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THE ABILITY OF 39 LIQUID CHELATING AGENTS TO FORM CEMENTS WITH METAL OXIDES, RESPECTING THEIR USABILITY AS ROOT-FILLING MATERIALS

A PRELIMINARY COMMUNICATION

by

T. Halfdan Nielsen

INTRODUCTION

In the course of time a great many and widely different root-filling materials have been used in dental practice. Just for that reason it seems that none of them has been quite satisfactory.

The most frequent objection to these materials, *viz.* shrinkage, probably is due to the fact, that, with a few exceptions, root-fillings are pastes, commonly used together with points: gutta-percha, silver etc. In a paste no cement-forming chemical reaction, and normally no chemical reaction at all, takes place between the liquid and the solid component. Consequently, the former gradually will be resorbed and/or evaporate. This gives rise to shrinkage, whereupon one cannot be sure, that the root-filling is still sufficient.

The most important demand, a bacteria-impermeable closure of the root-canal, might be fulfilled by a cement. This material is characterized by the fact, that the liquid and the solid component react chemically with each other. Provided the two components do possess certain properties, the reaction will result in the formation of a cement. In that case the possibility of evaporation and a subsequent shrinkage must be considered to be exceedingly small.

A cement as suggested at least must be constant in volume during the setting, or better: it must expand reasonably in order to effect a perfect contact with the walls of the root canal. Tardive contraction cannot be permitted. Further the cement must be of such a tightness in structure, that penetration of bacteria is effectively prevented. Finally, the cement must be physically and chemically resistant against relevant influences, when it is placed *in situ*.

CEMENTS SO FAR USED AS ROOT-FILLING MATERIALS

Such cements hardly belong to other than the following four types: —

1. *Zinc phosphate cements,* which all contract during setting. For this reason they are not usable for the present purpose.

2. *Zinc chloride cement* and further cements of this type (Sorel's cements) are formed by mixing ZnO with aqueous solutions of *e.g.* $ZnCl_2$ and $ZnSO_4$. All of them have tissue-injuring properties. For this reason they are unsuited for root-filling purposes.

3. *Epoxy resins* became available for root-filling purposes a few years ago (1). One of these was tested for shrinkage by the present author in the following, rather simple, way:

Two glass tubes of 20 mm length and about 1 mm lumen were closed at one end by melting. This made them resemble root canals. Then they were thoroughly filled up with the mixed epoxy resin until the surface of the "root-filling" was flush with the end of the tube. Root-filling spiral and vibration were employed in order to get the filling perfect. After closing by means of rubber stalls in order to prevent evaporation, the tubes were stored in a vertical position at 37° C for setting. One week later an examination revealed a shrinkage of about 1 mm (corresponding to about 50 %) for both of them. This property is probably found in other expoxy resins too, assuming the setting mechanism is of the same character in all these compounds.

Nevertheless, epoxy resins will possibly be sufficient as root-filling materials on account of the fact that they are very adherent to the dentine, but these cements were not known at the time, when the present screening was made and for that reason they were not further investigated in connection with the present work.

4. *Zinc oxide-eugenol cement* until now has been used to some extent for root-filling, in most cases along with points.

This cement, however, has the following deficiencies:

a. Even if it expands initially during setting until 11—23 ‰, this expansion is followed by a contraction of 2—3 ‰ in reference to the maximum expansion obtained (2).

b. Within about 50 days, its structure turns porous. This is found by means of the air bubble test method (2).

c. This cement is not resistant to carbonic acid, essentially not as HCO_3^-, since specimens of it are destroyed within two months when stored in a solution of $NaHCO_3 + CO_2$. The influence of carbonic acid must be considered relevant in the human root canal. The carbonic acid resistance test will be described later.

On account of the facts pointed out, it was decided to try to produce a number of new cements on the basis of chelating agent-metal oxide, quite analogous with the zinc oxide-eugenol cement. The purpose was to find a root-filling cement which was able to meet relevant demands in the best possible manner.

PREVIOUS INVESTIGATIONS

For many years the setting mechanism of zinc oxide-eugenol cement was rather unknown. *Copeland, Brauer, Sweeney & Forziati* (1955) showed, that:

a) the setting of zinc oxide-eugenol is conditioned by a metal chelate formed by the reaction between two molecules of eugenol and one molecule of zinc oxide. At the same time one molecule of water is formed,

b) during the setting, eugenol is sorbed in the cement without taking part in the chelate formation,

c) presence of water accelerates the setting process.

