Factors affecting the color stability of restorative resins

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Asmussen, E. Factors affecting the color stability of restorative resins. *Acta Odontol. Scand.* 1983, 41, 11–18. Oslo. ISSN 0001–6357.

The color change resulting from storage in water was measured on a number of experimental and proprietary composite resins. The experimental resins contained varying amounts of amine (DEPT or DEBA), benzoyl-peroxide (BPO) and inhibitor (MHQ). The proprietary resins had earlier been analyzed as regards the composition of the monomer and the content of amine and peroxide. The color change of DEPT-containing resins was positively correlated with the DEPT/BPO ratio, and negatively correlated with the monomer content of BISGMA. DEBA-containing resins were more color stable than resins containing equimolar concentrations of DEPT. The color change was independent of MHQ up to a certain concentration; above this the color change increased with the amount of MHQ. In general, the light activated materials were more color stable than the chemically activated materials. The color change was not affected by pH, but decreased when the oxygen had been removed from the storage water. The test for color stability using UV-light irradiation gave results for proprietary resins that were not correlated with the results obtained by water storage. □ *Discoloration; dental materials; operative dentistry*

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Clinical studies have demonstrated a discoloring potential of restorative resins (10, 11). The discoloration may arise for a number of reasons, including an internal color change of the resinous material itself (16).

Many laboratory investigations have focused on the internal discoloration of restorative resins, and it is known that several factors are involved in the color forming process. It has been found that the color change of chemically cured materials is associated with the type (5–7) and quantity (5, 7) of amine involved in the polymerization. Further, the inhibitor has been found to play a role (9). In the above laboratory studies the color change was assessed by the human eye.

Besides amine and inhibitor it has been conjectured that the monomer content of BISGMA (14) and peroxide (3) may influence the internal discoloration.

Bowen & Argentar (5) observed less formation of color when flushing the test solutions with nitrogen or argon. This suggests the influence of oxygen on color formation.

Laboratory investigations of color stability are frequently performed by means of irradiation with UV-light (5–7, 18, 19). However, the introduction of UV-light absorbers into the commercial resins possibly restricts the validity of this test to experimental materials: the commercial resins may show only little discoloration upon exposure to UV-light, but may discolor markedly in the clinical situation due to simple oxidation.

It was the aim of the present work to investigate on a quantitative basis the factors that govern the color stability of restorative resins.

Materials and methods

The color stability was investigated on experimental and commercial composite resins. The method has previously been described in detail (4). It involved the measurement of the change in color resulting from a 1 month storage in water at 60°C. This color change is well correlated with the color change induced by a long-term storing in water at 37°C, and may therefore be assumed to be clinically relevant. The measurements were performed on disc-shaped test specimens. Except when investigating the effect of oxygen, atmospheric air had free access to the storage water. The color change was measured by means of a

Hunterlab D25-A colorimeter and recorded as ΔE; ΔE has been defined in an earlier publication (4).

The experimental resins were identical with respect to monomer and filler: the monomer consisted of 50 mol % BISGMA and 50 mol % TEGDMA, and the silanized filler was of the conventional type. The filler content was 75.0% by weight. The content of amine, benzoyl-peroxide, and inhibitor are specified below.

Seventeen brands of commercial resins were investigated. Of these, 15 brands have previously been listed (4). The two additional brands were Heliosit (Vivadent, Schaan, Liechtenstein; batch 670680) and Visio-Dispers (ESPE, Seefeld, W. Germany; batch GO 28).

The investigation was divided in several sections to be described in the following.

Experimental composite resins

The test specimens were prepared by mixing equal amounts of an amine containing paste (universal paste) with a benzoyl-peroxide (BPO) containing paste (catalyst paste). The amine contents and BPO contents mentioned below are given as percentage by weight of the monomer in the unmixed pastes. The BPO used contained 20% of water, the weight of which for practical reasons is included in the given contents of BPO. Unless otherwise stated, the inhibitor of the pastes was only that which was present in the monomer when received from the supplier.

Effect of the amount of amine and BPO

The amine was DEPT (*N,N*-diethanol-*p*-toluidine). The universal pastes contained 0.5, 1.0, 1.5, 2.0, 2.5 or 3.0% DEPT in the monomer. The catalyst pastes contained 0.25, 0.50, 1.0 or 2.0% BPO in the monomer. The investigated combinations between universal and catalyst paste will appear from the results. One group of specimens were polymerized without amine by heating the catalyst paste with 1% BPO to 100°C for 4 h.

