	21.5	45.9	5.3	71.1	23.6
<i>TM66</i> -----	7.0	7.0	4.7	4.7	21.5	29.2	25.9	44.9	4.8	72.2	23.0
<i>TM77</i> -----	7.0	7.0	4.7	4.7	21.4	15.0	40.2	44.8	2.7	76.9	20.4
<i>TM88</i> -----	7.1	7.1	-----	-----	27.1	57.9	0.8	41.3	8.1	64.8	27.1

<sup>a</sup> *T* denotes test body; *M* indicates that the composition, as in the *M* series, lies on the line *xy*, fig. 1; the first digit denotes the chemical formula to be that of the correspondingly numbered body, table 5; the last digit indicates that the body was sent to the plant producing correspondingly numbered body, table 3.

<sup>b</sup> The feldspars used by the respective manufacturers, table 1.

The results of the factory tests substantiate in general the results obtained in the laboratory. One of the manufacturers reported a slight tendency toward jelling of casting bodies containing domestic kaolins and a somewhat slower rate of casting or filterpressing, as compared with bodies in regular use. The reports indicate that the substitution of domestic for English ball clay results in less shrinkage during drying and more during heat treatment, and a reduction, in some cases, of the plasticity and dry transverse strengths of the bodies. Terms used to describe the test bodies and their properties were "O. K.", "very fair", "quite satisfactory", and "good." However, in most

<sup>6</sup> J. Am. Ceram. Soc. 17, 262-267 (1934).

cases some modification would be required to make the test body entirely acceptable for replacement of the regular body. This fact was not surprising or discouraging since the ball clay contents of the test bodies had to be assumed, owing to lack of data, and the reports indicated that practically all the criticisms could be met by altering the amounts or types of ball clays in the test bodies.

## V. DISCUSSION

### 1. METHOD OF EXPRESSING BODY COMPOSITIONS

The expression of whiteware body compositions in terms of feldspar, flint, and clay only can be very misleading. The minimum temperature required to vitrify a given body in this system could be changed 20 to 40° C by merely changing the raw materials used. For this reason the RO-RO<sub>2</sub>-R<sub>2</sub>O<sub>3</sub> system was used but, because of the necessity for considering the physical properties prior to heat treatment, it was found imperative that the clay content be at least approximately specified.

The compositions of the RO, RO<sub>2</sub>, and R<sub>2</sub>O<sub>3</sub> components of most whiteware body mixtures are comparatively uniform. It seems, therefore, valid to represent such bodies in terms of the RO-RO<sub>2</sub>-R<sub>2</sub>O<sub>3</sub> system except when auxiliary fluxes are used. There would probably be less error involved in treating the RO, RO<sub>2</sub>, and R<sub>2</sub>O<sub>3</sub> in ordinary whiteware bodies as though each were a pure chemical compound than to assume that the properties of all clays or of all feldspars are alike—an assumption which is inferred by the specification of body compositions merely in terms of feldspar, flint, and clay.

### 2. SUBSTITUTION OF DOMESTIC FOR IMPORTED CLAYS

Explanations of the adverse effects on certain physical properties when substituting a combination of Florida and North Carolina kaolins for English china clay may be found in the fact that bodies containing more than 6 or 8 percent of the Florida kaolin are difficult to deflocculate. Also, the North Carolina kaolin is difficult to vitrify, possibly because of the comparatively large particle size of the fluxing minerals present,<sup>7</sup> although its RO content is considerable.

The fact that the English china clay bodies were slightly less refractory than the Georgia kaolin bodies, as evidenced by their apparent porosities and bulk densities, may be due to:

1. Water vapor given off by the muscovite in the china clay reduces the vitrification temperature. The effect of water vapor on vitrification was reported by Badger.<sup>8</sup> (This vapor might attack the fluxing materials and make a greater portion of the RO content free to react readily in the formation of glass. This reaction would begin to take place well below the pce of feldspars and might help to explain the fact reported by Schramm and Hall<sup>9</sup> that a body containing a feldspar of high pce might mature at a lower temperature than one containing a feldspar of lower pce.)

