NATIONAL BUREAU OF STANDARDS REPORT

9634

PROGRESS REPORT

July 1 through September 30, 1967

Development of Methods of Test
For Quality Control of Porcelain Enamels

by

M. D. Burdick and M. A. Rushmer

Porcelain Enamel Institute Research Associateship
National Bureau of Standards
Washington, D. C.

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

THE NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards[1] provides measurement and technical information services essential to the efficiency and effectiveness of the work of the Nation's scientists and engineers. The Bureau serves also as a focal point in the Federal Government for assuring maximum application of the physical and engineering sciences to the advancement of technology in industry and commerce. To accomplish this mission, the Bureau is organized into three institutes covering broad program areas of research and services:

THE INSTITUTE FOR BASIC STANDARDS . . . provides the central basis within the United States for a complete and consistent system of physical measurements, coordinates that system with the measurement systems of other nations, and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation's scientific community, industry, and commerce. This Institute comprises a series of divisions, each serving a classical subject matter area:

—Applied Mathematics—Electricity—Metrology—Mechanics—Heat—Atomic Physics—Physical Chemistry—Radiation Physics—Laboratory Astrophysics[2]—Radio Standards Laboratory,[2] which includes Radio Standards Physics and Radio Standards Engineering—Office of Standard Reference Data.

THE INSTITUTE FOR MATERIALS RESEARCH . . . conducts materials research and provides associated materials services including mainly reference materials and data on the properties of materials. Beyond its direct interest to the Nation's scientists and engineers, this Institute yields services which are essential to the advancement of technology in industry and commerce. This Institute is organized primarily by technical fields:

—Analytical Chemistry—Metallurgy—Reactor Radiations—Polymers—Inorganic Materials—Cryogenics[2]—Office of Standard Reference Materials.

THE INSTITUTE FOR APPLIED TECHNOLOGY . . . provides technical services to promote the use of available technology and to facilitate technological innovation in industry and government. The principal elements of this Institute are:

—Building Research—Electronic Instrumentation—Technical Analysis—Center for Computer Sciences and Technology—Textile and Apparel Technology Center—Office of Weights and Measures —Office of Engineering Standards Services—Office of Invention and Innovation—Office of Vehicle Systems Research—Clearinghouse for Federal Scientific and Technical Information[3]—Materials Evaluation Laboratory—NBS/GSA Testing Laboratory.

---

[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D. C., 20234.

[2] Located at Boulder, Colorado, 80302.

[3] Located at 5285 Port Royal Road, Springfield, Virginia 22151.

NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT
421.04-12-4212270

NBS REPORT
9634

PROGRESS REPORT

July 1 through September 30, 1967

DEVELOPMENT OF METHODS OF TEST
FOR QUALITY CONTROL OF PORCELAIN ENAMELS

by

M. D. Burdick and M. A. Rushmer

Porcelain Enamel Institute Research Associateship
National Bureau of Standards

NBS

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

SUMMARY

Work has continued on the development of a water soluble soil to be used in the cleanability test. Several new soils have been tried. The results thus far have not been reproducible.

The method of measuring the scratch-abrasion of porcelain enamels using a change in soil retention has been modified to give reproducible results.

I. CLEANABILITY

INTRODUCTION

The previously-developed method for comparing porcelain enamels with respect to their ease of cleaning is available, but it was thought that the usefulness of this method would be extended if the procedure could be made applicable to a wide variety of surfaces rather than only to those not affected by organic solvents.

Work has continued to alter the procedure and substitute reagents employed so that many surface finishes used in the domestic appliance field can be evaluated.

RESULTS AND DISCUSSION

A. The Composition of Soiling Agents

1. The desire to employ a dark-colored soiling agent originally led to the use of powdered graphite as a colorant. However, difficulty was encountered with the settling-out of this material from a liquid soiling agent. When colloidal graphite was substituted for the powdered graphite the settling was lessened but was not entirely overcome. In order to circumvent the possibility of settling, a water-soluble black colorant was substituted for the colloidal graphite. Recent tests have shown that soiling agents employing this material appear to be stable in this respect.

