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Influence of different kinds of rosins and hydrogenated resins on the setting time of Grossman cements

Influência de diferentes tipos de breus e resinas hidrogenadas sobre o tempo de endurecimento dos cimentos do tipo Grossman

Manoel Damião SOUSA NETO*
Luis Fernando GUIMARÃES**
Danilo Mathias Zanello GUERISOLI***
Paulo César SAQUY****
Jesus Djalma PÉCORA*****

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In this study, the effect on the setting time by the addition of different kinds of rosin and hydrogenated resin on the Grossman cement powder was evaluated. The experiments were carried out following the American Dental Association's specification number 57 for root canal sealers. For this analysis, different Grossman cement powders were prepared using different rosins (X, WW and WG) and hydrogenated resins (Staybelite and Staybelite ester 10). The study of the physicochemical properties of the Grossman cements obtained the different kinds of rosins and hydrogenated resins interference on the cement's setting time. The hydrogenated resin, having a higher pH, increased the setting time of the cement when compared to the X, WW and WG rosins.

UNITERMS: Dental cements; Time factors; Dental materials; Dental restoration; Permanent.

INTRODUCTION

The zinc oxide based cements have been used in Dentistry over the last six decades. These cements are nothing but formulas adapted to the circumstances and necessities of each time[13].

The root canal sealers proposed by GROSSMAN[6,7,8,9,10,11] (1962; 1974; 1936; 1958; 1976; 1946) are zinc-oxide eugenol based.

In 1936 GROSSMAN[8] developed, a root canal sealer that had the following composition: powder: silver, hydrogenated resin and zinc oxide; liquid: eugenol and 4% zinc chloride solution.

In 1958, observing that the silver produced sulfides that darkened the teeth, GROSSMAN[9] eliminated it from the powder composition. Regarding the liquid composition, he substituted the zinc chloride for almond oil. The addition of vegetal oil had the purpose of retarding the setting time, giving the dentist more time to work on the root canal.

Still researching, GROSSMAN[6] (1962) included anhydrous sodium tetraborate to the powder of his cement, with the purpose to retard the setting time. In 1974, this author concluded that the addition of almond oil to the eugenol was not necessary, since the anhydrous sodium tetraborate was able to keep a satisfying working time. Thus, alterations were made in the powder composition and the liquid, and the final formula is shown below:

Powder:
Zinc oxide 42%
Rosin or hydrogenated resin 27%
Bismuth subcarbonate 15%
Barium sulfate 15%
Anhydrous sodium tetraborate 1%
Liquid:
Engenol

According to the requisites that a root canal sealing material must have, the properties and qualities can be divided into physicochemical, antimicrobian and biological.

The investigation of these properties became standardized since the publication of the specification number 57 of the AMERICAN DENTAL ASSOCIATION[1] (1983), avoiding the problems caused by the lack of standardization of the realized tests[3], making the research results reproducible and also to enable accurate comparisons between the different materials and research results.

The different commercial brands of Grossman cements employ in their compositions hydrogenated resin or rosin, not having uniformity in the formula.

This way, it is necessary to study the influence of different kinds of rosins and hydrogenated resins on the setting time of the Grossman cements, to inform which product shows the best physicochemical characteristics.

MATERIAL AND METHODS

The setting time determination of the cements followed the specification number 57 of the A.D.A.

The cements tested were obtained from the formula proposed by GROSSMAN[10] (1976), the only difference between them being the kind of rosin or hydrogenated resin (Table 1)

TABLE 1 – Tested rosins and hydrogenated resins, their commercial brands and the manufacturers

Name	Manufacture	Origin
Breutex - X	Eucatex	Brazil
Tipo WG	Madeitex	Brazil
Tipo WW	Coimbra	Portugal
Stabylite ester 10	Hercules	USA
Stabylite resin	Hercules	USA

The powder/liquid relations for the modified cements and spatulation times were obtained as described by SOUSA NETO[15] (1997) and are shown in Table 2.

TABLE 2 – Powder/liquid relations and spatulation times in seconds for the modified cements

Cements obtained with the rosins below	Grammes of powder/ 0.20 ml of liquid					Mean values (in gr.)	Spatulation times (in sec.)					Mean values (sec.)
Staybelite ester 10	1.13	1.11	1.18	1.05	1.06	1.11	120	125	130	125	140	128
Staybelite	1.11	0.98	1.10	0.99	1.08	1.05	120	110	120	130	120	120
Kind X	0.92	0.94	0.96	0.93	0.98	0.95	120	110	110	120	120	116
Kind WG	0.90	0.92	0.89	0.94	0.85	0.90	120	120	140	130	120	126
Kind WW	0.80	0.75	0.78	0.82	0.82	0.80	140	120	135	125	115	126

In order to perform this test, rings of stainless steel with an internal diameter of 10 mm and wall thickness of 2 mm were manufactured. The rings were fixed with wax on their external surface on a glass plate (1 x 25 x 75 mm).

After this the cement was manipulated, following the proportion expressed in Table 2 and placed inside the metallic ring, until it was completely filled.