2. Some form of magnesium which accelerates the formation of glass and which is present in china clay and not in kaolin. Experi-

<sup>7</sup> *J. Am. Ceram. Soc.* **18**, 163 (1935).

<sup>8</sup> *J. Am. Ceram. Soc.* **16**, 107 (1935).

<sup>9</sup> *Am. Ceram. Soc.* **19**, 159-168 (1936).



ment has shown that the minimum vitrification temperature of a body can be lowered approximately 5° C by incorporating 0.2 percent of magnesium carbonate in its formula.

### 3. COMMERCIAL BODIES AND THEIR SIMULATION IN THE LABORATORY

Of considerable interest is the difference between the chemical formulas of bodies now used in the industry and those which were considered as typical 8 or 10 years ago. The variations are shown in table 7.

TABLE 7.—Comparison of bodies considered typical about 1930 with present commercial bodies

Body	RO	RO <sub>2</sub>	R <sub>2</sub> O <sub>3</sub>	Heat treatment <sup>a</sup> , 1 hr at
	%	%	%	°C
SV (type).....	2.5	74.3	23.2	1,225
P7.....	2.7	76.7	20.6	1,210
HT' (type).....	4.9	73.0	22.1	1,250
P3.....	6.3	69.7	24.0	1,235
P5.....	5.3	70.7	24.0	1,245
S (type).....	4.2	72.4	23.4	1,270
P1.....	4.6	70.4	25.0	1,260
P6.....	4.8	72.2	23.0	1,255
V (type).....	3.3	75.2	21.5	1,300
P4.....	4.9	73.1	22.0	1,250

<sup>a</sup> These minimum vitrification temperatures are based upon cast specimens containing no auxiliary fluxes, and the heating schedule employed (see p. 67). They are productive of maximum bulk specific gravity except in the cases of bodies SV and P7, which are semivitreous in type, having apparent porosities of about 12 percent.

In every case the commercial bodies tested contained more RO, making possible the same degree of vitrification with less severe heat treatment. The greatest difference is that between bodies P4 and V.

The chief cause of the difference in the effect of a given heat treatment on a dry-pressed body as compared with the same body when cast is probably is the arrangement or packing of particles. There seems to be less difference between specimens formed by plastic processes and those made by casting methods.

The wide variation in clay content of the bodies of the L series and the comparatively small effect of this variation upon most of the properties tested is of general interest.

Comparison of the properties of bodies L3 and L5 (table 4) heated to 1,165° C with those of body L7 heated to 1,210° C, shows the influence of RO content on the semivitrification temperature of white-ware.

### 4. EFFECT OF RO CONTENT ON VITRIFICATION

In the M series of bodies (located on the straight line *xy*, fig. 1), resorted to in the effort to correlate RO content of feldspathic white-ware bodies with vitrification temperature, there was a variation in total clay content of only 2.8 percent and changes in RO<sub>2</sub> and R<sub>2</sub>O<sub>3</sub> contents of equal successive amounts with equal increments in RO content. It was thought that the RO<sub>2</sub>/R<sub>2</sub>O<sub>3</sub> ratio might have considerable effect on the properties of the bodies, but indications are that this ratio can vary rather widely without affecting the properties tested.

The curve in figure 2 is probably one of a family comprised of more or less parallel curves for cast bodies, for plastic-process bodies, and for dry-pressed bodies. The location of the curves for each of these bodies would be determined by heating rate or, possibly, the use of an auxiliary flux or of a water-vapor atmosphere. Very likely a decided change in composition of the RO (e. g., change from pure potash to pure soda feldspar) would affect the shape of that end of the curve, where the RO contents of the bodies are greater.