Brauer, White & Moshonas (1958) investigated more combinations of liquid chelating agents and other metal oxides. Some of these formed cements too.

The presence of 2 decisive properties seems to be necessary for the formation of a cement:

a) an acid hydrogen in the chelating agent must take part in the reaction, and

b) the metal oxide must be soluble in acids.

Smith's investigations (1958) confirmed the results referred to above.

CHELATE CEMENTS AS ROOT-FILLING MATERIALS. APPROACH TO THE PROBLEMS

Besides the obvious demand of cement-formation to the powder liquid pair employed,

1) *the essential demand to the liquid component = the liquid chelating agent,* is that

it must be able to expel CO_2 from that (basic) carbonate, which corresponds to a given oxide. The argument for this is the following:

When used as a root-filling material a cement may be assumed to be soaked with tissue fluid oozing into the canal from the apical foramen. The normal content of HCO_3^- in this liquid is about 30 milli-equivalents per litre, according to *e.g. Gamble* (6). This HCO_3^- may destroy the cement, forming the (basic) carbonate from the metal used. If this takes place, no advantage has been obtained, when using such a cement.

On the other hand: if this demand is fulfilled, there is a reasonable security that the cement will not be destroyed, even under continuous influence of HCO_3^-.

2) *The essential demands to the powder component = the metal oxide.*

a) It must possess a maximum resistance against carbonic acid,

b) its x-ray contrast must be considerable.

The reason for a) is, that the oxide must be able to withstand the influence of the carbonic acid in the atmosphere. When used in a dentist's office, it is frequently exposed to air, perhaps several times a day. If an oxide, contaminated with carbonate in this way is used as a powder in a root-filling cement, it may evolve CO_2 when mixed with the liquid. A cement, which contains gas bubbles is likely to be insufficient as a root-filling material.

CHELATE CEMENTS. EXPERIMENTAL

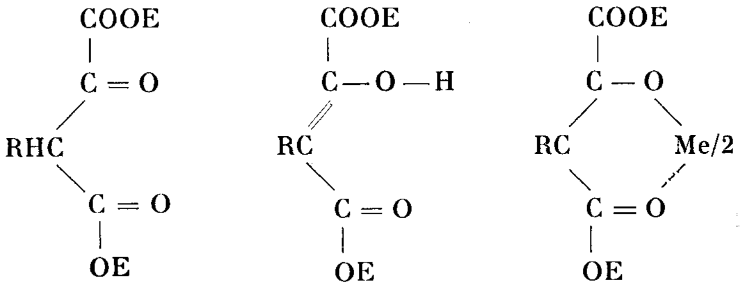
1. Selection of liquid chelating agents

Tables 1—5 contain the compounds, which were selected for investigation. Among these two are crystalline at room temperature: Guajacol, M.P. 28° C, and 8-hydroxyquinoline, also termed Oxine, M.P. 74° C. For this reason they could not be used directly. However, provided with certain substituents they formed liquid derivatives. These as well as derivatives from liquid compounds were investigated for cement-forming properties. Every compound and its derivatives are put down in a table of its own. Compounds given in brackets in no case were able to form a cement with any of the metal oxides used. The two liquid chelating agents: iso-eugenol and ethyl pyruvate were considered unsuited as liquids on account of their tendency to polymerize.

The only derivative of oxine: 7-n-propyl-8-hydroxyquinoline is an oily liquid. In the following it will be referred to as "Oxol".

