NOTE ON THE HARDNESS OF GLAZES¹

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ABSTRACT

Method of measurement.—The apparatus used (figure 1) consisted of a hardened tungsten-steel point which was allowed to bear on the glaze surface for 3 min. under a pressure of 50 lbs. The hardness was then computed from the dimensions of the resulting indentation. Results were reproducible to about 5 per cent. (See table III.) The presence of ridges and bubbles in the glaze was the principal cause of discordant readings.

Results and conclusions.—The enamels show the lowest and the porcelain glazes the greatest hardness, while the whiteware glazes occupy an intermediate position. The difference in hardness between the enamels and the whiteware glazes is quite marked. There is also a rather well defined difference between the whiteware and the porcelain glazes, but not a sharp separation between the lower and the higher fired porcelain glazes. Enough evidence has been accumulated to show that increased firing of the same glaze will increase the hardness. It appears also that increase in the alumina content brings about greater hardness.

Method

Manufacturers of white ware and table porcelain endeavor to produce as hard a glaze as possible which will resist the mechanical action of cutlery. This requirement may be considered to be a universal one for all types of glazed ware.

Unfortunately, however, the determination of hardness is a difficult task and there is no agreement as to the best method of measuring this physical quality. In general, hardness may be defined as the resistance offered by a body to the penetration of a still harder material. Probably the most satisfactory method is that of Brinell, in which the penetration of a sphere into the material to be tested is measured under a standard which causes the penetration.

In the present work an attempt has been made to estimate the hardness of several typical

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glazes and enamels by means of an adaptation of the Brinell test. The apparatus employed was very simple and is shown in figure 1. It consisted of a hardened tungsten steel point which was caused to penetrate the surface of the glaze under pressure. This procedure of making the test was a very simple one and consisted in placing a 50 pound weight, A, upon the platform B, and allowing it to remain in position for three minutes, after which time it was removed. The pressure upon the steel point was equivalent to several hundred thousand pounds per square inch. The indentation made in the glazed surface was then measured by means of a micrometer microscope, and several diameters of each impression were measured and a number of impressions made on every trial piece. The mean of the several measurements was taken to be the diameter of the impression. One of the difficulties in making this test was the presence of ridges and bubbles in the glaze, which are the principal causes of many discordant readings.

The computation is based on the relation:¹

$$t = \frac{D}{2} - \sqrt{\frac{D^2}{4} - \frac{d^2}{4}}$$

where t = depth of indentation, D = diameter of the rounded point, d = diameter of indentation, and p = load. The hardness may then be computed from the relation:¹

$$H = \frac{p}{\pi tD}$$

The hardness of different whiteware and porcelain glazes was determined as well as that of a number of enamels of the type applied on steel. The whiteware and porcelain glazes were applied upon specimens made in the laboratory. In the whiteware glazes of table II, glazes 1, 2, and 3 have the same molecular formula but different percentages of frit were added in each of the three mentioned.

Results

The observations made in connection with tests on a typical whiteware glaze, fired at cone 4, are given in table I. From

¹ Bureau of Standards, *Tech. Paper*, 11, "Comparison of Five Methods used to Measure Hardness," p. 5.

TABLE I—CHARACTER OF THE INDENTATIONS ON WHITEWARE GLAZES FIRED TO CONE 4

	Diameter of Impression in mm.	Appearance	Impression
1.	0.424	Hardly any bubbles	Sharp
2.	.460	Few bubbles	Sharp
3.	.464	Many bubbles	Ragged
4.	.490	Many bubbles and fractured at point of contact	Ragged & chipped
5.	.472	Fractured at point of contact	Ragged & chipped
6.	.478	No bubbles—crazed	Ragged
7.	.412	Few bubbles	Sharp
8.	.404	Few bubbles	Sharp
9.	.488	Bubbly, crazed at point of contact	Ragged & chipped
10.	.466	Few bubbles	Sharp
11.	.432	Few bubbles	Sharp
Same as above at Cone 6			
1.	.356	Few bubbles	Sharp
2.	—	Immature	Ragged
3.	.366	Slightly pitted	Sharp
4.	.372	No bubbles	do.
5.	.398	Few bubbles	do.
6.	.376	Few bubbles	do.
7.	.346	Few bubbles	do.
8.	.366	Slightly pitted	do.
9.	.372	Few bubbles	do.
10.	.354	Crazed when pressure was exerted	do.
11.	.374	Few bubbles	do.