The location of a curve, such as shown in figure 2, is probably governed by the temperature or heat treatment required to form enough glass of sufficient fluidity to produce a continuous film throughout the bodies. The surface tension of this continuous film of glass draws the particles closer together, causing the pore spaces to be filled or closed. The fluidity of the glass film allows the particles to move into a more compact arrangement. At the end of the curve (fig. 2) representing greater RO content the fluxing materials present may furnish sufficient glass to cause vitrification without appreciable solution of the nonfluxing materials, while at the end of the curve representing less RO content the glass furnished by the fluxing materials must dissolve appreciable amounts of the nonfluxing materials in order to produce a sufficient quantity of glass which, being more viscous, requires a greater temperature to produce vitrification.

The percentage apparent porosity of the specimens (table 5) at maximum bulk specific gravity shows correlation with RO content, decreasing from 0.3 to 0.0 percent as RO increases from 2.7 to 4.9 percent.

The volume shrinkages during heating of the vitrified specimens vary only 0.6 percent, with the exception of bodies *MS*, *MG*, *EC*, and *MM*. The cause of these exceptions is easily traced through the bulk specific gravities of the dry specimens to the degree of dispersion of the slips. The relatively great feldspar content of body *MS* and the addition of excess deflocculant to the other three bodies probably caused the dispersion of these slips to be less complete. These results indicate the importance of the properties of the body prior to heat treatment.

Bodies *MG*, *EC*, and *MM* vitrified at the same temperature, which was about 5° C less than that indicated by the curve in figure 2 for bodies of their chemical formula.

Although bodies *V8* and *V9*, table 2, contain different feldspars, the one in *V8* having 11.7 percent of RO and a K/Na ratio of 3.4, and the one in *V9* having 14.7 percent of RO and a K/Na ratio of 6.2, they are, allowing for experimental inaccuracies, almost identical in every property tested. These results substantiate the findings of Geller and Creamer<sup>10</sup> and of Schramm and Hall.<sup>11</sup>

##### 5. FACTORY TEST REPORTS

It is possible that the trouble which some cooperating manufacturers had with the casting bodies was due to incorrect amount or kind of deflocculant, since each undoubtedly used the kind he had on hand and may have been unable to spend sufficient time to determine the optimum amount required. At any rate, satisfactory casting slips of all the bodies tested by the manufacturers were made in the laboratory.

<sup>10</sup> J. Am. Ceram. Soc. 14, 30 (1931).

<sup>11</sup> J. Am. Ceram. Soc. 19, 159-168 (1936).

No insurmountable difficulty arising from the substitution of domestic kaolin for all of the imported china clay and of domestic ball clay for at least a portion (in some cases all) of the imported ball clay, was reported. In most cases such substitutions would apparently involve only minor adjustments in plant procedure which would not necessarily be difficult or costly.

The fact that practically all of the criticisms of the test bodies seem to be traceable to the ball clay would indicate that further study of the commercially available ball clays might be advisable.

## VI. SUMMARY

Domestic kaolins and ball clays were substituted for imported clays in important types of whiteware bodies. Substitutions were based on the compositions, in terms of  $RO$ ,  $RO_2$ , and  $R_2O_3$  of the bodies and raw materials, and on the physical properties of the raw materials and those required of the bodies. Specimens were formed by casting and were tested in the dried and heat-treated conditions. Laboratory results indicated that the properties of imported-clay bodies could be duplicated by domestic-clay bodies. Factory tests indicated that in most cases both domestic ball clays and kaolins could replace imported clays with minor changes in plant procedure. In a few cases the use of a very plastic ball clay is required to give the body special properties. The results in general indicate that body properties are as dependent on the method of body preparation or of forming the ware as on the raw materials employed. The plasticity and dry strength of a feldspathic whiteware body prepared and formed by a given method depend chiefly on the type and amount of ball clay used, while the minimum vitrification temperature depends chiefly on its  $RO$  content. Both  $RO$  and ball clay contents of feldspathic whiteware bodies can be varied widely with little effect on the physical properties of the products after heating on similar schedules to the same degree of vitrification.

WASHINGTON, May 14, 1937.