Table 1

Oxaloacetic acid, diethylate



Keto- Enol- Half a metal chelate

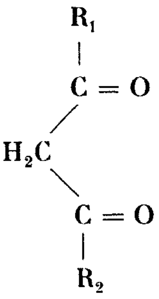
Oxaloacetic acid, diethylate, $R = H$

Derivative $R = C_6H_5^-$

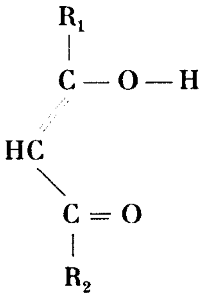
$E = C_2H_5^-$

Table 2

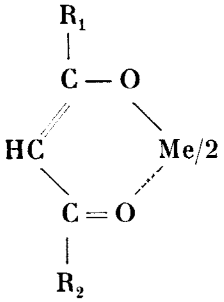
β-Diketo-compounds



Keto-



Enol-



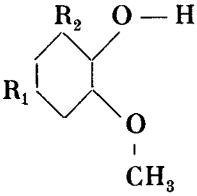
Half a metal chelate

No.	R_1	R_2	No.	R_1	R_2
1	methyl	methyl	14	φ	n-amyl
2	do.	n-butyl	15	φ	iso-propyl
3	do.	iso-butyl	16	φ	iso-butyl
4	ethyl	ethyl	17	φ	tert-butyl
5	do.	n-propyl	18	p-CH_3-φ-	iso-butyl
6	do.	n-butyl	19	φ-CH_2-	do.
7	do.	iso-butyl	20	furoyl	do.
8	n-propyl	n-propyl	(1)	ethyl	-OC_2H_5
9	do.	iso-butyl	(2)	n-propyl	do.
10	iso-butyl	iso-butyl	(3)	n-amyl	do.
11	φ	ethyl	(4)	iso-propyl	do.
12	φ	n-propyl	(5)	iso-butyl	do.
13	φ	n-butyl	6	φ	do.

$\varphi = C_6H_5^-$

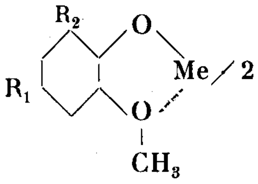
Table 3

Guajacol and derivatives



Guajacol

$(R_1 = R_2 = H)$

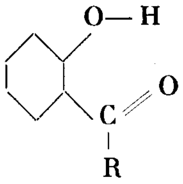


Half a metal chelate of Guajacol

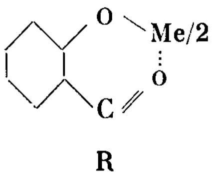
No.	R_1	R_2
1	allyl	H
2	n-propyl	H
3	methyl	H
(4)	H	allyl
(5)	H	n-propyl

Table 4

Salicylaldehyde and derivatives



Salicylaldehyde
R = H

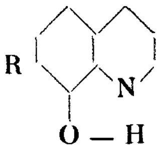


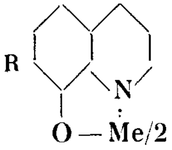
Half a metal chelate of
Salicylaldehyde
Me = metal

No.	R
1	H
(2)	CH_3-
(3)	C_2H_5-
(4)	-OCH_3
(5)	-OC_2H_5

Table 5

8-Hydroxyquinoline and derivative





8-hydroxyquinoline
called "Oxine"

Half a metal chelate of Oxine

R = H. M.P. = 74°C

R = n-propyl, only liquid derivative tested, referred to in this paper as "Oxol".

2. Selection of metal oxides

Among the metal oxides, these were tested: CuO, ZnO, CdO, and Bi_2O_3. All of them were able to form a cement in at least one case.

The following were not able to form a cement when mixed with any of the chelating agents tested: Al_2O_3, ZrO_2, Fe_2O_3, MnO_2, NiO, and WO_3.

CaO was not tested on account of its great tendency to form the carbonate, influenced by the atmosphere.

3. Experimental procedures

a. The cement formation test

Liquid and powder were mixed to a creamy consistency, well suited for a root-filling spiral. Normally the powder will be found in stoichiometric wide excess to the liquid. A sample of the mix was placed on a slide and put into a waterbath at 37° C.

As a practical criterion for cement-formation, the following was requested: Within 24 hours, the cement-paste should alter its structure, turning into a solid, which only could be broken when pressed with the edge of a mixing spatula. The pressure should be about that used for condensing amalgam. Sharp surfaces of fracture should appear upon breaking. The formation of a viscous cement was considered to be negative.

b. The carbonate test

Let us suppose that a given chelate-oxide combination forms a cement. In order to carry out the carbonate test for this combination, the same liquid is mixed with the (basic) carbonate corresponding to the oxide used. A sample of this mixture is placed in a test tube filled up with water at 37° C. This temperature is maintained during the experiment. Normally, the samples sank to the bottom when placed in the tubes.

A practical criterion for a positive result was that within 24 hours the sample either should ascend to just below the surface of the water, on account of the formation of gas bubbles in the sample, or if the sample did not ascend, its surface should be filled up with gas bubbles in such a manner that no doubt was possible.

Samples which neither ascended nor were filled up with gas bubbles were considered negative.

c. The carbonic acid resistance test

This test was introduced in order to obtain an effective countertest to the carbonate test. It was carried out in this way:

The cement selected for this test was made in several specimens of $2 \times 8 \times 16$ mm and allowed to set. The specimens were stored in water at 37° C for 8 days. Then 3 pieces were tested for transverse strength as follows: Each specimen was placed upon 3 peaks, and a steel ball 2 mm in diameter was pressed upon the upper middle of the specimen using known progressive pressure. The transverse strength was noted for the 3 specimens and the mean value was put down in a table as a reference value.

