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STANDARDIZATION OF DENTAL PROSTHETIC MATERIALS

by
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INTRODUCTION

For dental prosthetic polymer base materials several national standards exist (*British Standards Institution*, 1963; *Svenska Standardiseringskommittén för Tandvårdsmateriel*, 1966). These seem to be more or less similar and agree very well with the international standard for denture base polymers of the Fédération Dentaire Internationale (*British Standards Institution*, 1966). In 1963 a second international standardization organization for dental materials, ISO/TC-106 Dentistry, was established, with, among others, non-metallic denture base materials on the program (*British Standards Institution*, 1963).

All these standards are subject to improvement as technological development advances. This report is presented in order to give a contribution to the discussion of standardizing of denture base polymers and repair materials, known as powder and liquid.

MATERIALS AND METHODS

Physical tests on four dental prosthetic materials

The materials tested (powder and liquid) were:

A Heat-curing resin, coloured.

B Heat-curing resin, clear.

Received for publication, October 9, 1968.

C Heat-curing resin, coloured.

D Cold-curing repair resin, coloured.

A, B, C, and D were manufactured by different firms.

The following tests were carried out:

1. Deflection test according to ADAS No. 12 (*American Dental Association,* 1962).

2. Impact test according to DIN 53453 (»Normkleinstab mit Kerb») (*Deutscher Normenausschuss,* 1962).

3. Deflection temperature test, modified after ASTM, D 648—56 (*ASTM Committee D-20,* 1959).

4. Determination of residual monomer (*Smith,* 1956).

Production of the specimens and conditioning have been described previously (*Koppang,* 1966). It should be noted that in the material C, the exothermic reaction was allowed to elapse at 60°C, before the temperature bath was elevated to 73 ± 1°C. This procedure was followed in order to avoid porosity formation in this material.

Qualitative chemical analyses of dental prosthetic materials

The altogether 14 materials (powder and liquid) consisted of eight heat-curing and six cold-curing materials. Five of the cold-curing materials were repair materials, one was designated as a denture base as well as a repair material. The four materials tested physically belonged to the mentioned 14 materials. The four materials analyzed with respect to inorganic components of the powder, also belonged to the mentioned 14 materials.

The following test were performed:

1. The liquids were analyzed with a Wilkens Aerograph Moduline Gas Chromatograph, Model 1520, and infrared spectroscopy (*Koppang,* 1967).

2. The polymers in the powder were analyzed by a high frequency induction oven *a.m.* Simon, with subsequent analysis of the degradation products in a Wilkens Aerograph Moduline Gas Chromatograph, Model 1520 (*Koppang,* 1968).

3. The organic material of non-polymer character in the powder was analyzed by thin-layer chromatography, with subsequent analysis of the separated compounds by infrared spectroscopy (*Koppang,* unpublished work).

4. The inorganic material in the powder was analyzed by using a high vacuum X-ray fluorescence spectrograph, Philips, type PW1540 (*Koppang,* 1969).

For more exact details concerning both methods and results, the reader is advised to consult the following papers (*Koppang,* 1967, 1968, 1969).

RESULTS

The results of the physical tests (Figs. 1—3) and of tests for residual monomer (Fig. 4) have previously been reported (*Koppang*, 1966) and are here given diagramatically.

The chemical analyses of the liquid part of the materials indicated that the materials could be grouped in three types (Figs. 5, 6, and 7):

