NATIONAL BUREAU OF STANDARDS REPORT

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Progress Report

on

PRELIMINARY STUDY: TROPICAL
STORAGE OF DENTAL MATERIALS

by

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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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PRELIMINARY STUDY: TROPICAL STORAGE OF DENTAL MATERIALS

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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

PRELIMINARY STUDY: TROPICAL STORAGE OF DENTAL MATERIALS

Abstract

A preliminary survey of some dental materials stored for four years in Puerto Rico by the Armed Services was made to determine changes in properties of dental significance. Comparison was made with duplicates stored at the National Bureau of Standards. Alginate impression materials and investments were found to have deteriorated to an unusable state. Methyl methacrylate monomer (liquid) containing dissolved polymer had polymerized. Some items which had volatile and low melting constituents were shown to be improperly packed and melted. The tests substantiated the present practice of phase buying and preferential storage. The survey indicates the desirability for further study of the effect of storage on many dental items.

1. INTRODUCTION

Deterioration of dental materials during transport and storage is of particular interest to the Armed Services. Long periods of storage, often under extremely adverse conditions, can be a military necessity. Materials which are unusable or in an inferior condition on arrival at the operational level cause a loss of time and money as well as an interruption in

dental service.

In 1951, while a guest worker at the Dental Research Section of the National Bureau of Standards, Col. T. E. Fischer, USAF (DC), planned an investigation to determine critical time limits for the storage of certain dental materials in tropical climates. Although circumstances prevented carrying out the investigation as originally planned, a number of materiel items have been returned to the National Bureau of Standards after four years of storage, and their condition examined by visual observation and applicable specification tests.

2. CONDITIONS OF STORAGE

To avoid variations in composition, date of manufacture, and packaging, samples for storage at three locations were selected with the same batch number.

The dental materials listed under Column A, Table 1 were stored in a constant temperature and humidity room in the Dental Research Laboratory of the National Bureau of Standards. The samples were sealed in a packing case with a moisture-proof liner. The room is maintained at approximately a temperature of 70°F and a relative humidity of 60%.

The items listed in Column B, Table 1 were stored on open shelves in the penthouse of the Rodriguez Army Hospital, San Juan, Puerto Rico. The prevailing temperature at this site was the highest of the three locations.

The materials listed under Column C, Table 1 were stored on open shelves at the Tropical Research Laboratory, San Juan,

Puerto Rico, where they were exposed to year round relative humidities of 75 to 79%.

3. RESULTS AND DISCUSSION

3.1 General Effects of Storage

The appearance of the packaging of individual samples reflected storage conditions. Metal parts of containers showed varying amounts of rusting. Containers stored in the moisture-proof case at the National Bureau of Standards were clean and relatively free of rust; the penthouse containers were spotted with rust; and the seaside samples were very rusty (as may be seen in Figure 1). Cardboard cartons containing materials with volatile or low melting point ingredients were stained by these ingredients. Figure 2 shows cartons of a protective coating material. The penthouse sample, "B", which had been subjected to higher temperatures, is badly discolored.

Materials which were obviously affected by storage or which had become unusable are marked by an asterisk in Table 1. They are discussed in detail below.

3.2 Investment

The investment samples showed no caking or lumping and appeared in usable condition; however, consistency tests, performed according to Federal Specification U-I-546, proved samples from the two tropical locations to be unsatisfactory.

Figure 3 shows typical results of the consistency tests. Samples stored under "A" conditions show normal slumping. Samples stored under "B" and "C" conditions set so rapidly that the test specimens supported their own weight in less

than two minutes, a setting rate too fast for dental use.

Since such behavior is most likely caused by partial hydration [1], samples of investments from "A", "B", and "C" were dried to constant weight at 110°C. The results, as shown in Table 2, show the varying water content and setting times.

Assuming that all water in the sample is in the calcium sulfate and is removed completely by the drying process, calculations on "A" sample of investment indicate that there were approximately 30 grams of calcium sulfate hemihydrate per 100 grams of the investment. This is a reasonable proportion for investments of this type. Comparing the percent weight lost by "B" and "C" samples to that lost by "A" samples, it is readily apparent that partial hydration of the material stored at "B" and "C" had occurred. Further calculations suggest that in "B" samples approximately 9% of the hemihydrate might be considered to be hydrated to the dihydrate form; and in "C", approximately 15%.

