# THE UNITED STATES POTTERS ASSOCIATION

TELEPHONE: FULTON 6-4225 EAST LIVERPOOL, OHIO 43920

E. S. MORSE
TREASURER




July 13, 1967

Dr. Robert A. Kehoe, M. D.
University of Cincinnati
Kettering Laboratory
Eden & Bethesda Aves.
Cincinnati, Ohio 45219

Dear Dr. Kehoe:

I was pleased to receive your letter of June 22nd and think that your suggestion is excellent. However, I think we will wait until October at which time all of the members will have monthly determinations on their lead glazes covering one year.

It is very magnanimous of you to offer your services on an out-of-pocket expense basis and, as soon as we can crystalize on a date, I shall be in touch with you as to whether it is agreeable.

Very truly yours,

B. W. Merwin

B. W. Merwin, Chairman
Research Committee

BWM/A

June 22, 1967

Mr. B. W. Merwin, Chairman
Research Committee
The United States Potters Association
East Liverpool, Ohio 43920

Dear Mr. Merwin:

I was greatly pleased by your letter of June 19th, in which you describe the progress that has been made toward the goal which was set some years ago for collecting information on the problem of your industry in relation to lead-containing glazes. I was the more comforted, in relation to my own shortcomings, with respect to furnishing your group with a full report of our findings and our views concerning them. I am fully aware of the fact that both findings and views were presented to your group in a less formal, and probably a less effective manner, but I am also aware that this was not enough. Perhaps I can still make amends.

A great deal of water has gone over the dam, with respect to the environmental aspects of the distribution and use of lead, since we talked together. I think, in view of the comments in your letter, that it would not be amiss, if your group can afford the time, for us to get together again, and discuss the position of your industry and come to a decision as to what should be done. There are several matters to consider. I agree that it would be wise to discuss the situation with the appropriate health officials, but I am not certain, at this point, whether this involves the Public Health Service. I believe that the Food and Drug Administration is the official authority in this matter. On the other hand, it may be advisable to consult informally with appropriate representatives of the Public Health Service. I believe that it would be wise to write to Dr. Goddard of the Food and Drug Administration and to Surgeon General Stewart of the Public Health Service, informing them briefly of the matter and suggesting that one or the other or both of them might wish to designate a representative to confer, informally, with your group, as to the part, if any, that should be played by an official agency. Let me make a specific suggestion. I shall be glad to act for you in this and other matters, to consult with you, and to be present, if you choose, in any discussions which you may have with governmental people. You may come to the conclusion that this is unnecessary or inadvisable, and if so, I shall not be offended. However, I am offering my services, at the cost to you of my out-of-pocket expenses, partly because of my keen interest in this matter, and partly because, having fallen down to some extent in my own contribution, I wish to assure you and your associates that I have not abandoned you. (I even expect to prepare the report of which I have spoken repeatedly. I have gathered together all of the necessary material, against the time when I could free myself of other pressing duties long enough to attend to it.)

Let me have your opinion on these matters at your convenience. I have but one fixed engagement in the near future. You referred to it in the last

sentence of your letter. I have planned to be in Montana in August, and I should not like to delay or interrupt my rendezvous in the wilderness for any reason, for I can hardly arrange it, as matters now stand, at any other time.

Sincerely yours,

Robert A. Kehoe, M.D.
Professor Emeritus of
Occupational Medicine

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# THE UNITED STATES POTTERS ASSOCIATION

TELEPHONE: FULTON 6-4225 EAST LIVERPOOL, OHIO 43920

E. S. MORSE
TREASURER



June 19, 1967

Dr. Robert A Kehoe, M.D.
University of Cincinnati
Kettering Laboratory
Eden & Bethesda Aves.
Cincinnati, Ohio 45219

Dear Dr. Kehoe:

The Research Committee and Lead Industries Association are nearing the completion of our investigation at Rutgers University and, feel we have compiled a great deal of information on the formulation of lead bearing glazes as regards lead solubility.

Since October, 1966 all members of the U.S.P.A. have been sending cups glazed with production glazes to Pittsburgh Testing Laboratory to be checked for lead release by the dithyzone method. Our aim is to accumulate some history on present production glazes so that we will be able to talk more intelligently on acceptable limits.

A year ago I wrote you stating that A.S.T.M. had agreed to start the wheels in motion, to move the dithyzone test from a tentative standard to a full standard. I failed to follow this close enough and this spring found that nothing had been done. However, with a little prodding they have now started to make this move and I hope by this fall to have the method classified as a full standard.

We feel that we are about ready to consider the possibility of arriving at an industry standard and are in a quandary as how to proceed. Mr. Harry Thiemecke of the Homer Laughlin China Company and I feel that the U. S. Public Health Department should be involved since we are just a group of engineers and have limited knowledge and neither background nor training in the physiological aspects of lead.

Due to the fact that you have had considerable contact and experience with these people, we thought possibly you would be able to tell us who to contact. Also we would appreciate your thought along this line. Maybe we are thinking of the wrong approach as we are neophytes and are well aware of it.

I am enclosing a copy of my research committee report at our annual meeting in Pittsburgh this past December. You will note that I included a part of your last letter to me in the report. This report should pretty well bring you up to date on what has transpired this past year.

I hope you will be able to get your annual fishing trip to Montana and have an enjoyable time.

Yours very truly,

B. W. Merwin,

B. W. Merwin, Chairman
Research Committee

BWM/A
Enc.

12-6-66

# REPORT OF THE RESEARCH COMMITTEE

Considerable publicity has been given to lead during the past year, as evidenced by the following incidents.

The New York City health department during November and December, 1965, had a case of lead poisoning traced to Japanese mugs. Mr. Edwin Ludewig, Assistant Commissioner of Environmental Sanitation, was in charge of these hearings, where it was brought out that the entire pigment was removed from the interior of said mugs when filled with 4% acetic acid and allowed to set overnight. As a result, the New York City health department placed an embargo on the mugs in question. Mr. Don Fowler of the Lead Industries Association was in contact with Mr. Ludewig at this time and acted as our representative as well as the Lead Industries Association. He was informed that no decisions would be made until we could advise them.

This past spring and summer a geochemist from California Institute of Technology, Mr. Claire Patterson, stirred up quite a controversy aimed at lead in air due to the tetra-ethyl lead additive, used in most of the present day gasoline for use in automobiles, which escapes to the atmosphere via automobile exhausts. Extensive hearings were held in Washington, D. C. by Sen. Muskie's committee. Dr. Kehoe of the Kettering Institute at Cincinnati, Ohio was one of the expert witnesses for industry and

was credited with doing an excellent job in spite of harassment. These hearings obtained national coverage via TV.

Lead from glazes was not mentioned at the hearings, however, it is only a matter of time until some eager politician may pick up this subject and try to make something of it. The following paragraph from a communication from Dr. Kehoe after the hearings, I believe, quite capably covers the ramifications of these hearings: "In addition, I was under attack, both directly and covertly, as being a pawn of industry, and the potential effect of this on certain policies and plans of the Kettering Laboratory, as well as associations of scientists generally, with industry and industrial managers, was considerable. I believe these matters have been settled for a time, but I believe they are merely quiescent, and will recur. This problem, in my view, is a serious one for the future. Not that it will affect me greatly, but rather that the controversy created here by a man from the California Institute of Technology, and abetted by quite a number of inconsequential people, plus a number who should know better, is quite capable of poisoning the scientific atmosphere that is so essential in our time for dealing with the many problems of occupational and environmental health."

I might mention in passing, that at the American Public Health Association meeting held in San Francisco, California this past November, two professors from the Columbia University School of Public Health and Administrative Medicine reported on a 16 country

study of lead in human blood and urine and are quoted as follows:

"These studies do not support the contention that increased burning of gasoline and wider use of lead in industry are causing additional exposures to lead in our environment.

"No significant change in lead levels of the blood and urine in the last three decades have been shown."

The data presented included lead measurements from [illegible] natives living in the hills of New Guinea away from [illegible] civilization. They had blood levels higher than either urban or rural Californians.

A copy of the Indian Standard specification for [illegible] water [illegible] was obtained. Their leaching test is more severe than our standard test, A.S.T.M. C555-66T, and they specify 0.5 p.p.m. as the maximum lead solubility allowed. At a conference, we asked Dr. John Koenig of Purdue University to run comparative tests between our standard method and the Indian standard method on the same glazes. Two glazes that gave 0.07 p.p.m. with our ASTM test gave 0.48 and 0.30 p.p.m. when boiled per the Indian method. One glaze that gave 1.05 p.p.m. with our test showed 10.4 p.p.m. with the Indian method. The committee feels that the Indian test is not very realistic as they hold the acetic acid, used for leaching, at the boiling point for 30 minutes. We would be hard pressed to find food that contains 5% acetic acid which is boiled for 30 minutes during preparation.

We were pleasantly surprised this past year when the University advised Lead Industries Association and your Research Committee that the original commitment would be sufficient to enable our investigation an additional year. Consequently, this investigation, Lead Glazes for Dinnerware, will terminate on September 1, 1957 rather than 1956.

Dr. Hodkin has consented to prepare a manual based on the final report of this effort, encompassing new concepts of formulation, proper firing conditions of glazes for dinnerware, research findings on the effect of colors and opacifiers on lead solubility, and generally should provide a worthwhile addition to the literature.

A meeting of the Research Committee was held at the Pittsburgh Airport this past August to bring all members up to date and review our position on lead release from glazed ceramic surfaces.

The committee agreed that it would be wise to have some history of lead release from production glazes so that our position will be as strong as possible whenever the subject comes up in government circles. Consequently, we voted to request each member of the association have the Pittsburgh Testing Laboratory run one test per month on production ware representing each type of glaze in production. This test to be carried out for one year so that the volume of data needed will be obtained. I am happy to

report all members have agreed to cooperate and that the monthly tests were started in October. We requested an adjustment in the charge per test from Pittsburgh Testing Laboratory and they agreed to do these tests for $15.00 each provided they could set up and run these tests once each month. Consequently, we have asked all member companies to have the glazed cups in their hands by the 10th of each month.

Committee C-21 of ASTM has commenced to take the necessary steps to move our dithizone procedure from a tentative standard to an adopted standard. We feel this is needed to strengthen the effectiveness of the data from our tests in case of legal involvement.

The following progress report was just received from Dr. John E. Hennig at Rutgers University, relevant to the investigation we are jointly sponsoring with Lead Industries Association -

> I am glad the results of this research serve to confirm further what you have long known. For example, especially when the research was initiated and at various times since, we have run the standard test on Cone 3-5 clear glazes. These data show lead release values of less than 0.5 PPM for these glazes and in a number of cases less than 0.1 PPM or less than 1 part in ten million. Thus the cone 3-5 clear glazes, which constitute the large part of all commercial dinnerware glazes used, show very low lead release as has been found in a number of other laboratories during the past three decades.

2 - Considerable effort has been given to investigation of the effect of color oxide and stain additions on the lead release of glazes, since earlier work has shown that certain additions can give an adverse reaction to the lead solubility of a glaze. Direct additions of the coloring oxides have shown the detrimental effects of CuO especially for the lower temperature glazes. Also CuO should not be used in a stain. As you know the low temperature copper green glaze was abandoned years ago.

Of more practical significance is the normal practice involving the use of prepared compositions or stains, which include the coloring oxides but are designed to be compatible with specific frit glazes and their maturation. A number of typical commercial stains, representing those most commonly used compositions along with the appropriate clear base glazes, were tested. None of these affected the lead release of the base glaze adversely showing these have been well-designed.

3 - It was also requested by you that the effects of opacifying oxide mill additions be studied. Various amounts of zircon, $SnO_2$ and $TiO_2$, added to various fritted lead glazes, have not affected the lead release adversely and in some cases of glazes showing higher lead release may prove beneficial.

4 - Another objective was to determine the effects of processing parameters on the solubility of specific glazes. While the technology is highly developed in this respect, the purpose as stated is to relate such variables to lead release using the standard test. In

our early work in this area, we have been very much concerned with variation in individual values from specimen to specimen involving assumedly the same bisque, glaze, and processing variables. We have just completed a factorial design experiment of lead release in relation to production parameters. These specimens are ready for test and it is hoped this statistical approach will be more conclusive.

5 -- Further phases of interest have included: concentration profile for lead in various type glazes; volatility of lead under various conditions; effects of interfacial action, and relation of such considerations to depletion tests.

6 -- The major effort involves the design of glazes to maintain the well established of the lead content. This includes a number of experimental compositions fired from Cone 07 to Cone 01 which are prior or borderline in respect to lead release.

Briefly stated this includes: borates, silicates, borosilicates, aluminosilicates, boraluminosilicates of lead, to which various alkali, alkaline earth, and oxide additions are being made to gain a more complete understanding of the relation of lead release to both composition and structure.

7 -- We hope to complete all the experimental work by July 1967. A manual is under preparation and should be completed during the summer of 1967.

8 - As mentioned previously, we could run more Dithizone tests without slowing up our experimental work. So if any plant would like to submit sets of cup specimens, which might show trends because of variations in composition or production parameters, we could test such specimens and give the plant the lead release data. This service could be given on the basis that all the significant information (composition, firing data, etc.) could and would be included in our report. The name of the plant submitting specimens would not be included in the report. We would very much like to have this cooperation since these would be specimens prepared and fired under commercial conditions.

Respectfully submitted,

B. W. Merwin, Chairman

# Further Investigations of the Extraction of Lead From Glazed Ceramic Surfaces

This report describes the results obtained when a number of glazed ceramic surfaces were treated repeatedly with hot Heinz's vinegar to determine the extent of the extraction of lead by the vinegar.

## Materials and Procedures:

Test #1. A single cup of each of six colors of Ceramaston manufactured by The Laurel Pottery Co. of California was filled partially with 150 ml. of Heinz's vinegar at 100°C and allowed to remain for 30 minutes as in the tests described in our reports dated July 12, 1961 and January 31, 1962.

Test #2. Cups of the two colors which released the greatest amounts of lead to the vinegar were then treated repeatedly with 150 ml. portions of Heinz's vinegar at 100°C and 60° Centigrade. For purposes of comparison, three cups of each of glazes Az and Ba, from another source, which had been tested previously in this manner with hot 5% acetic acid, were also so treated repeatedly with Heinz's vinegar at 60° Centigrade. Cups used in all tests were given a wash with luke warm Calgon solution (one tablespoon per gallon of water) between each treatment with the vinegar.

In carrying out these tests the analyst first used Heinz's vinegar at 100°C followed by a number of treatments with the vinegar heated to 60° Centigrade. In order to establish whether there was a significant difference between the extraction of lead at 100°C and 60°C, a cup of Ceramastone of a third color was treated three times with Heinz's vinegar at 60°C, following an initial treatment with

Heinz's vinegar at 100° Centigrade.

The amount of lead removed from the glaze during each treatment was determined by analyzing a suitable portion of the vinegar by the standard dithizone procedure, as used in the Laboratory.

Results:

In Table #1 are recorded the concentrations of lead leached from each cup by a single period of contact with 150 ml. of Heinz's vinegar at 100° Centigrade.

In Table #2 are recorded the results obtained when two glazed cups of Ceramastone, which had yielded the most lead in the initial testing program, were treated repeatedly with 150 ml. portions of hot vinegar. A third cup of a tangerine colored glaze of the Ceramastone ware was tested first with vinegar heated to 100°C, and then to vinegar at 60°C, in order to compare the quantities of lead leached out by the vinegar at the two temperatures. Included in the table are the results yielded by glazes Az and Ba when vinegar heated to 60°C was introduced repeatedly into the cups for periods of 30 minutes.

Discussion:

The analyst used vinegar heated to 100°C initially, but changed to the use of vinegar heated to 60°C in subsequent tests. As is shown by the data in Table #2, the quantities of lead extracted by vinegar at the two temperatures did not differ significantly.

The repeated filling of the cups with hot vinegar resulted in the loss of lead at a nearly constant rate only slightly lower than that observed initially and recorded in Table #1. The testing was not continued further because of the obvious trend, which indicated

that these glazes, themselves were involved in a destructive or disintegrating process.

Glazes Az and Ba, differing from the Ceramastone glazes, yielded much less lead than they had in the tests carried out initially and described in our report of July 12, 1961. The reason for this is not clear. The specific cups representing these glazes in these tests had not been subjected to any prior tests and were employed in triplicate. The results obtained from the three representatives of each glaze and shape were averaged in each instance. Their variability may be due, in part, at least, to the fact that the cups used were from different batches of ware prepared at different times. It is of interest to note that there is no evidence in these data of a trend toward a decrease in the rate (or extent) of the extraction of lead from these glazes. Whether or not such a diminution will occur gradually or abruptly, in time, is a question of some importance, as is that of what happens to the glaze itself. This would appear to be worthy of investigation if some method of observation, based upon the physical structure of the glazes, is available or can be devised.

From The Kettering Laboratory in the Department of Preventive Medicine and Industrial Health, College of Medicine, University of Cincinnati, Cincinnati, Ohio

Report by:

J. Cholak, Ch.E.
L. Ertle, D.Sc.
R. Burkey, B.Sc.
E. Parkinson, B.Sc.

Approved: Robert A. Kehoe

Robert A. Kehoe, M.D.
Director

Table #1

The Extraction of Lead From Ceramastone (Laurel Pottery Co.) Glazes by Hot (100°C) Heinz's Vinegar

| Glaze | PPM |
|---|---|
| LN #9183-32 - Granite | 23.3 |
| LN #0183-34 - Yellow | 34.8 |
| LN #0183-36 - Tangerine | 27.8 |
| LN #0183-38 - Blue | 22.6 |
| LN #0183-40 - Cocoa | 39.3 |
| LN #0183-42 - Pink | 42.2 |
| Heinz's Vinegar - Blank | 0.012 |

## Table #2

### Lead Leached Out of Various Glazes in Successive Tests of Cups With Heinz's Vinegar Heated to Two Temperatures

| Description | Test # | PPM 100°C | PPM 60°C |
|---|---|---|---|
| LN #0183-40 - Cocoa Laurel Ceramastone | 1 | 39.3 | |
| | 2 | 24.2 | |
| | 3 | 26.1 | |
| | 4 | 24.4 | |
| | 5 | | 23.6 |
| | 6 | | 25.8 |
| LN #0183-42 - Pink Ceramastone Laurel | 1 | 42.2 | |
| | 2 | 30.4 | |
| | 3 | 31.4 | |
| | 4 | 32.7 | |
| | 5 | | 32.9 |
| | 6 | | 32.9 |
| LN #0183-36 - Tangerine Ceramastone Laurel | 1 | 27.8 | |
| | 2 | | 22.0 |
| | 3 | | 27.0 |
| | 4 | | 29.8 |
| Az - Red Harlequin Shape | 1 | | 0.42 |
| | 2 | | 0.49 |
| | 3 | | 0.71 |
| | 4 | | 0.91 |
| Ba - Green Harlequin Shape | 1 | | 0.53 |
| | 2 | | 0.18 |
| | 3 | | 0.26 |
| | 4 | | 0.41 |