I Heat-curing,
II Heat-curing, of type »Quick Cure»,
III Cold-curing

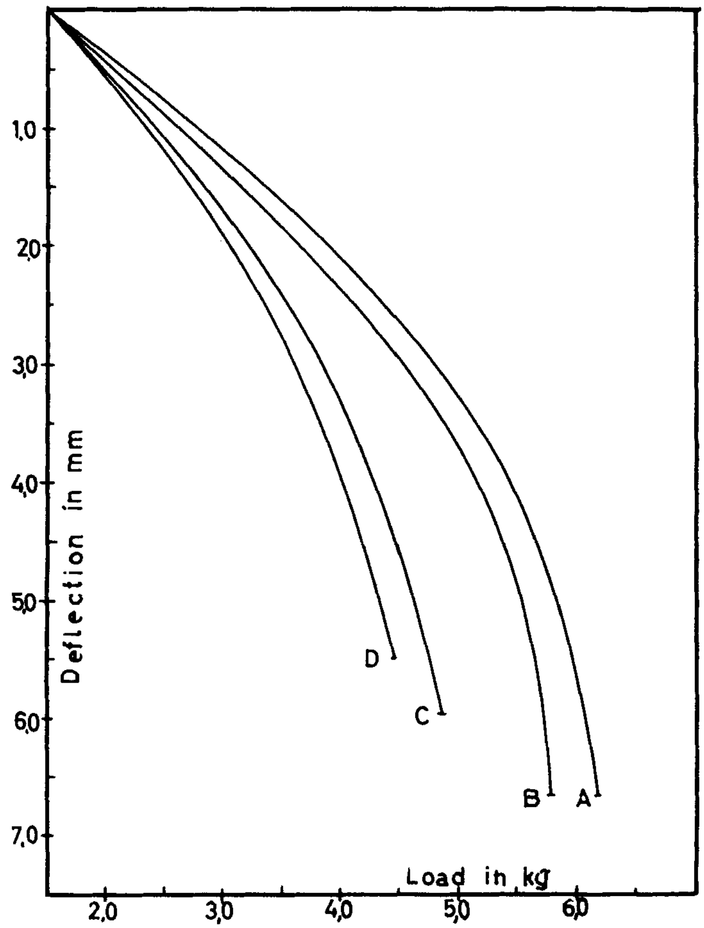

Fig. 1. Deflection test, performed in accordance with ADAS No. 12. Each diagram represents the mean value of three test series.

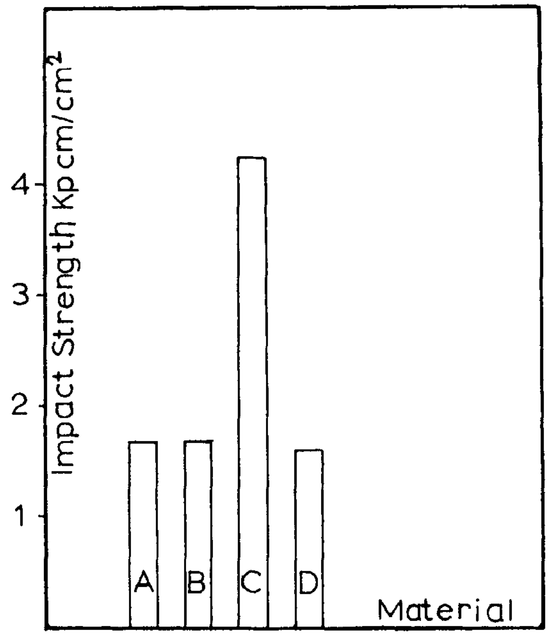

Fig. 2. Impact test, performed in accordance with DIN 53453 (»Normkleinstab mit Kerb«). Each column represents the mean value of four test results.

The heat-curing material, I, differed essentially from the two other types, II and III, which contained a co-initiator (N, N-dimethyl-p-toluidine) and an U. V. absorber, [2,2-dihydroxy-4-methoxy-benzophenone, 2-hydroxy-4-methoxy-benzophenone or 2(2-hydroxy-5-methylphenyl) benzotriazole].

The monomer admixture differed somewhat from material to material, as will be seen from Figs. 5, 6, and 7, but the main component was methylmethacrylate. Other monomer components demonstrated were n-butylmethacrylate, iso-butylmethacrylate, laurylmethacrylate, ethylene-glycol-dimethacrylate, and a non-linear methacrylic ester.

The chemical analyses of the polymer part of the powder indicated (Figs. 8 and 9) that the polymers belong to two types:

1. Polymers consisting of methylmethacrylate,
2. Co-polymers (or mixed polymers) consisting of methylmethacrylate as the principal component.

