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USE OF P^{32}, SR^{89}, AND CA^{45} IN MECHANICAL DISHWASHING STUDIES

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The problem of measuring and evaluating the amount of inorganic film formed on dishes when they are mechanically washed with alkaline detergents in hard water supplies has been of interest to detergent manufacturers for many years. Many papers have been published on methods of measuring food soil removal from artificially soiled glass and ceramic surfaces, but little has been published on measuring the hard water film build-up. Mendenhall and Wilson (1944) have described a photometric study, but this method has several limitations. It must be performed with a flat glass surface; it is not sensitive enough to evaluate minute films, and there are general limitations due to reflections from surfaces.

Our interests have been in films on ceramic, plastic and metal, as well as on glass surfaces, and also in studying minute film formations. These films are responsible for retaining food soil and harboring bacteria on dishes and utensils.

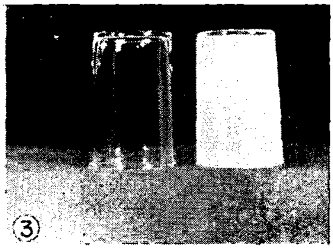
In the course of work performed by Martin and Wilson for the Quartermaster Corps, many methods were tried to evaluate minute films, mostly food soil, without notable success. Reflected light, flourescence, phase microscopy, electrography, replica films, dyeing the film, and measuring the strength of the films were considered.

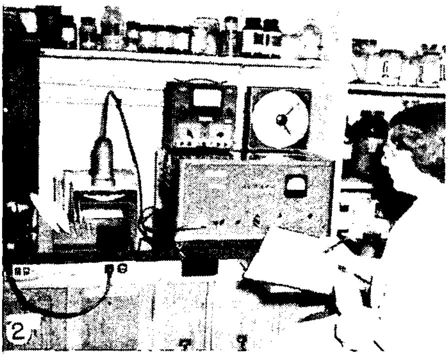
The use of radioactive phosphorus as part of the phosphate component of the detergent, or the use of calcium or strontium in the water supply appeared to be a feasible means of forming a radioactive film on the various materials of which dishes and utensils are made.

Use of P^{32} in Detergents

P^{32} was obtained from Oak Ridge in the form of very dilute phosphoric acid. This can be added to trisodium phosphate in this form, or it can be incorporated in the phosphoric acid used for making the complex phosphates such as tripolyphosphate or as polyphosphate.

The first tests were made with trisodium phosphate and waters of various hardness, which combination is known to produce a heavy calcium phosphate film on dishes and the dishwashing machine. A General Electric portable home type dishwasher was used (Fig. 1). This type of machine is manually controlled and thereby very flexible in its ability to vary the length of washing and rinsing and the number of washes or rinses. The test pieces were racked in the upper rack. The inner circle contained four 5″ x 5″ glass squares for evaluation by both the photometric method and radioactive count; the outer circle contained 4″ discs of melamine plastic, aluminum, stainless steel, and monel, and saucers of porcelain and melamine plastic. After washing, rinsing twice, and air drying, they were all counted for radioactivity. Fig. 2 shows





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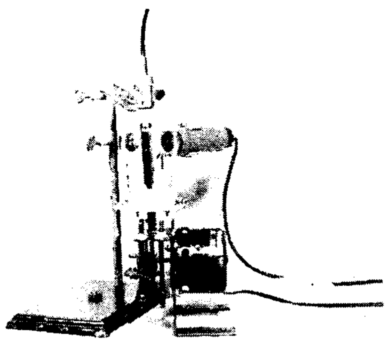

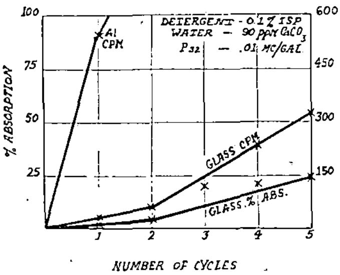

FIG. 6

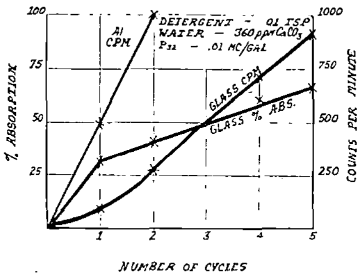

FIG. 7

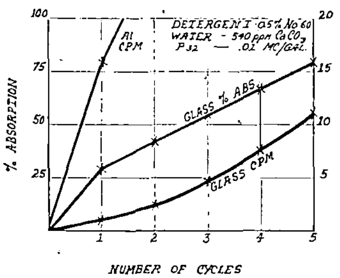

FIG. 8

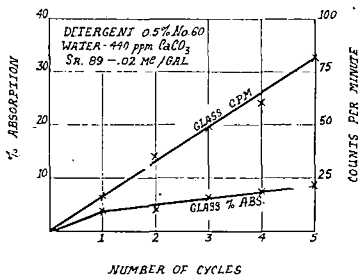

FIG. 9

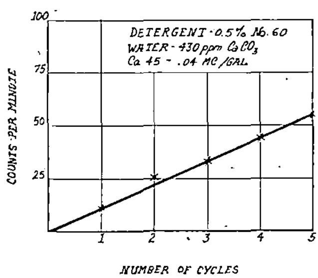

FIG. 10

the counting setup. The saucers or discs are positioned on the shelf below the GM tube. Fig 3 shows an example of badly filmed tumblers; Fig. 4 shows badly spotted tumblers.