The setting rate of the hydrated investment may be slowed, and acceptable consistency obtained, by increasing the ratio of water to investment powder when mixing. This procedure is not recommended because it weakens the investment [2] and changes both the setting and thermal expansion [3]. An inlay cast into a mold made of this partially hydrated material is not likely to fit satisfactorily.

3.3 Resin Materials

Dental resin materials are procured for the Armed Services in powder/liquid form. In addition to samples of the standard supply items, samples of several brands of "filling" resin kits were also stored.

Past experience with resin liquids has indicated the necessity for phase buying and preferential storage of these materials to avoid premature polymerization induced by heat. In this study, "A" samples of denture base resin liquids were found to be still liquid while "B" and "C" samples had polymerized into clear solids, which, of course, are useless in the dental laboratory. Figure 4 shows the effect of four years of storage at "C" on a methyl methacrylate liquid.

It is interesting to note that all of the filling resin liquids were still in the liquid phase. The liquid of one brand had changed in appearance from optically clear to a cloudy pink. The available sample was too small for analysis. However, it is suggested that the change might be due to some chemical reaction involving the tertiary amine initiator. Another brand had not polymerized but the plastic seals on the bottle caps were broken and a large portion of the liquid had evaporated. The remaining samples were unaffected by storage.

These observations substantiate the practice of preferential storage (below 37°C) and phase buying of denture base resin liquids to avoid loss due to short shelf-life. It also

appeared that the self-cured (filling) resin liquids are more resistant to polymerization when stored at elevated temperatures than are the heat-cured resin liquids.

Tests for polymer content were positive for the unpolymerized heat-cured resin liquids and negative for the self-cured resin liquids. Samples giving positive tests for polymer content solidified in less than 23 hours when stored in a constant temperature oven at 85°C. Samples giving a negative test resisted polymerization for more than 168 hours when stored under these same conditions.

Tests for traces of polymer were negative for twelve of fourteen ADA certified denture resin liquids currently on the market. The two brands of resin liquids, which showed polymer content, polymerized into an unusable hard mass in less than 17 hours when stored in the constant temperature oven at 85°C. Two brands of resin liquids, picked at random from the twelve brands without traces of polymers, showed no evidence toward solidification (increased viscosity) after 72 hours in the 85°C oven.

From these results it appears that resin liquids without polymer content can be expected to have a longer shelf-life. A more definitive study of this type might prove the desirability of a change in Federal Specification U-R-179 for Resin, Acrylic, Dental which permits the resin liquid to be "methyl methacrylate monomer or methyl methacrylate monomer which has been partially polymerized."

3.4 Alginate Impression Material

All samples stored had deteriorated to an unusable condition. On mixing at standard temperature and humidity, a gummy, grainy mass was formed in less than one and one-half minutes.

Pfeiffer [4] demonstrated that alginate impression material deteriorates rapidly when stored at temperatures exceeding 37°C. The fact that samples stored under standard temperature and humidity conditions were unusable suggests some factor in addition to temperature affects this material. Procurement and supply agencies now avoid loss of these materials by both phase buying and preferential storage.

3.5 Materials with Volatile Solvents and Low Melting Point Ingredients

This group of materials would be expected to be adversely affected by high temperatures during storage. Some items were stored only in the roof-top location, while others were stored in two or all three locations.

A protective coating material of the theobroma type was stored at all locations, but only the samples stored at "B" were affected to any extent. The metal tube containers had lost approximately one-third of their contents. The remaining portion was easily expressed from the tubes but appeared drier and more grainy than the samples stored at "A" and "C". The material was still usable for protecting restorations. The loss in volume was due to the effect of elevated temperatures

which caused this low melting point material to liquefy and evaporate.

Cellulose acetate cast lacquer samples stored at "A" and "C" had separated into a liquid phase and a gel phase. Samples of this material from "B" had completely lost their solvent (95% chloroform, 5% alcohol, by volume) through evaporation.

Wax shapes and a brand of sheet casting wax from "B" were found to have lost a part of their more volatile ingredients, making the materials unusable for the purposes intended. This deterioration occurred only to the samples where higher temperatures were encountered. Another brand of sheet casting wax and samples of a baseplate wax were unaffected by the higher temperatures.