Components demonstrated in co-polymers (or mixture of polymers) apart from methylmethacrylate, were ethylacrylate, ethylmethacrylate, iso-butyl-

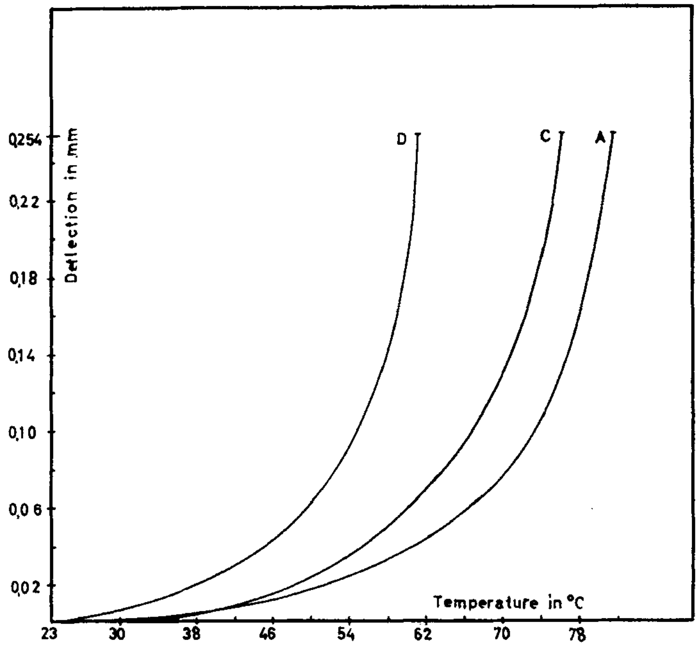

Fig. 3. Deflection temperature test, performed in accordance with ASTM, D 648—56, with a modified specimen fitting the deflection apparature descibed in ADAS No. 12. Each diagram resprensents the mean value of two test series. Fiber stress is 264. psi. Heating rate is 2°C/min.

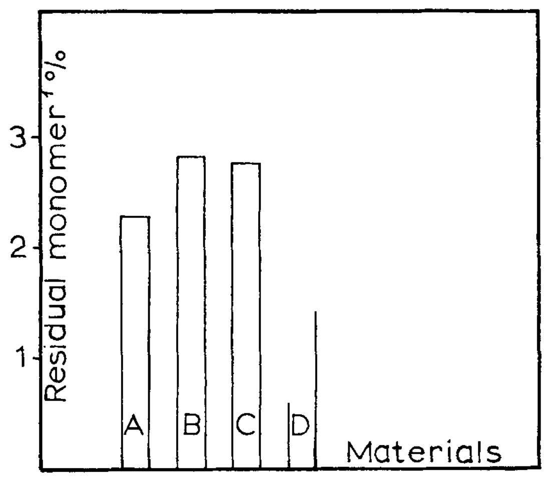

Fig. 4. Residual monomer calculated with respect to methylmethacrylate. Each column represents the mean value of three parallels.

[1]) D only partially soluble in glacial acetic acid.

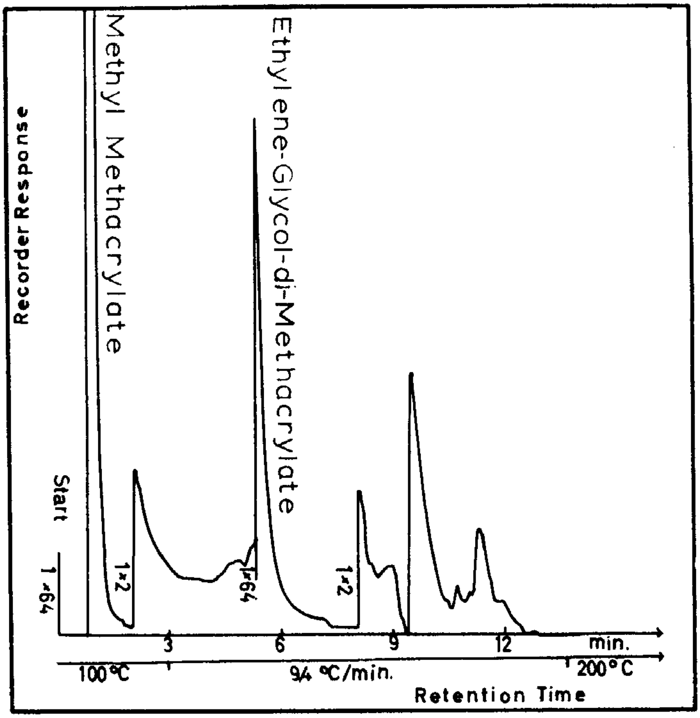

Fig. 5. Gas-chromatogram of the liquid part of a heat-curing dental prosthetic material.

methacrylate, n-butylacrylate, and styrene. The organic material of non-polymer character in the powder demonstrated a more fundamental difference from one material to another than seemed to be stated for the liquids and the polymers.