2. The water-soluble soiling agents had a tendency to dry up during the dry-wiping procedure employed. If some degree of lubricity could be retained for a longer period during the cleaning

process, a more reproducible procedure might be obtained. Soil XII, Table 1, represents an attempt to prepare an oil-in-water emulsion to impart a film forming tendency to a water-soluble soil. Preliminary trials were made to emulsify a small amount of paraffin oil in glycerol and water. These emulsions prepared in a food blender appeared to be quite stable. When the colorant and the fluorescent tracer were added, however, the oil came to the top of the preparation and its stability was lost.

3. Soil XIII was an attempt to improve the consistency of Soil X through the use of a surfactant. The use of this soil, described in a later paragraph, did not achieve satisfactory results.

4. Polyethylene glycol as a water-soluble base for soil composition was tried in Soils XIV through XVII as outlined in Table 1. No improvement in lubricity or drying characteristics was obtained.

B. Experiments with Polished Plate Glass.

A series of cleanability tests was made using six plate glass specimens soiled with Soil X and mechanically cleaned on each of six days. A separate extraction bottle was used to extract the soil remaining on these specimens after one minute cleaning time. The experiment was designed in such a way that at the end of six days each specimen had been extracted with each extraction bottle according to arrangement 1 shown in Table 2. These data were also arranged in two other ways so that an analysis of variance could be employed to evaluate the variance associated with different specimens, different extraction bottles or the different days on which the determinations were made. Only two data arrangements were required to isolate differences between specimens, bottles and days, hence only two are shown in Table 2.

The results of this experiment are given in Table 3. The results of an analysis of variance, at the bottom of the table, suggest that there may be real differences between the degree of cleanability of these plate-glass specimens. However, this is not conclusively shown because of the F ratio for specimens is only slightly larger than the critical value. These data show no evidence of significant differences among the various bottles. Assuming that there are only minor differences among the bottles, one would expect to rank the several specimens in any column of Table 3 in the same relative order. If the six specimens in each column are ranked from 1 for the highest to 6 for the lowest of the specimen group, marked differences in rank can be observed. Four out of the six specimens have differences of four ranks, i.e. ranked highest in one column and next to lowest in another, or lowest in one column and next to highest in another. These variable results in specimen ranking indicate that greater reproducibility is desirable in order to show conclusively whether specimen differences exist.

The almost significant day-to-day variability suggested that blank determinations on these specimens might be helpful in assigning the cause.

Blank determinations were made on the same washed and dried specimens by omitting the soiling and cleaning steps in the procedure. These blanks would reflect the combined effects of unclean specimens, extraction bottles, transfer beakers and the cuvette in which the fluorescent solution was measured. It was found many times that the value of the blank was about ten percent of the amount of retained soil determined in a regular test.

A series of blank determinations was made using the same specimens and a similar format as outlined in Table 2, Arrangement 2. The specimens were washed in the regular way after each blank determination. The results of this series are given in Table 4. Here it can be seen that the day-to-day variation was significant, in fact it was also significant at the 99 percent level. This indicates that from day to day one does not get the same blank values. The washing of the specimens must be a rather critical operation. It can also be noted that on the fifth and sixth days, in this series, the value of the blanks, on the average, dropped to less than half of that previously obtained. This perhaps reflected the effect of the four or five washings that the specimens, bottles and beakers had received in the early days of the series.

C. Experiments on Porcelain Enamels and Other Surfaces.

A group of nine appliance finishes, including many organics, were made available for cleanability tests. More than 225 tests were performed on these and on porcelain enamels. The soiling agent selected for use was Soil XIII and the following conclusions were drawn:

1. The combination of the soiling agent and the test procedure used did not produce acceptable, reproducible results.

2. The soiling and cleaning operations visibly altered the surface texture (and thus the cleanability) of several of the softer organic finishes.

3. Repeat determinations on the finishes, visibly altered in the first test, resulted in amounts of soil retained of about 60 percent of that found in the first test.

4. Blank determinations reflect the cleanliness of the specimens (and utensils) at the time the blank was run. The value of the blank is not necessarily applicable to any other time. This indicated the need for more reproducible preparative techniques (washing and rinsing procedures) for use as a part of a cleanability test.

5. It was originally planned to present the results of this work at the PEI Forum in November, but the difficulties encountered indicate that formal presentation at this time would be premature.