Effect of the type of amine

Equimolar amounts of DEPT or DEBA (*N,N* - diethanol - 3,5 - di - tert - butyl - aniline) were used. The universal pastes contained 1% DEPT or 1.5% DEBA in the monomer. The catalyst pastes contained 0.25, 0.5 or 1.0% BPO in the monomer.

Effect of the amount of inhibitor

The inhibitor was MHQ (hydroquinone-monomethylether). The MHQ content of the monomer was 0.25, 0.50, 0.75 or 1.0‰ by weight. The universal pastes contained 2% DEPT and the catalyst pastes 1.5 or 2.5% BPO in the monomer.

Commercial composite resins

Effect of brand

The above-mentioned 17 brands were investigated. Eleven brands were chemically cured; six brands were cured by light.

Effect of pH and oxygen

Specimens were produced using a chemically cured resin. The color change was investigated after storing in 1) demineralized water, 2) water containing 1% by weight of acetic acid, or 3) water from which atmospheric oxygen had been removed. The oxygen was removed from the water by boiling for 5 min and flushing with nitrogen while cooling the water to the test temperature of 60°C. After introducing the test specimens into the water, the container was sealed by means of a slide fitting stopper and vacuum grease.

Effect of UV-light irradiation

Specimens were produced using two brands of chemically cured material. The color change was measured after storing in water at 60°C for 1 month or after a 24-h exposure to UV-light from a powerful UV-light source (Osram Ultra Vitalux, GUR 31) as described in the ADA Specification No. 27 (19).

For each of the above-mentioned sets of

experimental variables the color change was measured on three test specimens.

Results

The results are presented in Figs. 1–7. Each point (Figs. 1–3) or bar (Figs. 4–7) represents the mean of the results obtained with three test specimens. As will appear from the discussion, the standard deviation of this mean was estimated to equal 0.44 units (f = 15). This implies that two mean values 1.1 unit of ΔE apart are different from each other at the $p = 0.05$ level of statistical significance.

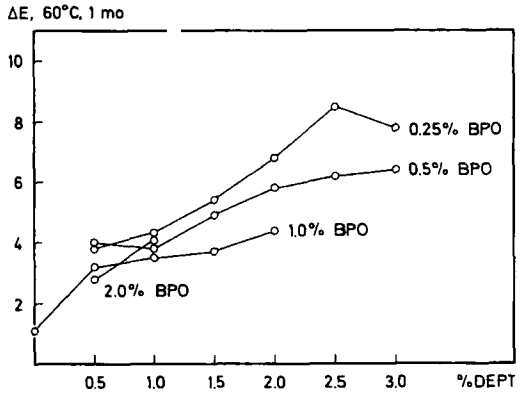

Fig. 1. Color change of experimental resins (ordinate) in relation to monomer content of DEPT in the universal paste. The monomer content of BPO (including 20% water) in the various catalyst pastes is stated in the diagram.

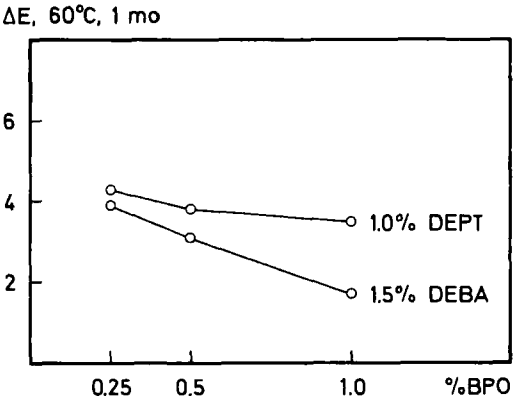

Fig. 2. Color change of experimental resins (ordinate) in relation to monomer content of BPO (including 20% (mol %) in the monomer of the mixed materials. The color change was corrected for variations in the amounts of DEPT and BPO.