The analyses of these materials have not yet been finished, but the dominant component demonstrated was n-dibutylphtalate. Also methylphtalylethylglycolate and benzoylperoxide were found.

The analyses of the inorganic materials in the powder from two American (U.S.A.), one German, and one Norwegian dental prosthetic material, showed very few qualitative differences (Table I).

DISCUSSION

As mentioned in the introduction, all standards are subject to improvement as technological development advances. Whether the improvements are proceeding at a rate comparable to technological development, may, how-

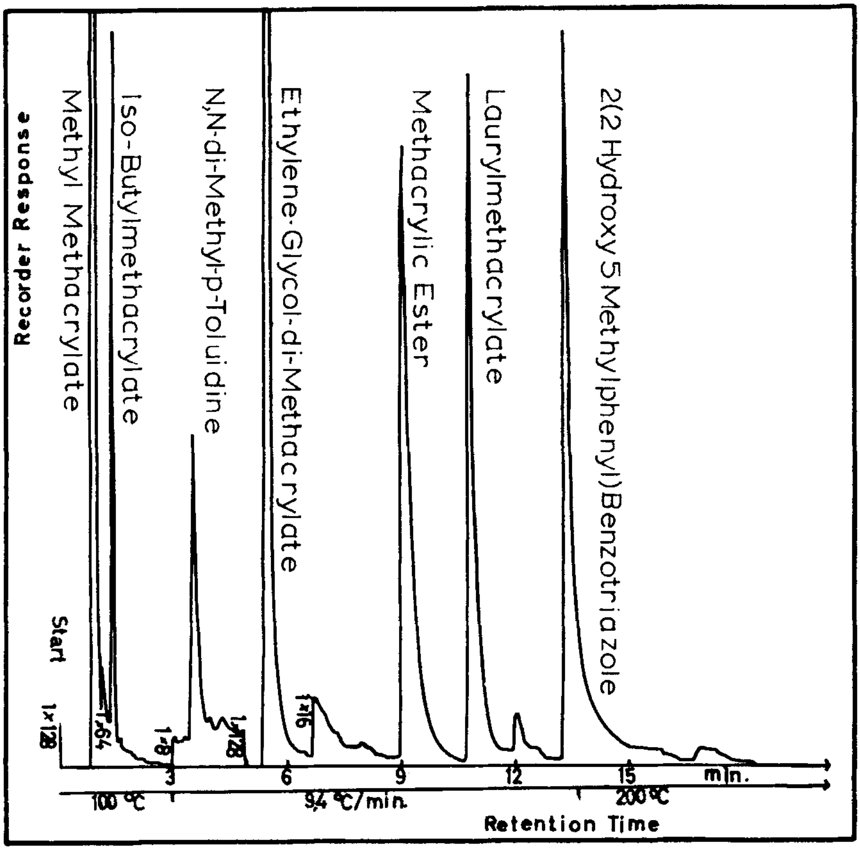

Fig. 6. Gas-chromatogram of the liquid part of a heat-curing dental prosthetic material of the type »Quick Cure».

ever, be left open to discussion. The rapidity with which the improvements proceed, naturally is partly a result of positive critisism of existing standards, but unfortunately also of the actual economical situation, as well as the supply of highly qualified persons able to solve the problems.

New directions in the physical testing of denture base materials have previously been argued for (*Koppang*, 1966). As will be seen from the results of the physical tests, the bending test will not give adequate answer as to the properties of the material. The aim of material testing (physical, chemical, and biological) is the development of non-destructive methods, so that the individual prothesis could be submitted to testing before being delivered to the patient. Such methods are, however, still hypothetical.