PLANS FOR THE NEXT PERIOD

Work will be aimed toward the development of a soiling agent with great lubricity. It is possible that other methods of soil removal may be found which will minimize the need for lubrication and the tendency for the soil to dry up during the cleaning process. Several water-soluble lubricants have been obtained for this purpose.

Improved preparative treatments for specimens and utensils are required in order to yield uniformly low blank values for soil retained, if the use of blank determinations is indicated.

SCRATCH-ABRASION

INTRODUCTION

The resistance of porcelain enamels to scratching or abrasion is an important property but is one that has not been measured quantitatively in a manner which agrees with field results. It was found during the last report period that measuring the change in soil retained before and after abrasion seemed to rank the abrasion damage to four enamels in the same order, independently of the method used to abrade them and further,this ranking agreed with visual estimates of abrasion damage.

RESULTS AND DISCUSSION

It was planned during this report period to measure the change in soil retained on enamels abraded for different periods of time to determine if the enamels followed the same time-soil retained curve regardless of the method used to abrade them. However, the first attempts to do this indicated that differences in soil retained for duplicate sets of specimens abraded for the same length of time were greater than the change in soil retained for specimens abraded for different times. This condition is intolerable.

It was originally thought that this was caused by a delayed spalling of the enamel. Therefore many determinations were made waiting different times between abrading and soiling to determine whether this "spalling" was reproducible after any given time period. It can be seen in Table 5 that these results were extremely erratic - enamels abraded for the same time and waiting the same time before soiling might have three times as much soil retained one time as the next. An analysis of variance of these data indicated that the differences among three specimens abraded, soiled and cleaned at one time were insignificant, but the differences between specimens abraded at different times were highly significant.

This irreproducibility still seemed to be caused by some "conditioning" either before the specimens were abraded or before they were soiled and cleaned since 1) the unabraded specimens could be soiled and cleaned reproducibly and 2) the specimens in any one set could be abraded, soiled and cleaned reproducibly. This seemed to limit the possibility for the non-reproducibility to the conditioning of the specimens before abrading and/or soiling. Therefore the next five sets of specimens were oven dried and cooled in a dessicator before abrading and soiling. The results of these trials are shown in Table 6. An analysis of variance of these data indicated no significant difference existed between either the three specimens in one set or between sets of specimens abraded on different days.

PLANS FOR NEXT REPORT PERIOD

It is still planned to compare the effects of abrasion time on the change in soil retention using both the PEI and the Mechanical Abrasion techniques in order to specify the type and time of abrasion which might be used in a standard test method.

1966 EXPOSURE TEST OF NATURE-TONE ENAMELS ON STEEL

The specimens were returned to the exposure racks at Kure Beach, North Carolina - 80 feet from the ocean and The South

Florida Test Service Site in Miami, Florida. The next inspection of these specimens is scheduled for January 1968 after one-year's exposure.

The exposure racks were installed at the Gaithersburg, Maryland site and the specimens were put on exposure. The first inspection of these specimens will be after six-months' exposure.

CONTINUITY OF COATING

The results from two of the three companies participating in the Round Robin Test for Continuity of Coating have been received. However, in order to provide a more comprehensive report these will not be discussed until all the results have been received.

TABLE 1. COMPOSITION OF WATER-SOLUBLE SOILING AGENTS.

Ingredients	X	XII	XIII	XIV	XV	XVI	XVII
Glycerol	92.4	82.70	91.6	--	--	19.8	--
Polyethylene Glycol M.W. 400	--	--	--	98.0	87.0	68.7	94.09
Polyethylene Glycol M.W. 20,000	--	--	--	--	--	--	2.16
Paraffin Oil	--	10.89	--	--	--	--	--
Distilled Water	5.8	4.35	6.0	--	11.0	9.5	--
Keco Acid Black a/	0.9	1.00	1.3	1.0	1.0	1.0	2.59
Uranine b/	0.9	1.00	1.0	1.0	1.0	1.0	--
Riboflavin	--	--	--	--	--	--	1.16
Triton X-100 c/	--	0.06	0.1	--	--	--	--

a/ Water soluble dye.

b/ Uranine is the sodium salt of Fluorescein, $C_{20}H_{10}O_5Na_2$

c/ Emulsifying agent

TABLE 2. EXPERIMENTAL PATTERN USED IN CLEANABILITY TESTS OF POLISHED PLATE GLASS

Arrangement Number 1.