Two of three brands of preformed plastic patterns were also affected by the higher temperatures met in the roof-top location, but the two brands were affected in different ways. One brand had lost its plasticizer and had become very brittle, whereas samples of the other brand had flowed together and were so sticky and gummy that they could be separated neither from themselves nor their cardboard mounts.

3.6 Cement Filling Materials

Silicate cement stored at "B" and red copper cement stored at "A", "B", and "C" gave no evidence of deterioration. Fischer [5] has shown that deterioration of these materials is due to loss of water from the cement liquid. At the present time, procurement specifications require that cement liquids

be packaged in sealed glass ampoules. This improvement in packaging has been effective in preventing deterioration of these materials during storage.

4. SUMMARY

Deterioration of some materials is avoided only through phase buying and preferential storage, measures which cannot always be utilized. Improved packaging appears to be all that is necessary to insure long shelf-life for other materials. The following recommendations are the result of inspecting and testing dental materials after storage for four years:

1. The condition of investments stored in humid climates shows that the investments are inadequately protected from moisture by the snap-in-lid metal containers in which these materials are now supplied. Better containers should be used.
2. Low melting point materials packaged in screw-cap metal tubes need to be more adequately protected from high temperature by puncture-to-open seals.
3. Specifications for the procurement of preformed plastic patterns should contain a temperature stability requirement.
4. An improvement in the storage stability of denture base resin liquids is desirable.
5. There is a need for a more storage-stable elastic impression material.

BIBLIOGRAPHY

1. Farmer, G. J., and Skinner, E. W., Effect of relative humidity on the setting time of plaster of paris. Northwestern Univ. Bull. 43, 12-16 Dec. (1942).
2. Souder, W., and Paffenbarger, G. C., Physical properties of dental materials. Circular of National Bureau of Standards C433, page 88. U. S. Govt. Printing Office, Washington, D. C. (1942).
3. Volland, R. H., and Paffenbarger, G. C., Cast gold inlay technic as worked out in the cooperative research at the National Bureau of Standards. J.A.D.A. 19, 185 Feb. (1932).
4. Pfeiffer, K. R., Harvey, J. L., and Brauer, G. M., Deterioration during storage of alginate hydrocolloidal dental impression material. U.S.Armed Forces Med. Jnl. 6, 1315-1320 Sept. (1954).
5. Fischer, T. E., and Schoonover, I. C., Deterioration of silicate cements in the tropics. U.S.Armed Forces Med. Jnl. 2, 907-913 June (1951).

Table 1. Materials Stored

A	B	C
NBS at 70°F, 60% R.H.	Puerto Rico, Roof-top	Puerto Rico, Seaside
Investment	Investment*	Investment*
Denture Resin Liquid	Denture Resin Liquid*	Denture Resin Liquid*
		Self-cure Resin P/L
Acrylic Resin Powder	Acrylic Resin Powder	Acrylic Resin Powder
Clear Resin Kit P/L	Clear Resin Kit P/L*	Clear Resin Kit P/L*
	3 Brands "Filling" Resin Kits P/L*	
Alginate Material*	Alginate Material*	Alginate Material*
Protective Coating	Protective Coating*	Protective Coating
Baseplate Wax	Baseplate Wax	Baseplate Wax
Wax Shapes	Wax Shapes*	Wax Shapes
3 Brands Casting Wax	2 Brands Casting Wax	3 Brands Casting Wax
	3 Brands Preformed Plastic Patterns*	
Cast Lacquer*	Cast Lacquer*	Cast Lacquer*
Cavity Varnish	Cavity Varnish	Cavity Varnish
	Silicate Cement P/L	
Copper Cement P/L	Copper Cement P/L	Copper Cement P/L

*Items marked by an asterisk were found to have been adversely affected by storage.

Table 2. Water Content and Setting Time of Investment

Sample	Water Content[a] (%)	Setting Time[b] (min)
A	1.8	20
B	2.2	2
C	2.5	1.5

a Average of two determinations of weight loss on heating to constant weight at 110°C.

b On undried samples.

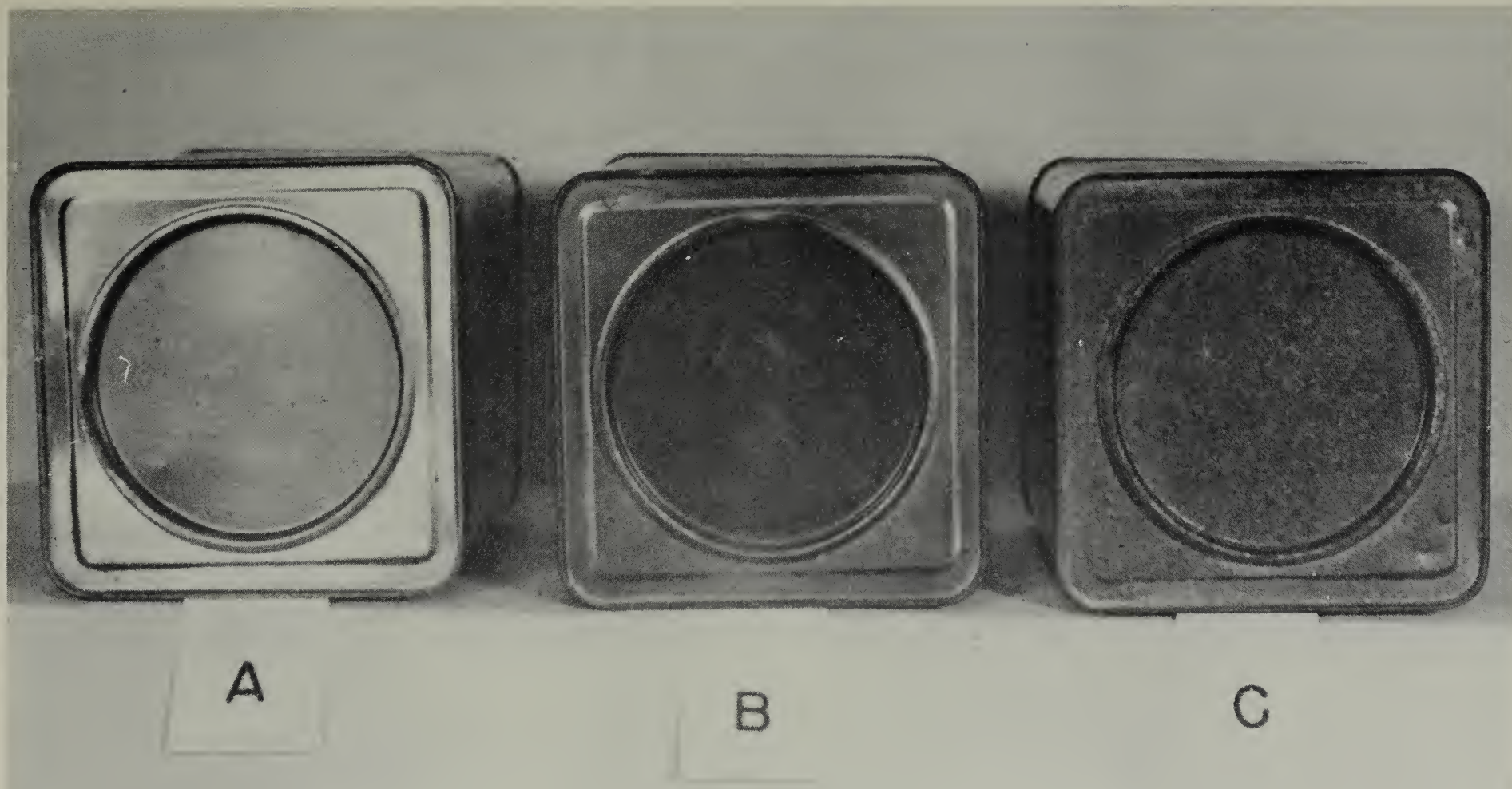

Figure 1. The metal container, "A", stored in a moisture-proof case, is clean and relatively free of rust. Containers "B" and "C", stored on open shelves in the hospital penthouse and pavilion of the Tropical Research Laboratory, are progressively more rusty indicating the effect of the increased humidity at the site of storage.