The graphs in Figs. 6-8 show the rate of filming as indicated by photometric readings and by radioactive counts per minute. Fig. 6 is the rate of filming with 0.1% TSP in a soft water. The lower line shows the rate of filming as indicated by the photometer method. After five complete washes the film on the glass slides absorbs 27% of the light, showing a fairly uniform rate of increase. The next line shows the increase in radioactive counts per minute on the same glass slides. All of the test pieces approximated this curve except the aluminum one, in which the curve rises very fast, as indicated by the line to the left. The count for the aluminum piece reads 9500 per minute after five wash cycles, as compared to an average of 340 for the other materials. This is probably due largely to the formation of an aluminum phosphate, and not to heavy calcium phosphate film.

In using an extremely hard water and a TSP concentration of 0.1% the data shown in Fig. 7 are obtained. Again, the rate of build-up as indicated by measuring the radioactivity is fairly uniform. The aluminum count is again high in comparison. The rate of film build-up shown by the photometric method is uniform after the first wash cycle. We are inclined to believe that the rate of build-up as indicated by the radioactivity is the probable rate, and suspect that the excess light absorption after the first cycle is due to some special cleavage in the optical properties due to the initial stages of the film build-up.

If the P^{32} is incorporated in a tripolyphosphate and used in a dishwashing compound of sodium silicate, sodium carbonate and sodium tripolyphosphate but no TSP, the data shown in Fig. 8 are obtained. The photometric film indicated by the mdidle line shows a heavy film build-up in five wash cycles, but the radioactivity of the film is very small, as shown by the lower line. This indicates that very little phosphate is in the film. As before, though, the radioactivity of the aluminum specimen is higher than the rest.

Data from these three graphs are summarized in the following table:

Detergent	Water Hardness	% Absorption	Counts per minute
0.1% TSP	90 ppm	27	340
0.1% TSP	360 ppm	67	900
0.5% No. 60	540 ppm	78	11

It is apparent that when water hardness increases, film formation and the radioactive count also increase when TSP is used. By using a still higher water hardness with a commercial dishwashing product containing no TSP, we can produce a heavier film as measured photometrically, but the count indicates that the phosphate content is but a small fraction of this film. The film is predominately carbonate and silicates, making it impractical to use P^{32} as a tracer in film studies, since many commercially important dishwashing formulations contain no TSP and have phosphorus present only as Polyphosphate.

Use of Sr^{89} and Ca^{45}

We needed a tracer which would make the film radioactive regardless of whether the film was composed mainly of carbonate, silicate, or phosphate. Two elements are available: Strontium ^{89} with a strong *B* or beta and Ca^{45} with a weak *B* or beta radiation. Strontium was available first, so we started with it.

Fig. 9 shows data obtained with a hard water and a commercial dishwashing product. Using 0.02 mc of Sr^{89} per gallon, we obtained a significant count with a relatively small amount of film.

As soon as Ca^{45} became available, we used that in place of Sr^{89}, since calcium is usually the main cation present in films encountered in dishwashing practice. Somewhat similar curves were obtained with Ca^{45}.

Water spotting and filming of glass tumblers are widely used as criteria of the value of a dishwashing product or process. Tumblers are not very suitable for photometric evaluation, hence evaluation is usually based on a visual estimate as to whether they are good, fair, or poor after five, ten, or fifteen washes. This is not a quantitative evaluation that can be used for an exact comparison from year to year or relied on from one individual observer to another. It does not lend itself to determining small improvements in product quality. But since the visual appearance is of very great practical importance, it is very desirable to find tracer methods which lend themselves readily to quantitative evaluation and at the same time correlate well with visual appearance of dishes and eating utensils.

Correlation has not yet been established for many conditions of practical importance. Our present testing program is being carried on with soiled and unsoiled tumblers in an endeavor to determine at what stage in the washing process it is best to add the Ca^{45} for the best tagging of the film. There is the choice of adding it to the soil, the washwater, one of the rinses, or by special treatment after the utensil is dried, or a combination of two or more such means.

A rotating stand, shown in Fig. 5, is used to hold the tumbler when it is being counted. One tube counts the outside and another is used inside. Usually, we make separate counts on the two sides. Fig. 10 shows a film build-up as measured by activity on the outside of glasses when we have Ca^{45} in the wash and both rinses. The inside readings have not been uniform nor have the readings on milk soiled surfaces been reliable to date. Results of preliminary tests would seem to indicate that there is more film on the outside and that a clean surface holds more hard water film than a milk soiled one. Our present objective is to check this unusual condition and its cause.

SUMMARY

The use of P^{32} incorporated in phosphate detergents provides a means of measuring some types of hard water film formation on glass,

ceramic, plastic, and metal surfaces of dishes or utensils washed by mechanical methods.

The use of Sr^{89} or Ca^{45} as a portion of the water hardness enables one to measure the hard water film formation when the detergent contains a complex phosphate that would not appreciably enter into the film formation.

LITERATURE CITED

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