After 120 ± 10 seconds from the beginning of the spatulation, the whole apparatus was placed over a grate inside a hermetically sealed plastic container. The device was kept at 37° C and 95% relative air humidity.

After 150 ± 10 seconds from the beginning of the spatulation, a 100 g, 2 mm active point Gillmore needle was positioned vertically on the surface of the material.

This test was repeated each 60 seconds until the needle stopped to mark the surface of the cement. The setting time was considered as the amount of time passed from the beginning of the spatulation until the Gilmore needle did not leave any visible mark on the cement's surface.

The setting time was considered as the average of 5 measures.

RESULTS AND DISCUSSION

The data obtained for the setting times, shown in Table 3, were submitted to a statistical analysis. The sample parameter study pointed to a non-parametric distribution. The Kruskal-Wallis test indicated a H_0=0,03% for a 1% significance.

TABLE 3 - Flow test of the studied cements (data in millimeters)

Cements obtained with the following rosins and hydrogenated resins	Setting time (in seconds)					Mean
Staybelite ester 10	5520	5880	5160	5820	6180	5712
Staybelite	3900	3540	4200	3300	3720	4188
Rosin X type	2100	2160	2400	2040	2210	2182
Rosin WG type	1060	1480	1360	1560	2240	1540
Rosin WW type	1120	1280	1160	1220	1180	1192

Once determined by the Kruskal-Wallis test that significant statistical differences between the cements existed, the sample average comparison was made, and the results are presented in Table 4.

TABLE 4 - Setting time: Comparison between the sample average of the tested cements.

Compared samples (two by two)	Difference between the averages	Significance
Staybelite ester 10 X Staybelite	5.0000	*
Staybelite ester 10 X Rosin X kind	10.8000	*
Staybelite ester 10 X Rosin WG kind	15.2000	*
Staybelite ester 10 X Rosin WW kind	19.0000	*
Staybelite X Rosin X kind	5.8000	*
Staybelite X Rosin WG kind	10.2000	*
Staybelite X Rosin WW kind	14.0000	*
Rosin X kind X Rosin WG kind	4.4000	ns
Rosin X kind X Rosin WW kind	8.2000	*
Rosin WG kind X Rosin WW kind	3.8000	ns

* Significant to the level of 0.01 = 4.6068; ns = non significant

The setting times of the cements obtained from hydrogenated resins and different kinds of rosin are statistically different between them.

SOUSA NETO[15] (1997) analyzed the pH and conductivity of different kinds of rosins and hydrogenated resins to verify their relation to the different physicochemical properties, and these data are shown on Table 5.

TABLE 5 - pH and conductivity values of different kinds of rosin and hydrogenated resins versus time

Rosins and hydrogenated resins	pH x time (min)							conductivity $(ohm^{-1} cm^{-1})^2$ x time (min)						
	1	2	5	10	20	30	60	1	2	5	10	20	30	60
Staybelite ester 10	3.9	4.5	5.0	5.3	5.6	5.6	5.6	14	16	17	29	59	62	68
Staybelite	4.7	4.9	4.9	5.1	5.1	5.1	5.1	24	25	34	44	44	47	59
Rosin X type	5.2	5.2	5.2	5.2	5.1	5.2	5.0	26	29	39	45	65	88	105
Rosin WG type	4.2	4.7	4.7	4.8	4.8	4.7	4.7	66	145	270	336	415	580	710
Rosin WW type	4.6	4.3	4.2	4.3	4.0	4.0	3.6	32	98	141	167	193	223	347

Conductivity is a property that indicates the amount of ions present in a solution. The higher the value, the higher the amount of ions in the medium.

When different kinds of rosins were compared, we observed that the X kind presented low conductivity. This characteristic can be justified by the purification method to which this rosin is submitted during its manufacturing process.

The X kind rosin has an uniform light yellow color, different from the WG and WW types, which have a dark yellow color and differences in pigmentation, indicating the presence of impurities (inorganic ions).

The WG rosin has a high conductivity value, indicating high quantities of inorganic ions in its composition.

The hydrogenated resins are obtained from the rosin hydrogenation. This process consists of adding hydrogen to a molecule, through a reaction with gaseous hydrogen, with or without the presence of a catalyst, lowering the number of double links of an unsaturated chain.

The low conductivity found in the hydrogenated resins is due to the hydrogenation process, which removes the impurities from the rosin and saturates the chain. These resins showed the least quantity of inorganic ions among the studied rosins.

The GROSSMAN[6,7,9] cement (1962; 1974; 1958) is a zinc-oxide eugenol based cement. Other components are added in order to obtain better physicochemical properties. Thus, the setting reaction is due to the reaction between the zinc and the eugenol.

The setting reaction of the zinc and eugenol is basically an ionic reaction, where the eugenol acts as a proton donator (H^+). The phenolic hydrogen in eugenol is substituted by the zinc ions to form a zinc-oxide eugenol chelate[5].