these results it is apparent that the presence of bubbles in the glaze will lower its hardness decidedly. From the appearance of the indentation it seemed that there was an extremely thin but exceedingly hard layer or film on the surface of the glaze, similar to the enamel on teeth. There was a distinct difference between the surface and the material below it, which showed a crushed appearance. If there were a succession of hard layers the steel point would crush through each, leaving a series of ellipses. This was actually found in the case of the harder glazes, but was absent in those of a softer character.

In order to determine the effect of increased firing on the hardness of the whiteware glazes, the latter were applied to whiteware discs and fired to cone 4—4½ and cone 5½—6. In the cone 4 tests, the hardness fluctuated from 248 to 296, although several specimens were entirely out of this range and were discarded as immature. The hardness of the specimens fired to cone 5½ was from 268 to 298. Another set of whiteware glazes were fired at cones 4 and 6 and the hardness found to vary from 214 to 258 at cone 4, and 261 to 300 at cone 6.

In general, firing to higher temperature, therefore, appears to yield harder glazes. The hardness values for the series of white ware glazes are given in table II. Table III shows the hardness

TABLE II—INCREASE OF HARDNESS WITH INCREASE OF TEMPERATURE

	Whiteware Glazes								Cone 4		Cone 6	
	K ₂ O	Na ₂ O	CaO	PbO	ZnO	Al ₂ O ₃	B ₂ O ₃	SiO ₂	R	H	R	H
1.	0.173	0.032	0.456	0.217	0.122	0.238	0.271	2.30	0.212	246	0.178	249
2.	.173	.032	.456	.217	.122	.238	.271	2.30	.230	226		
3.	.173	.032	.456	.217	.122	.238	.271	2.30	.232	224	.183	284
4.	.173	.139	.343	.219	.124	.240	.278	2.32	.245	214	.186	280
5.	.177	.243	.233	.222	.125	.243	.279	2.35	.236	220	.199	261
6.	.230	.318		.289	.163	.317	.361	3.06	.239	218	.188	276
7.	.266	.211		.334	.189	.366	.417	3.54	.206	253	.173	300
8.	.317	.059		.399	.225	.437	.497	4.22	.202	258	.183	284
9.	.295	.290		.265	.150	.375	.331	2.79	.244	213	.186	280
10.	.368	.182		.288	.162	.452	.359	3.01	.233	224	.177	296
11.	.478	.045		.305	.172	.570	.380	3.05	.216	240	.182	286

R = Radius of indentation in mm.

H = Hardness of glaze.

TABLE III—ILLUSTRATING THE VARIATION OF THE RESULTS USING A SINGLE GLAZE APPLIED TO 29 DIFFERENT WHITEWARE TEST DISKS.

Composition of glaze suitable: CaO 0.55, K₂O 0.25, PbO 0.20, Al₂O₃ 0.27, B₂O₃ 0.39, SiO₂ 2.96.

	Cone 4		Cone 6	
	R	H	R	H
Mean of 29 tests	0.191	272	0.187	280
Average deviation from the mean	a.d.			
Max. dev. from mean	.0068	10	.004	6
Precision Measure	.019	24	.013	18
	$\sqrt{\frac{a.d.}{29}}$			
	.0013	2.22	.00088	1.33

R = radiation of indentation.

H = hardness of glaze.

of the same whiteware glaze applied to 29 specimens on discs of the same body composition. The specimens were all prepared at the same time. The table shows the range of values that may be encountered in the same glaze on a number of pieces of ware.