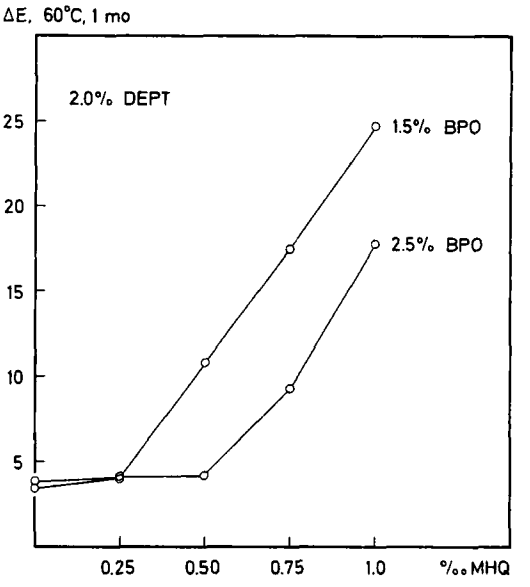

Fig. 3. Color change of experimental resins (ordinate) in relation to monomer content of MHQ. The monomer of the universal pastes contained 2% DEPT, and the monomer of the catalyst pastes contained either 1.5% or 2.5% BPO (including 20% water).

Effect of the amount of amine and BPO

The results are presented in Fig. 1. It appears that in general the color change increased with the amount of DEPT, but decreased with the amount of BPO. The specimens cured without amine showed the least color change.

Effect of the type of amine

The results can be seen in Fig. 2. The resins cured with DEBA were more color stable than the resins cured with equimolar amounts of DEPT. With 1% BPO the difference is significant at $p = 0.02$. As in Fig. 1, the color change decreased with increasing amount of BPO.

Effect of the amount of inhibitor

The results are presented in Fig. 3. At low concentrations of inhibitor the color change was virtually independent of inhibitor content, but above a critical point the color change was found to increase markedly with

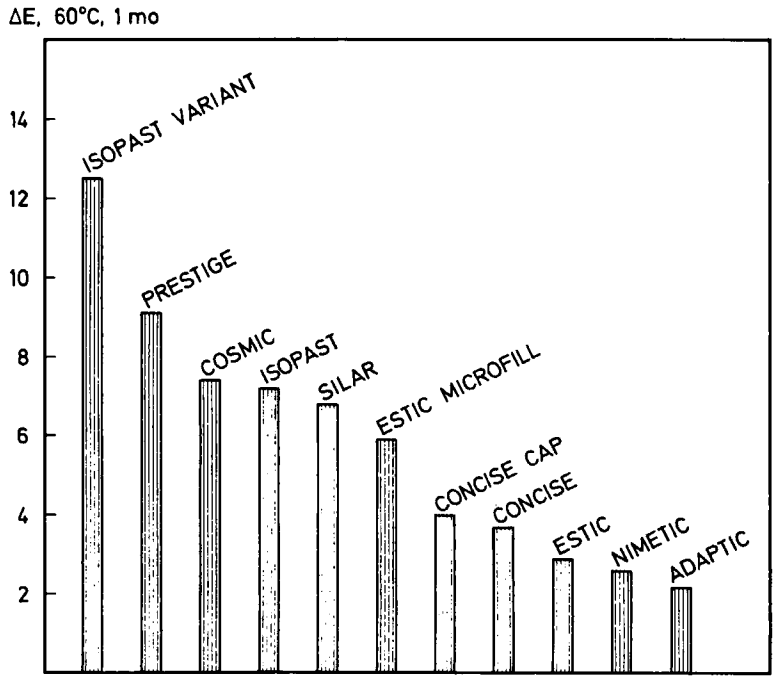

Fig. 4. Color change of chemically cured proprietary 1979 resins.