The setting mechanism of zinc-oxide eugenol based cements is a result of equimolars mixtures of zinc oxide and eugenol, consisting of zinc-oxide involved in a long crystal matrix of zinc eugenolate chelate. Any excess of eugenol is absorbed either by eugenolate and zinc oxide[4].

SAVIOLI[14] (1992) clearly showed the effect of rosin on the setting reaction of the zinc oxide based cement, reinforcing Grossman findings. The addition of rosin to the powder acts as an accelerator.

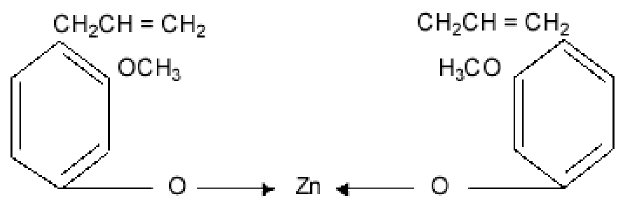
Based on the works of FRAGOLA[5] et al. (1979); BRAUER[4] (1967); GROSSMAN[11] (1982) and SAVIOLI[14] (1992) the influence of the pH on the setting reaction can be explained in this manner:

The reaction between zinc and eugenol is of ionic nature.

The pH indicates a higher hydrogenionic concentration (H^+). Thus, the higher the quantity of H^+, the

$$ZnO + H_2O \rightarrow Zn\,(OH)^2 \quad (I)$$

$$Zn\,(OH)_2 + 2H^+ \rightarrow Zn^{2+} + 2H_2O \quad (II)$$



(III)

quicker the reaction (II) that produces zinc in its ionic form (Zn^{2+}).

A higher quantity of Zn^{2+} makes the reaction (III) quicker, accelerating the setting time. This mechanism explains the absence of hardening in cements that contain hydrogenated resins with the pH around 7 (neutral). In this pH there is no H^+ excess able to release Zn^{2+}. GROSSMAN[12] (1982) relates that the cements containing hydrogenated resins with pH around 7 in their formulas did not set.

In this experiment, the long time the cements prepared with hydrogenated resin took to set , can be explained by its pH and low conductivity. The pH of the hydrogenated resins is higher than the rosins and their conductivity is lower.

The rosins, due to the concentration of abietic acid, have a low pH — indicating a high concentration of H^+ in the medium, accelerating the reaction between zinc oxide and eugenol.

BATCHELOR; WILSON[2] (1969) stated that consistency and setting time in the cements are related and both are affected by variables like temperature and humidity. Thus, before the realization of the tests in this study, the powder-liquid ratio was established to achieve the ideal consistency for the cements as stated by GROSSMAN[10] (1976).

The setting of the material on the glass surface is not related to the clinical conditions, where temperature and oral humidity will interfere in the process. The amounts of material used under clinical and laboratory conditions are also different. To avoid variations in the results, ADA specifications were used for ambient conditions: 37°C and 95% relative humidity.

In this study, it was observed that different kinds of hydrogenated resins and rosins interfere on the setting time of the cements. The hydrogenated resin has a higher pH than the rosin, increasing the setting time when compared to the more acid rosin kinds X, WW and WG.

CONCLUSIONS

1. Different kinds of hydrogenated resin and rosin interfere on setting time

1.1. The more acid the pH of the rosin, the quicker will be the setting reaction.

1.2. The setting time follows a crescent order: WW rosin, WG rosin, X rosin, Staybelite ester 10 resin and Staybelite resin.

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No presente estudo, analisou-se o efeito da adição de diferentes tipos de breus e resinas hidrogenadas ao pó do cimento de GROSSMAN sobre o tempo de endurecimento. Os experimentos foram realizados de acordo com a Especificação 57 para materiais obturadores de canais radiculares da American Dental Association (ADA). Para análise, foram aviados pós do cimento de GROSSMAN com diferentes tipos de breu (X, WW e WG) e resinas hidrogenadas (Stabylite e Stabylite éster 10). Os estudos das propriedades físico-químicas dos cimentos tipo GROSSMAN obtidos de diferentes tipos de breus e resinas hidrogenadas interferem no tempo de endurecimento do cimento. A resina hidrogenada, obtida do processo de hidrogenação tem o pH mais alto, provocando um aumento do tempo de endurecimento do cimento em relação aos breus tipo X, WW e WG, que têm pH mais ácido.

UNITERMOS: Cimentos dentários; Materiais dentários; Restauração dentária permanente; Fatores de tempo.

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* Professor Titular da Universidade de Ribeirão Preto - USP.

** Professor Doutor da Faculdade de Ciências Farmacêuticas de Ribeirão Preto - USP.

*** CD Estagiário de Endodontia, **** Professor Associado e ***** Professor Titular da Faculdade de Odontologia de Ribeirão Preto - USP.

Faculdade de Odontologia da Universidade de São Paulo

Avenida Lineu Prestes, 2227 - Caixa Postal 8216
Cidade Universitária Armando de Salles Oliveira
05508-900 São Paulo SP - Brazil
Tel.: (55 11) 3091-7861
Fax: (55 11) 3091-7413

eMail

pob@edu.usp.br