The other specimens were distributed in 100 ml Erlenmeyer flasks, 3 pieces in each. Further in each flask was poured 50 ml of this solution: water 600 ml, $NaHCO_3$ 12.5 g, and 1 "sparklet" of CO_2. The solution was made in a special flask for home fabrication of soda water. After this each flask was closed with a rubber stopper and secured with metal-wire on account of the internal pressure. Storage at 37° C. Every week the solution in the Erlenmeyer flasks was replaced by fresh solution.

After 1, 3 and 6 weeks, 3 specimens were tested for transverse strength each time. The mean value of every test was put down in the table for comparison.

RESULTS AND DISCUSSION

1. Evaluation of the cement-formation and the carbonate tests

All the results are shown in Table 6.

a) *Oxaloacetic acid diethylate and its derivative.* Both are setting slowly and the cements formed are too fragile. On account of this they were abandoned as unsuitable for the purpose.

b) *β-Diketones.* Among these, No. 20 seems to be the best. It forms a suitably quickly setting cement when mixed with ZnO. Its odour is not as unpleasant as that of eugenol. The carbonate test is positive. Tests revealed a linear expansion (2) of 22 ‰ without tardive contraction within a time of observation of 180 days. Nos. 1—4 are of high viscosity and for this reason are not suited for convenient mixing with powder. Diketones Nos. 1, 2, 3, 4 and 12, 13, 17 and 18 theoretically might be accepted in connection with CuO. Later on, however, it was demonstrated, that every chelate cement with CuO discolours serum broth. They were therefore dropped as not being suited for root-fillings. It is remarkable that the β-diketones Nos. 5—10 are not able to set within 24 hours, even when the corresponding carbonate tests were positive. The cements formed from these were viscous.

c) *β-keto-ethylate No. 6* was the only one which was able to form a cement. Still, the carbonate test was negative except in connection with copper carbonate.

d) *The guajacol group.* Liquid No. 1: eugenol, seems far from the ideal. The carbonate test is negative for this liquid as well as for the rest of the group. Nos. 4 and 5 were not able to form cements, probably because of a steric hindrance from the side-chain in the 6-position.

e) *Salicylaldehyde* has a rather bad odour. So much so that doubt about its usability in the clinic may arise. A practical study of a salicyaldehyde-ZnO-cement which was stored in water, revealed that the cement in the course of a few days became coated with a thin, stinky, dark layer of unknown origin. If this layer was removed, a new one soon formed. Nos. 2—5 were not able to form cements.

Table 6

Cement-formation tests and carbonatetests

Liquid chelating agent	Cadmium		Zinc		Copper		Bismuth		Number of cements per liquid
	oxide	carbonate	oxide	basic carbonate	oxide	basic carbonate	oxide	basic carbonate	
Oxaloacetic acid, 1	12 h	—	12 h	—	—	+	—	o	2
diethyl ester 2	12 h	—	—	+	16 h	+	—	o	2
β-Diketone 1	1 m	—	2 m	+	2 m	+	—	o	3
do. 2	6 m	—	2 m	+	4 m	+	—	o	3
do. 3	20 m	—	7 m	+	25 m	+	—	o	3
do. 4	4 h	—	7 m	+	25 m	+	—	o	3
do. 5	—	—	—	+	1 h	+	—	o	1
do. 6	—	—	—	+	2 h	+	—	o	1
do. 7	—	—	—	+	6 h	+	—	o	1
do. 8	—	—	—	+	2 h	+	—	o	1
do. 9	—	—	—	+	2 h	+	—	o	1
do. 10	—	—	—	+	2 h	+	—	o	1
do. 11	30 m	—	4 h	+	1 h	+	—	o	3
do. 12	20 m	—	4 h	+	10 m	+	—	o	3
do. 13	30 m	—	3 h	+	12 m	+	—	o	3
do. 14	40 m	—	10 h	+	12 h	+	—	o	3
do. 15	4 h	—	—	+	18 h	+	—	o	2
do. 16	4 h	—	—	+	18 h	+	—	o	2
do. 17	4 h	—	—	+	10 m	+	—	o	2
do. 18	4 h	—	2 h	+	30 m	+	—	o	3
do. 19	3 h	—	5 h	+	2 h	+	—	o	3
do. 20	8 m	—	12 m	+	2 h	+	—	o	3
β-keto ester 6	20 h	—	—	—	2 h	+	—	o	2
Guajacol 1	30 m	—	1 h	—	—	—	—	o	2
do. 2	30 m	—	2 h	—	—	—	—	o	2
do. 3	30 m	—	2 h	—	—	—	—	o	2
Salicylaldehyde	40 m	—	25 m	+	25 m	+	—	o	3
Oxol	mom	+	mom	+	mom	+	30 m	+	4
					Number of cements formed:				64