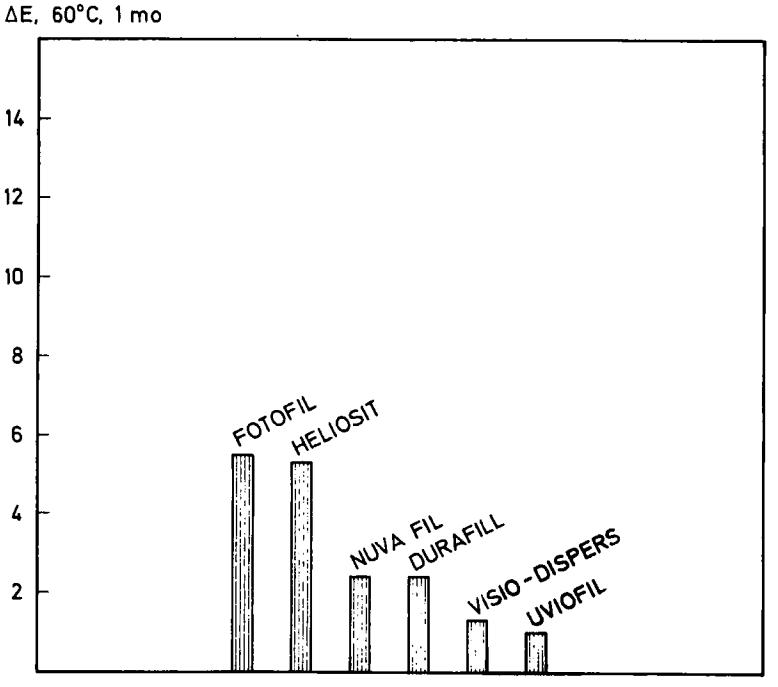

Fig. 5. Color change of light-cured proprietary 1979 resins.

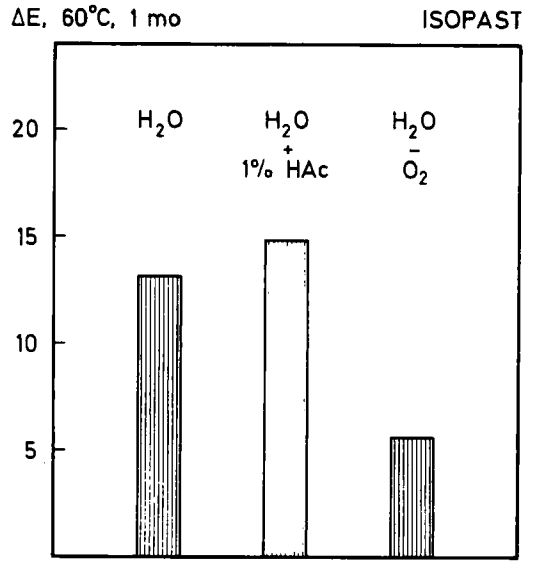

Fig. 6. Color change of a proprietary 1979 resin resulting from storage in three different media. To the left demineralized water was used, in the middle the water contained 1% acetic acid, and to the right the atmospheric oxygen had been removed from the storage water.

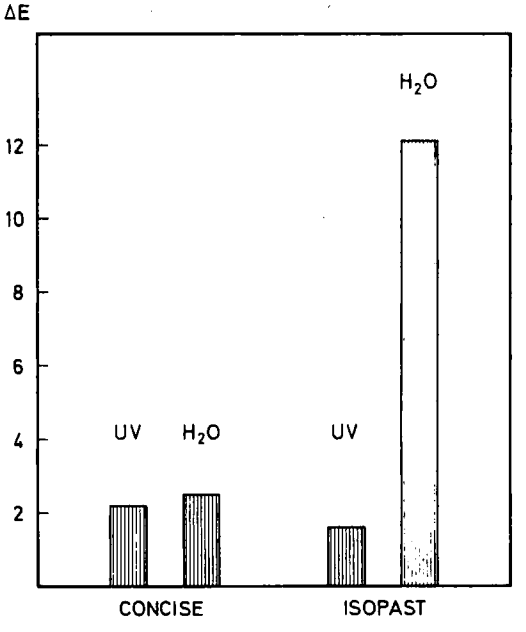

Fig. 7. Color change of two proprietary 1979 resins. For each material the column to the left represents the color change resulting from UV-light irradiation, and the column to the right the change induced by water storage.

the content of inhibitor. The concentration of inhibitor at the critical point increased with the amount of BPO.

Effect of brand

The color change of the chemically cured brands is presented in Fig. 4, and in Fig. 5 the results with the light cured brands are given. It appears that large differences occur between the individual brands. Taken as groups, the light cured materials were more color stable than the chemically cured materials ($p < 0.05$).

Effect of pH and oxygen

Fig. 6 shows that a reduction in pH had only little effect on color formation, but that color change was greatly reduced when the oxygen had been removed from the storage water. This demonstrates the oxidizing nature of the color forming process.

Effect of UV-light irradiation

The results are shown in Fig. 7. The color change provoked by UV-light was rather small for both materials, whereas a large difference occurred as a consequence of water storage.

Discussion

It appears from the above that the color change of restorative resins is affected by several factors.