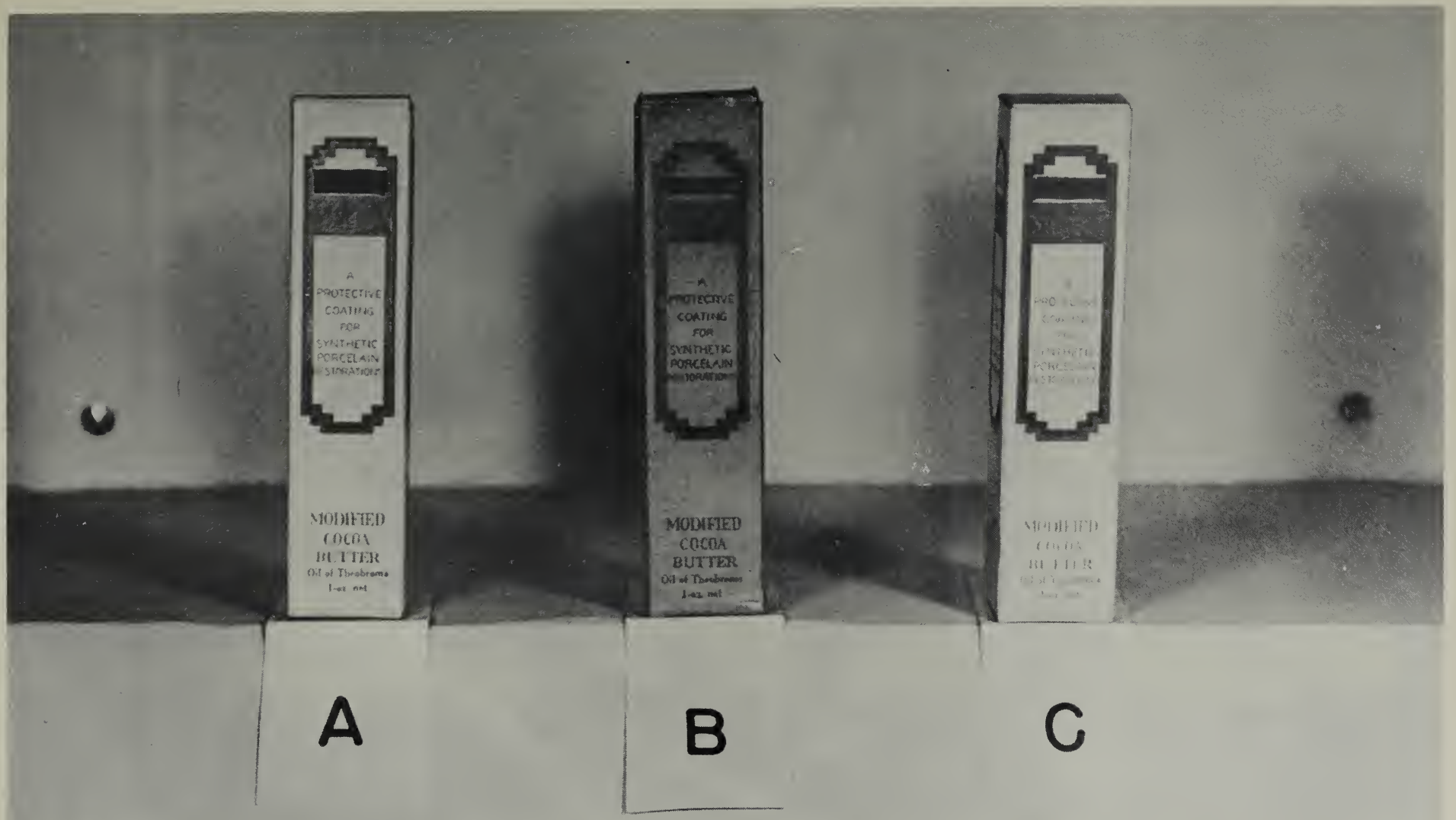

Figure 2. Discoloration of the cardboard carton containing a low melting point material is shown by "B" which was stored in the Rodriguez Army Hospital penthouse. Excessive temperatures during storage reduced the volume of this sample approximately by one-third of its original volume.