H_{37}: Approximate time of setting under water at 37°C.
+: Bubbles of CO_2 formed during the carbonate test.
o: not investigated. mom = setting almost momentarily.

f) *"Oxol", 7-n-propyl-8-hydroxyquinoline,* seems to possess very strong cement-forming properties. Mixtures of this liquid with each of the 3 oxides will harden *sub spatula.* Only a mixture with Bi_2O_3 as the powder component will set within 30 minutes.

Oxol seems in all decisive respects to fulfil relevant demands to the liquid component in a root-filling cement. It is *chemically stable,* since it has proven to be constant in its cement-forming properties during 4 years; it is *physically stable* except in colour. Like all phenols, it turns dark with time. Its viscosity is very convenient, *viz.* a little more fat oily than that of eugenol. Its odour is very weak and not unpleasant. Finally, it is positive to the carbonate test with all the cement-forming metals, yet only with freshly precipitated $(BiO)_2CO_3$. It seems as if an ageing of this compound takes place. This question will be subjected to further investigation.

Table 7

The carbonic acid resistance test

Cement tested	Transverse strength after		
	1 week	3 weeks	6 weeks
ZnO — eugenol	700 gr	183 gr	<100 gr
ZnO — β-diketone No. 20	750 gr	670 gr	600 gr
Bi_2O_3 — "Oxol"	950 gr	1000 gr	1100 gr

2. Evaluation of the carbonic acid resistance test

The results for the 3 cements are given in Table 7. The carbonate-negative eugenol-ZnO cement is quite destroyed within 2 months while the 2 cements which are positive to the carbonate test seem to withstand the influence of HCO_3^-. Investigations bearing on this vital point are in progress.

PRELIMINARY CONCLUSIONS

The results of the tests here referred to seem to indicate: —

1) The zinc oxide-eugenol cement may not be efficient used as a root-filling cement, with or without points.

2) The cement from β-diketon No. 20 and zinc oxide may possibly be sufficient as a root-filling cement.

3) The Bi_2O_3-oxol cement seems to possess the best possibilities to form a well suited root-filling cement, with as well as without points. In comparison with the zinc oxide-eugenol cement

a) it is harder,

b) its transverse strength is greater and, in addition, rises during 6 weeks even when influenced by HCO_3^-,

c) it yields an excellent x-ray contrast.

Investigations, already made, but not to be reported in this paper, have shown that

d) its middle expansion can be adjusted to about 10—15 ‰ (2),

e) it possesses a powerful bactericidal effect even 2 months after setting (2),

f) the influence of HCO_3^- is more than 3 times less on Bi_2O_3 than on ZnO (2),

g) contamination of the Bi_2O_3 with the basic carbonate will possibly not give rise to formation of CO_2 during setting, according to the previous chapter, section 1. f,

h) the particle size of Bi_2O_3 can be lowered to a degree which ensures the required density of the cement with the view to preventing penetration of bacteria (2).

The preparation of a suitable Bi_2O_3 appeared to be rather critical, but at present our work in this respect has progressed so far, that the "Bi-oxol-cement" can be subjected to clinical tests in the near future.

SUMMARY

The author intends to make a root-filling cement based upon the principle of a liquid chelating agent mixed with a metal oxide, analogous with zinc oxide-eugenol cement.

The following groups of (liquid) chelating agents or derivatives of the latter were investigated for formation of cement: —

1) oxaloacetic acid diethylate	Table 1
2) β-diketones and β-keto esters	Table 2
3) guajacol	Table 3
4) salicylaldehyde	Table 4
5) 8-hydroxyquinoline	Table 5.

The following oxides were able to form at least one cement: CuO, ZnO, CdO, and Bi_2O_3.

Not able to form cements were: Al_2O_3, ZrO_2, Fe_2O_3, MnO_2, NiO, and WO_3.