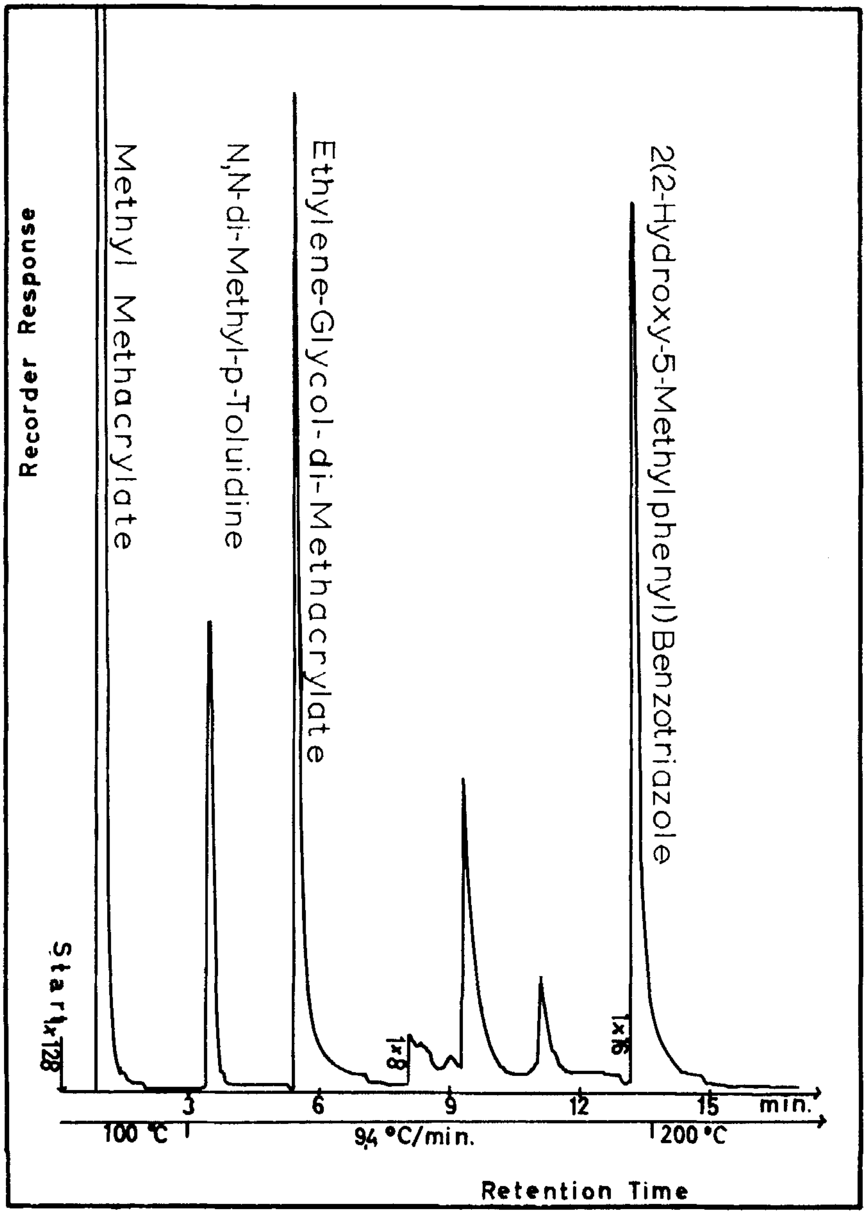

Fig. 7. Gas-chromatogram of the liquid part of a cold-curing dental prosthetic material.