The results obtained on porcelain glazes are compiled in table IV, and those for enamels in table V. It is apparent that a distinct

TABLE IV—HARDNESS OF SOME PORCELAIN GLAZES FIRED AT CONE 16

	CaO	K ₂ O	Al ₂ O ₃	SiO ₂	Al ₂ O ₃ :SiO ₂	R	H	
1.	0.7	0.3	0.30	3.0	1:10	0.146	356	
2.	.7	.3	.375	3.0	1:8	.140	370	
3.	.7	.3	.500	3.0	1:6	.150	346	
4.	.7	.3	.600	3.0	1:5	.156	334	
5.	.7	.3	.750	3.0	1:4	.162	321	
6.	.7	.3	.400	4.0	1:10	.170	306	immature
7.	.7	.3	.500	4.0	1:8	.155	336	
8.	.7	.3	.666	4.0	1:6	.152	342	
9.	.7	.3	.800	4.0	1:5	.147	354	
10.	.7	.3	1.000	4.0	1:4	.149	349	
11.	.7	.3	.500	5.0	1:10	.162	321	
12.	.7	.3	.625	5.0	1:8	.144	361	
13.	.7	.3	.833	5.0	1:6	.142	366	
14.	.7	.3	1.000	5.0	1:5	.151	340	
15.	.7	.3	1.250	5.0	1:4	.153	344	
16.	.7	.3	.700	7.0	1:10	.150	346	
17.	.7	.3	.875	7.0	1:8	.145	362	
18.	.7	.3	1.166	7.0	1:6	.148	350	
19.	.7	.3	1.400	7.0	1:5	.139	372	
20.	.7	.3	1.750	7.0	1:4	.138	374	
21.	.7	.3	.900	9.0	1:10	.155	336	
22.	.7	.3	1.125	9.0	1:8	.160	325	
23.	.7	.3	1.500	9.0	1:6	.158	330	
24.	.7	.3	1.800	9.0	1:5	.148	351	
25.	.7	.3	2.250	9.0	1:4	.147	352	
26.	.7	.3	1.100	11.0	1:10	.144	361	
27.	.7	.3	1.375	11.0	1:8	.143	362	
28.	.7	.3	1.833	11.0	1:6	.151	340	
29.	.7	.3	2.200	11.0	1:5	.138	374	

R = Radius of indentation in mm.

H = Hardness of glaze.

TABLE V—HARDNESS OF SOME TWO-COAT AND GREYWARE ENAMELS

	1	2	3	4	5	6	7	8	9	10
R	0.250	0.252	0.260	0.260	0.258	0.250	0.246	0.250	0.260	0.258
H	208	206	200	200	201	208	210	208	200	201

R = Radius of indentation in mm.

H = Hardness of glaze.

difference in hardness is to be noted. The greatest hardness is shown by the porcelain glazes and the lowest by the enamels. Attention must, however, be called to the fact that the results obtained for one and the same glaze are more or less discordant. The thickness of the glaze is evidently an important factor as well as the varying degree of firing which the specimens may have undergone. It cannot be expected that the results are more than rough approximations. They simply indicate the order of magnitude of the hardness. It is evident that the difficulties in the way of making exact determinations are very great. It is obvious that the chemical composition must have an important bearing on the hardness of the glazes, but no conclusive evidence can be deduced on this point.

One point of interest may be noted, however, namely, that an increase in the alumina content appears to bring about a distinct increase in the hardness of the glaze.

In the following summary table, the maximum and minimum hardness, together with the average hardness of each type of glaze, is given:

		Low	High	Total average
Whiteware Glaze No. 1	Cone 4	213	258	230
	Cone 6	249	300	279
Whiteware Glaze No. 2	Cone 4	248	296	270
	Cone 6	265	298	281
Porcelain Glaze	Cone 16	306	374	348
Two-Coat and Greyware Enamels		200	210	204