The best cement was formed from the liquid: 7, n-propyl, 8-hydroxyquinoline, termed ”Oxol”, mixed with Bi_2O_3 (Table 6). Compared with the zinc oxide-eugenol cement it possesses these advantages:

1) greater hardness,

2) fair expansion during setting without tardive contraction,

3) withstands HCO_3^- during 6 weeks without damage, contrary to the zinc oxide-eugenol cement, which is totally destroyed within the same period under similar conditions (Table 7).

It is expected that this new cement will be tested clinically in the near future.

ACKNOWLEDGEMENTS

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RÉSUMÉ

ÉTUDE DE 39 AGENTS DE CHÉLATION LIQUIDES EN CE QUI CONCERNE LEUR APTITUDE À FORMER DES CIMENTS AVEC LES OXYDES MÉTALLIQUES ET LA POSSIBILITÉ DE LEUR EMPLOI POUR L'OBTURATION DES CANAUX RADICULAIRES

L'auteur se propose de préparer un ciment pour obturation des canaux radiculaires basé sur le principe du mélange d'un liquide, agent de chélation, avec un oxyde métallique, à la manière du ciment à l'oxyde de zinc-eugénol.

Les groupes suivants d'agents de chélation (liquides) ou des dérivés de ceux-ci ont été étudiés en ce qui concerne la formation de ciment:

1)	acide oxaloacétique (diéthylate)	Tableau 1
2)	β-dicétones et esters β-cétoniques	Tableau 2
3)	gaïacol	Tableau 3
4)	aldéhyde salicylique	Tableau 4
5)	hydroxy-8-quinoléine	Tableau 5.

Les oxydes suivants étaient en état de former un ciment au moins: CuO, ZnO, CdO et Bi_2O_3.

Les oxydes suivants n'étaient en état de former aucuns ciments: Al_2O_3, ZrO_2, Fe_2O_3, MnO_2, NiO et WO_3.

Le ciment le meilleur était celui formé par le mélange du liquide 7, n-propyl, hydroxy-8-quinoléine, appellé Oxol, avec Bi_2O_3 (Tableau 6). Par rapport au ciment à l'oxyde de zinc-eugénol il présente les avantages suivants:

1) dureté supérieure,

2) expansion acceptable pendant la prise sans contraction tardive,

3) résiste à HCO_3^- pendant 6 semaines sans être attaqué, tandis que le ciment à l'oxyde de zinc-eugénol se trouve complétement détruit pendant la même période dans des conditions similaires. (Tableau 7).

L'auteur compte faire subir très prochainement des essais cliniques à ce ciment.

ZUSAMMENFASSUNG

ÜBER DIE ANWENDUNG VON 39 FLÜSSIGEN CHELATBILDNERN UND METALOXIDEN ZUR BILDUNG VON ZEMENTEN MIT HINBLICK AUF IHRE BRAUCHBARKEIT ALS WURZELFÜLLUNGSMATERIALIEN

Der Verfasser versucht ein Wurzelfüllungszement herzustellen nach dem Prinzip mit flüssigen Chelatbildnern und Metaloxiden analog mit dem Zinkoxid-Eugenolzement.

Folgende Gruppen von (flüssigen) Chelatbildnern oder Derivaten davon sind hinsichtlich einer Zementbildung untersucht worden:

1) Oxalessigsäure-diaethylester	Tafel 1
2) β-Diketonen und β-ketoestern	Tafel 2
3) Guajacol	Tafel 3
4) Salicylaldehyd	Tafel 4
5) 8-oxychinolin	Tafel 5.

Folgende Oxide waren in der Lage mindestens ein Zement zu bilden: CuO, ZnO, CdO und Bi_2O_3.

Nicht in der Lage Zemente zu bilden waren: Al_2O_3, ZrO_2, Fe_2O_3, MnO_2, NiO und WO_3.

Das beste Zement wurde von der Flüssigkeit: 7-n-propyl-8-oxychinolin, "Oxol" genannt, gemischt mit Bi_2O_3 als Pulversubstanz erzeugt (Tafel 6). Dem Zinkoxid-Eugenolzement gegenüber weist es folgende Vorteilen auf:

1) eine grössere Härte,

2) eine gute Expansion während der Abbindung ohne Spätkontraktion,

3) es wiedersteht in einem Zeitraum von 6 Wochen HCO_3^- ohne Beschädigung, im Gegensatz zu dem Zinkoxid-Eugenolzement, das unter den gleichen Bedingungen innerhalb derselben Zeit völlig zerstört wird (Tafel 7).

Man erwartet, dass das neue Zement in der nächsten Zukunft klinisch überprüft wird.

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