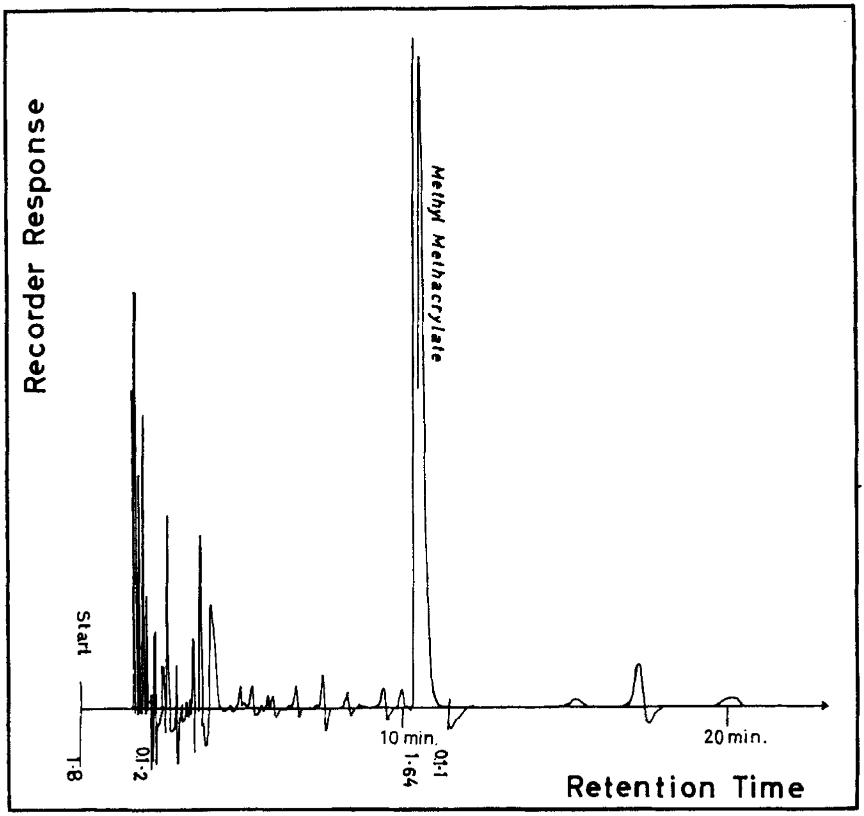

Fig. 8. Pyrolysis-gas-chromatogram of the polymeric part of a dental prosthetic materia (powder and liquid). (Ferromagnetic conductor: Fe, — 700°C).

The standards of each of the physical tests performed, require test specimens of different dimensions. It must be considered an invaluable advantage if a single specimen applicable for as many test methods as possible, could be standardized.

Already the polymerization of specimens for physical testing indicated the presence of three different types of materials known as powder and liquid. This indication seemed later to be verified by the chemical analyses of the liquids.

The material C, known as a heat-curing material, was classified as a type II material. The deflection test for material C gave approximately the same results as for the cold-curing material D. This result is probably not caused

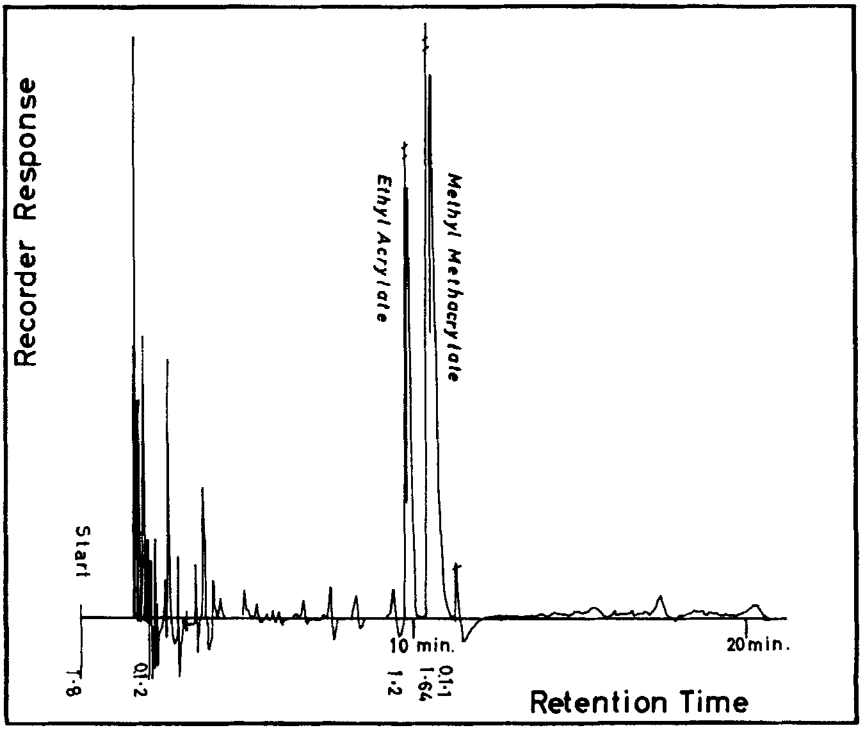

Fig. 9. Pyrolysis-gas-chromatogram of the polymeric part of a dental prosthetic material (powder and liquid). (Ferromagnetic conductor: Fe, — 700°C).

by the initiator system, but by a combination of the chemicals constituting the prosthetic material. This assumption seems to be proved by the results of the other physical tests.

The chemical analyses seem to indicate that a standardization of the chemical composition of base and repair materials of the type powder and liquid, known as acrylics, should not be unrealistic. This would increase the possibilities for controlling impurities present, and further be of great value in screening out components undesired from a biological point of view.

The initiator system differences, demonstrated by the chemical analyses, seem to indicate that time has come for the classification of a new base material. On the other hand it may, however, prove a better policy, not to classify the materials as heat-curing and cold-curing, etc., but to standardize only how materials should be »handled» and the subsequent results. The marketing of materials with the only designation that a certain standard is

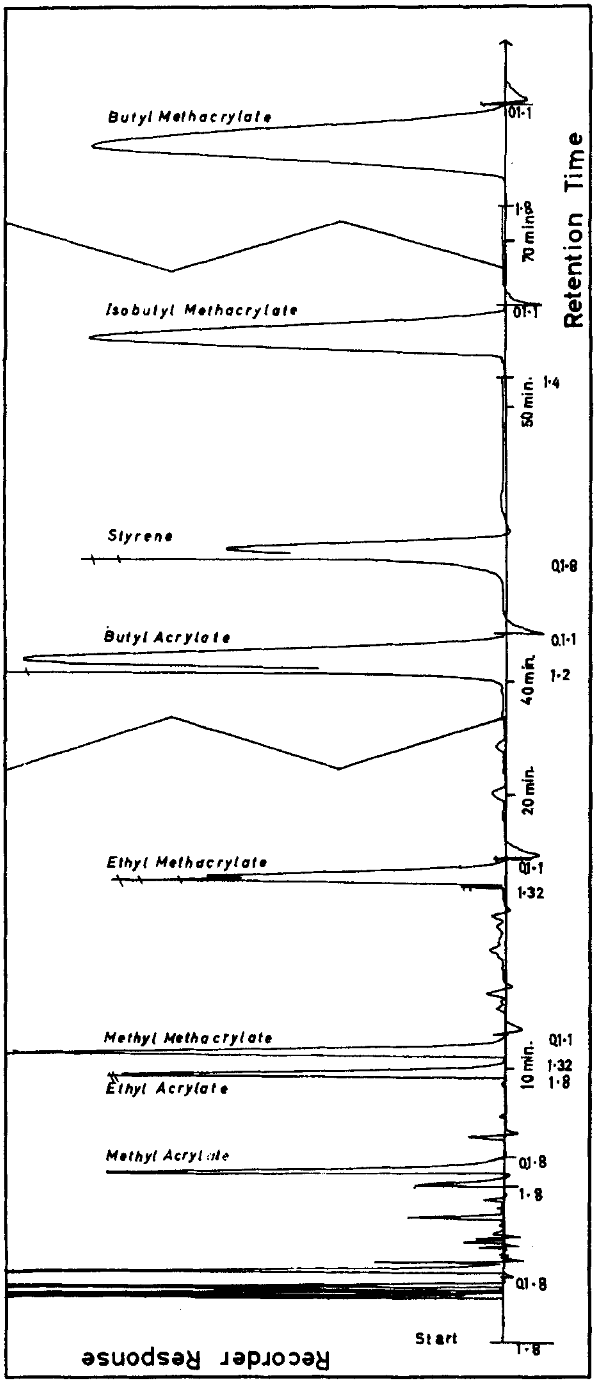

Fig. 10. Pyrolysis-gas-chromatogram of the mixture of polystyrene and copolymer of methylacrylate, ethylacrylate, butylacrylate, methylmethacrylate, ethylmethacrylate, isobutylmethacrylate, and butylmethacrylate. (The monomers were not purified. Ferromagnetic conductor: Fe, — 700°C).

Table I.

Inorganic material demonstrated in dental prosthetic materials by X-ray fluorescence. Series a represents the precipitate from the benzene solution of the powder. Serie b represents the direct analysis of the powder. + = demonstrated, 0 = not demonstrated, ? = probable, ?? = uncertain.

Material		Cd	Se	Ti	Ca	Zn	K	Ba	Fe	Cu	Pb	As	Nb	Co	S	Cl
I a	(Cold-curing)	+	+	+	+	+	+	?	+	+	+	?	0	0	+	0
II a	(Heat-curing »Quick Cure«)	+	+	+	+	+	+	0	+	+	+	?	+	0	0	0
III a	(Heat-curing	+	+	+	+	+	+	0	+	+	+	?	0	0	+	0
IV a	(Cold-curing)	+	+	+	+	+	+	0	+	0	+	?	0	+	+	+
I b	(Cold-curing)	+	?	+	+	?	+	0	+	0	??	??	0	0	??	0
II b	(Heat-curing »Quick Cure«)	+	?	+	+	?	+	0	+	+	??	??	0	0	??	0

satisfied, must be considered unsatisfactory, as seen from the results of the physical tests. In the future each material should be supplied with the exact results of physical tests, and the exact chemical composition. Such a procedure would give the practitioner correct and valuable information and therefore offer him the opportunity to select the best material for the individual patient.