The body of the table indicates on which of six days the experiments were made.

Specimen No. \ Extraction Bottle	A	B	C	D	E	F
7	1	6	5	4	3	2
12	2	1	6	5	4	3
13	3	2	1	6	5	4
14	4	3	2	1	6	5
16	5	4	3	2	1	6
17	6	5	4	3	2	1

Arrangement Number 2.

The body of the table indicates the specimen numbers used.

Extraction Bottle \ Day	1	2	3	4	5	6
A	7	12	13	14	16	17
B	12	13	14	16	17	7
C	13	14	16	17	7	12
D	14	16	17	7	12	13
E	16	17	7	12	13	14
F	17	7	12	13	14	16

A through F represent six extraction bottles
7 through 17 represent six specimen numbers
1 through 6 represent six different days

TABLE 3. THE AMOUNT OF SOIL X RETAINED ON PLATE GLASS SPECIMENS AFTER ONE MINUTE CLEANING TIME, MICROGRAMS PER SQUARE CENTIMETER

The data are shown in arrangement 1 of Table 2.

	Extraction Bottle						
Specimen	A	B	C	D	E	F	Ave
7	1.34	1.53	1.55	1.23	1.45	1.48	1.43
12	1.21	1.27	1.60	1.60	1.21	1.30	1.36
13	1.84	1.48	1.55	1.66	1.76	1.56	1.64
14	1.28	1.65	1.87	1.27	1.39	1.87	1.56
16	1.21	1.31	1.34	1.34	1.31	1.45	1.33
17	1.58	1.25	1.27	1.60	1.27	1.24	1.37
Average	1.41	1.42	1.53	1.45	1.40	1.48	1.45

Results of an Analysis of Variance

Variable	F Ratio	Critical Value of F at 95% Level	Arrangement
Specimens	2.78	2.60	1 (above)
Bottles	0.40	2.60	1 (above)
Days	1.74	2.60	2 (not shown)

TABLE 4. BLANK CLEANABILITY DETERMINATIONS ON POLISHED PLATE GLASS

The results of blank determinations below, in μg/cm^2, are the amounts of Soil X equivalent to the fluorescent intensities measured. The data are shown in arrangement 2 of Table 2.

Extraction Bottle / Day	1	2	3	4	5	6	Ave
A	0.10	0.19	0.24	0.13	0.03	0.05	0.12
B	.15	.20	.22	.28	.02	.05	.15
C	.13	.29	.10	.08	.02	.10	.12
D	.09	.15	.19	.10	.10	.10	.12
E	.08	.13	.16	.12	.10	.03	.10
F	.06	.06	.16	.13	.03	.10	.09
Average	.10	.17	.18	.14	.05	.07	--

Results of an Analysis of Variance

Variable	F Ratio	Critical Value of F at 95% Level	Arrangement
Days	5.77	2.60	2 (above)
Specimens	0.85	2.60	1 (not shown)
Bottles	0.95	2.60	2 (above)

TABLE 5. CHANGE IN SOIL RETAINED FOR SPECIMENS ABRADED 150 SECONDS AND WAITING VARIOUS LENGTHS OF TIME BEFORE SOILING AND CLEANING.

Time Between Abrading and Soiling Operations	Change in Soil Retained			
	Individual Specimens			Average
min.	μg/cm²			μg/cm²
0	1.30	1.22	1.42	1.31
0	1.45	1.85	1.76	1.69
0	0.45	0.65	0.86	0.65
0	0.63	0.60	0.34	0.52
15	1.12	0.67	1.06	0.95
15	1.11	0.44	0.48	0.68
15	0.97	0.74	1.10	0.95
240	1.01	0.88	0.97	0.94
420	0.56	0.45	0.36	0.46

TABLE 6. CHANGE IN SOIL RETAINED FOR ENAMELS THAT WERE OVEN DRIED BEFORE ABRADING AND SOILING

Change in Soil Retained - μg/cm^2			
Individual			Average
1.32	0.86	1.40	1.19
1.01	0.98	1.41	1.13
1.55	1.16	1.34	1.35
1.47	1.08	1.27	1.27
1.15	1.26	0.84	1.08

DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS