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Your Ref. Subscription to, or
interest in our journal and/or the (lead)solubility of glazes.

For some years now, unfortunately the publication of our journal KM/SCC has been postponed. The main reason has been lack of time for editing, because of, for the last 1½-2 years, the editor has been keenly engaged in the study of lead-glaze-solubility and the risc of lead-poisening to the general user of pottery. This problem has been well known for over 2oo years at least, but may be a little more severe today, as we are becoming inoeasingly exposed to lead and similar heavy metals from other sources. With two grandfathers having been doctors, and some observations of the poisoning trough easily soluble lead-boro-silicate-glaze (coloured!) near at hand, I have found the c o m b i n e d medical and glasstructural study of this necessary and worth while. Please let me try to compensate the long waiting for our journal a little, by giving you some brief information on the subject of my 'research'.

Lead-content: In general principal, it appears that one can achieve relative low solubility at any level of lead-content for glazes to be fired above 1o5o°C although it can easily be demonstrated, that one can also find dangerously high solubilities of lead with quite low content of lead in the glaze, as well as a high firing-temperature of, say, 1loo°C. It is against this background, that we have published the enclosed advertisement in the year-book of the Technical Museum in Stockholm, the text of which is -roughly translated:

> Ceramic glaze: homogenous glasscoating - wishful thinking
> Phaseseparation means 'different properties side by side'
> — one of the reasons for surprising variation
> in the chemical durability of, for instance, leadbearing glazes.

We have -in collaboration with the Swedish Institute for Public Health- investigated the lead-solubility of a constant glazecomposition, in which we only altered the content of boric acid (if frit-compositions given by the frit-manufacturers are quite reliable). From o.3 moles B_2O_3 onwards, we found a sharp increase in the solubility, the rise of which becomes almost vertical between o.45 and o.5o mol boric acid (PbO = o.7, SiO_2 = 2.o). The diagram has the shape of an "S", starting (at o.3 B_2O_3) with 1 ppm (=mgPb/liter) and ending at 915 ppm (at o.82 B_2O_3). Our preliminary view is, that a soluble second phase (dominantly a borate-glass) starting to form as droplets in a rather stable silicatephase begins to become interconnected when the curve becomes almost vertical. Above the solubility of looo ppm Pb, one begins to approach the absolute leadcontent of the glazed surface, which is in the order of lo ooo mg Pb per square decimeter (5o wt-% Pb, o.2 mm glaze-layer). The scale of the diagram is logarithmic. Phaseseparation in glass (glaze) is not an exeption, but almost a regular, at least a common phenomenon to be found in very many phase-diagrams of interest for glazes. However, the significance of this for the safe use of lead (as well as some other hazardous elements) in glazes and frits does not seem to have been described in the literature, as far as we are aware. On the other hand is phaseseparation in glasses, at the time beeing, almost t h e theme most often found in the abstracts dealing with research on glass.

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Colour in glazes: "Already" in 1939 GELLER & CRAEMER wrote in the Journal of the American Ceramic Society on "Solubility of Coloured Glazes in Organic Acids". In the excellent volume "CERAMICS - A Symposium", published 1953 by the British Ceramic Society, the paper by A N SMITH "The Structure of Glazes" contains a sentence which I have found most significant, in connection with a review of WEYL's "Coloured Glasses" (a classical monograph):

> "Colour is due to fields of force that are not fully saturated or balanced, weak binding-forces usually giving rise to strong colours."

If this is generally correct, and we have found no reason to doubt it, the only conclusion would be to avoid any (large) coloured surfaces i n s i d e such pottery which is liable to be in contact with food and drink. For stoneware and hard porcelain with leadless glazes, this, of course, would apply only for any on-glaze-decoration fired on subsequently, for it is rare to find such "enamel"-colours which are quite free of lead, or similar fluxing elements (like bismuth).

Acids in food & drink: Are YOU aware, that both animal- and vegetable f a t consists of fatty acids? In 1829 SIMEON SHAW in "History of the Staffordshire Potteries" (chapter 'Rise and Progress of the Staffs. Potteries') wrote:

> When vessels of this kind are employed in either baking or boiling food, it is now ascertained, that the lead glaze is very soluble during the time of heat, and that it intermixes with animal fat, or the acid juices of fruits, or vinegar when cold, and that it is partially soluble even when any of these remain awhile in the vessels cold; ...

That fruit acids, as a rule, are able to dissolve more material from a glaze than, for instance, acetic acid (vinegar), is not always known, nor is it appreciated in wider circles, that just this family of acids are almost as effective in a strongly d i l u t e d concentration as they are in higher percentage. Many drinks contain some or other acid, without tasting sour at all, for example wine, spirits and coffee often contain some succinic acid. Also carbonic acid can be rather aggressive, and only relative recent glassresearch has been able to find the present type of window-glass-composition which is relatively stable against the action of the very slight carbonic acidity of rain. It is therefore not surprising, that really most (almost all) known cases of poisoning due to soluble lead from glazes have occured in connection with vessels for different types of drink. (There must be many unknown slighter cases never discovered.)

Resorption of lead: lead poisoning as an occupational disease is probably most often due to breathing lead-bearing dust, white lead being about the greatest risk in this connection. While almost all lead taken into the lungs (even as a frit) is -sooner or later- being absorbed through the effective action of body-fluids which are very effective to dissolve lead in most forms, it is -as a rule- taken that ingested lead is absorbed only to a surprisingly small degree (10-20 %), the rest being excreted in due course. We have strong evidence, that when lead dissolved by fruit-acids (for example as lead-citrate) enters the digestive system, it is much more readily absorbed. People who suffer from lack of stomach-acid (=HCl), which would be expected to transfer a citrate into chloride -at least partially-, do appear to become more readily leadpoisoned. Also Vitamin D-2, "Calciferol", which is known to enable the absorption of calcium by the body, appears to increase the ability for leadabsorption. This vitamin depends on ultraviolet light for its formation in fats and milk, for example, which would help explain why the frequency of lead-poisoning is much greater during the summer-months (see CHISOLM's paper "Lead Poisoning" in Scientific American, February 1971, where the seasonal pattern of 85 % of all lead-poisoning cases occuring from May through October is brought out most clearly, though only partly explained).

Sorry this is becoming longer than I had planned... (=3 pages together)

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Lead-Poisoning: Volumes could and have been written about this. This need therefore not even be an introduction, the only intention is to point out one or two things worth remembering. It is quite surprising and most satisfactory to find, that almost all the literature I have studied on lead-poisoning appears to be in fullest agreement about symptoms (and their possible absence) and effects -brain-damage and different forms of paralysis, sterility as well as death beeing the severest-. Also, a high degree of agreement is to be found regarding the maximum daily dose of lead, above which chronic poisoning is liable to occur: ½ mg/day. I could also quote 1 mg lead per day as the 'boarder-line' from some authors, or even very little more. This depends highly on the rate of absorption, governed by individual differences, as well as on age, sex (the female sex said to be from 1-3 times more vulnerable than the male) and outer factors. Since, according to several investigastions the average human beeing has a "normal" and regular daily intake of 0.3 (one third!) mg Pb daily /most coming indirectly from the lead in petrol via our food/, it is evident, that there is not much margin for any addition. I might also point out, that not all doctors are quite familiar with the 'slighter' symptoms of lead-poisoning, especially in areas where this disease is uncommon as it is nowadays, fortunately.

T E S T I N G: A German paper from "Sprechsaal für Keramik, Glas, Email" of 1873 by Prof. Alex. Schmidt: "Bleiglasur oder bleifreie Glasur" (=Lead- or Leadless Glaze) gives a most simple but reliable method for a qualitative test. Almost exactly the same procedure was recommended by Gordon BARNES in Tactile, the magazine of the Canadian Guild of Potters, March 1970 in his paper: "Lead Glaze Solubility Problem". Gordon Barnes also demonstrated this method during the WORLD CRAFTS CONFERENCE in Dublin, August 1970:

Leave a glazed vessel filled with vinegar for about 12 hours.
Add a small volume of sulphide-solution.
A white precipitate is only colloidal sulphur, liberated by the acid.
If the precipitate is yellow, brown or black, this is due to the presence of lead in the vinegar, the dark compound beeing lead-sulphide.
One can easily compare a yellow precipitate with that formed by putting some sulphide-solution to f r e s h vinegar, where the cloudy w h i t e precipitate is known to be lead-free.

Any water-soluble sulphide will serve the purpose well. "Liver of sulphur" beeing potassium-sulphide is quite handy, so is sodium-sulphide, and the concentration of the solution is not important. (It's allright if it smells)

All the more or less expensive tests give you a figure of your solubility, but the above test (which can be speeded up by heating the vessel) ought to be known and tried by every potter. The nearest chemist should have the sulphide-salt for you.

Different Countries have more or less differing official testing-procedures for glazed utensils. A treatment during 24 hours with 4 % acetic acid is the commonest. The German "lead-law" of 1887/88 prescribed the boiling during ½ hour with 4 % acetic acid (testing as by G.Barnes/Prof.Schmidt, above), when "no lead" should have gone into solution. This means less than 3 mg Pb/liter of the solution, and this is the level of the highest permissibbe lead-content according to the Swedish law. Here, however, three ½-hr-boilings are combined, before the dissolved amount of lead is determined, in relation to the volume of the vessel. This procedure has several times been reported to be due to become replaced by the commoner 24-hr at room-temp.-method, but it was recently decided, that further investigations were necessary, before the method might be changed, since it is by boiling, that the highest figures of solubility are attained.

Conferences: In 1956, the "Symposium on Structure and Properties of Glazes", by the British Ceramic Society, was held in Sheffield, see Transactions Vol 55 No 1o.

During the 1970 Fall Meeting of the American Ceramic Society on 2nd October, 1970, there was a "Session on LEAD IN GLAZES", reprints of this have been distributed by the Lead Industries Association, Inc., Nw York.

The British Ceramic Society arranged a Symposium on "The Solubility Problem in Glazes and Decoration in Stoke-on-Trent on 1oth Nov. 1970, and a new meeting is due in Hanley on the 16th March, 1972 on "LEAD RELEASE - the present position" END.