The liquids and polymers seem to consist essentially of acrylic and methacrylic esters, with methylmethacrylate as the main component. The physical properties of the materials will naturally vary according to the monomer admixture, and the quantity of each monomer present both in the liquid and in the starting admixture for the suspension polymer. Fundamental works on these relationships in connection with the glass temperature, have been performed (*Kanig*, 1963; see also *Illers*, 1963).

The organic material of non-polymer character in the powder, most probably consists of initiators (peroxides), wetting agents for the pigments, plasticizers, and other organic components with special effects (such as water solubility, etc.) on the material. The plasticizers may be introduced as solvents for the peroxides, as wetting agents for the pigments, or as regulators for the polymerization. All the compounds mentioned were present to a minor degree and are not considered likely to have a fundamental influence on the physical characteristics of the dental prosthetic materials.

The inorganic materials, or pigments, from four dental prosthetic materials (two base and two repair materials), seem qualitatively very similar from one material to another.

SUMMARY

Physical and chemical analyses of dental prosthetic materials, powder and liquid, seem to indicate:

1. The bending test described by ADAS No. 12 does not give adequate information of the physical properties of the material.

2. The chemical analyses seem to indicate no fundamental differences between the materials with regard to the main components, the initiator systems being excluded, as the essential components present consist of acrylic and methacrylic esters.

Based on the results of these physical and chemical analyses, the following suggestions are made:

I. To standardize a single test specimen for a wide choice of diverse standardized test methods, with available standardized testing apparatures.

II. To standardize the chemicals and the chemical composition of these materials (powder and liquid).

These standards should involve the supply of each product with the physical test results, and a statement of the chemical composition.

RÉSUMÉ

NORMALISATION DES MATÉRIAUX POUR PROTHÈSES DENTAIRES

Les analyses physiques de matériaux pour prothèses dentaires, poudre et liquide, semblent indiquer que:

1. l'essai de flexion décrit dans la spécification No 12 de l'ADA ne donne pas une information adéquate sur les propriétés physiques du matériau.

2. les analyses chimiques ne semblent pas révéler de différences fondamentales entre les différents matériaux en ce qui concerne les principaux composants, si l'on exclut les systèmes initiateurs, puisque les principaux composants présents consistent en esters acryliques et métacryliques.

Se basant sur les résultats de ces analyses physiques et chimiques, l'auteur propose:

I. que soit normalisé un échantillon unique pour un large choix d'essais suivant différentes méthodes normalisées et en ùtilisant des appareils normalisés pour les essais.

II. que soient normalisés les composants et la composition chimique de ces matériaux (poudre et liquide).

Ces normalisations impliqueraient la nécessité de fournir avec chaque produit les résultats des essais physiques et une déclaration de la composition chimique.

ZUSAMMENFASSUNG

STANDARDIZIERUNG DENTALER PROTHESENMATERIALEN

Von physikalischen Testungen und kvalitativen chemischen Analysen dentaler Basis- und Reparationsmaterialen (Pulver und Flüssigkeit) können folgende Konklusionen gezogen werden:

1. Die Biegetestung allein, als von ADAS No. 12 beschrieben, gibt keine zufriedenstellende Information über die physikalischen Eigenschaften der Materialen.

2. Die chemischen Analysen neigen keine fundamentalen Unterschieden zwischen die Materialen zu indikieren, abgesehen von den Initiatorsystemen, da die essentiellen Komponenten von Akryl- und Methakrylsäureestern bestehen.

Basiert auf den Resultaten dieser physikalischen und chemischen Analysen, werden folgende Vorschläge hervorgewurfen:

I. Das Standardizieren von einem einziegen Testungskörper für eine Menge verschiedener Testungsmethoden, mit zugänglichen standardizierten Testungsapparaturen.

II. Das Standardizieren der Chemikalien und der chemischen Zusammensetzung dieser Materialen (Pulver und Flüssigkeit).

Die Standarden sollten auch die Resultate physikalischer Testungen und die genaue chemische Zusammensetzung jedes Materials involvieren.

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