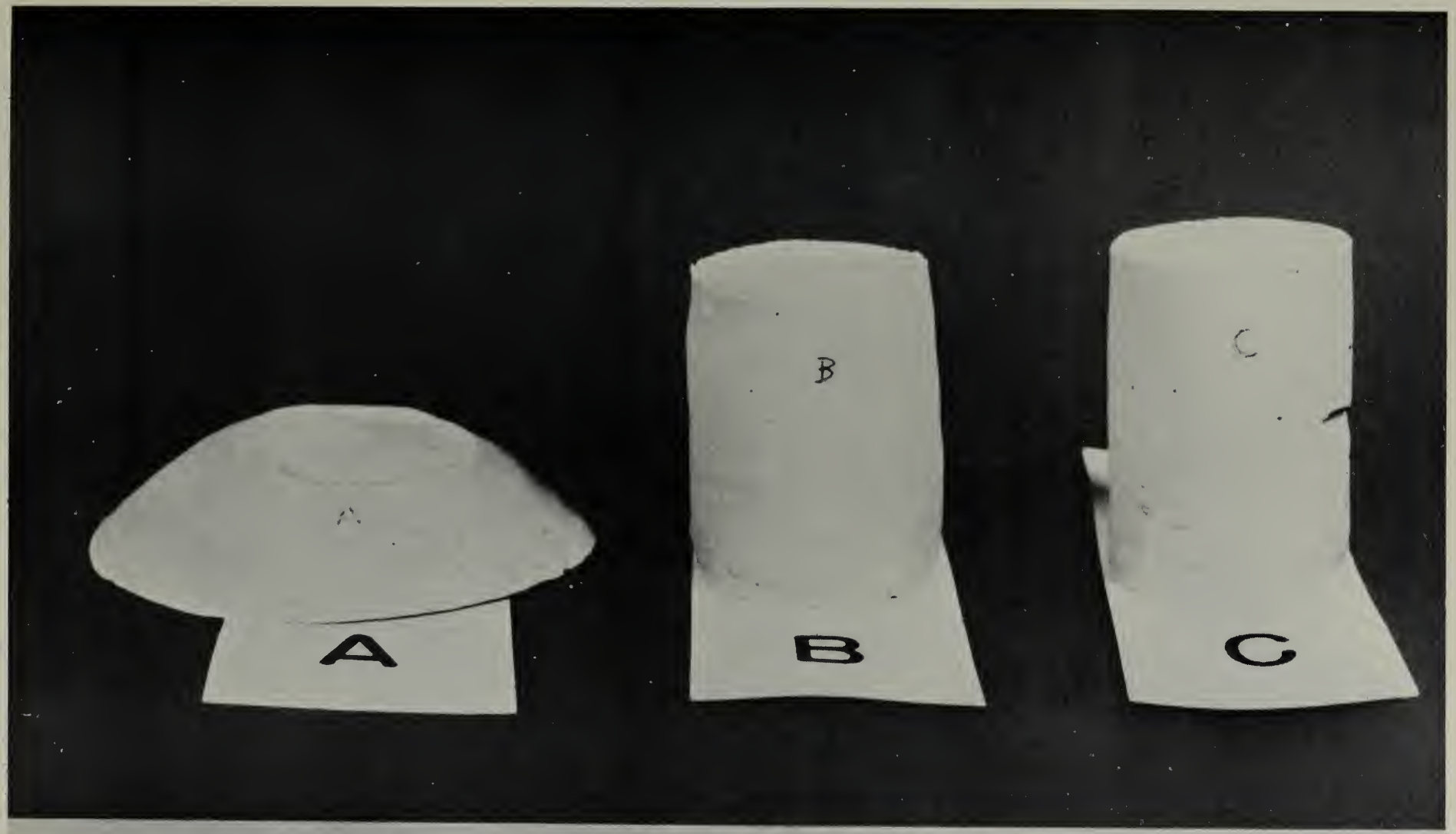

Figure 3. "A" shows normal slumping of investment mixed at the water/powder ratio recommended by the manufacturer for accurate dental castings. "B" and "C" set too rapidly to be of use in the dental laboratory. This behavior is due to moisture contamination.

Figure 4. The clear, solid mass which resulted from storage of the denture base resin monomer pictured here is of no value in making dentures. The material, normally a liquid, solified at elevated temperatures reached during four years of storage in Puerto Rico.

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