The results presented in Fig. 1 (except for the heat cured case) was treated statistically by means of regression analysis (8). The dependent variable was ΔE, and as independent variable the quantity $A/(k + B)$ was used. In the latter expression A represents the amount of amine, and B the amount of pure BPO in percentage by weight of the monomer in the mixed pastes. The constant, k, was fitted in such a manner that the coefficient of correlation assumed its maximum value. At $k = 0.1$ a maximum value of $r = 0.964$ occurred. This value differs from zero at the $p = 0.001$ level of statistical sig-

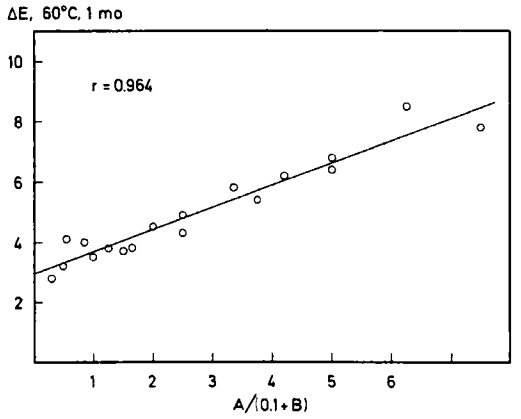

Fig. 8. Color change of experimental composite resins (ordinate) in relation to A/(0.1 + B). A represents the percentage of DEPT, and B the percentage of BPO in the monomer of the mixed pastes.

nificance. The standard deviation about the regression line was 0.44. The relationship between ΔE and $A/(0.1 + B)$ is presented in Fig. 8. It appears that the color change does not depend on the absolute amount of amine but is approximately given by the ratio between amine and BPO. The demonstrated relationship may be explained if it is assumed that the quantity on the abscissa is a measure of the amount of amine present in the material after the reaction with BPO.

As mentioned in the introduction, it is known that the type of amine affects the color stability of restorative resins. DEPT and DEBA have been identified in modern composite resins (2). The good color stability of the DEBA polymerized resins shown in Fig. 2 and of Nimetic (2) shown in Fig. 4 is probably imparted by the special structure of the DEBA molecule: the bulky, tertiary butyl groups present a steric hindrance for the color forming oxidizing attack on the benzene ring of the amine.

The influence of the amount of inhibitor presented in Fig. 3 may be explained as follows: at low concentrations the inhibitor is almost completely consumed during polymerization of the material. By these processes the material undergoes a change in color, influencing the initial color of the material. However, the reacted inhibitor is no longer chromogenic and does not affect the color stability of the polymerized resin. At high concentrations the inhibitor is incompletely reacted during polymerization; hence, the remaining, unreacted inhibitor may cause a change of color in the polymerized resin. The higher the concentration of BPO, the more inhibitor will react during polymerization, and the less inhibitor will remain in the polymerized resin. This implies that the higher the concentration of BPO, the less inhibitor-induced color change will occur in the set material, as depicted in Fig. 3.

Figs. 4 and 5 show less discoloration in the light cured than in the chemically cured materials. This finding is in agreement with a number of clinical studies (9, 10, 12, 15, 17).

The reason for this is probably to be found in the fact that chemically cured materials are made to polymerize by means of a chromogenic compound, i.e. an aromatic, tertiary amine. On the other hand, the light cured materials are polymerized by a mechanism in which aromatic amines are not necessary.

In Fig. 8 the relationship between color change in experimental resins and $A/(0.1 + B)$ is demonstrated. A similar relationship was investigated using the results obtained with the commercial materials. Of the 11 brands shown in Fig. 4, 10 brands are polymerized by DEPT (2). These brands have earlier been analyzed quantitatively with respect to monomer content of DEPT, BPO and BISGMA (1–3; Asmussen, unpublished results). The results of these analyses are summarized in Table 1. On this basis three dimensional regression analysis was carried out (8). ΔE was taken as the dependent variable, and as independent variables were used the content of BISGMA and the quantity $A/(k + B)$ previously described. The constant k was fitted in such a manner that the residual variation was minimized. As was the case with the experimental resin, this occurred at $k = 0.1$. Both regression coefficients were found to differ from zero at the $p = 0.01$ level of statistical significance. The two variables 'explained' 80% of the total variation. Fig. 9 shows the relationship between color change and content of BISGMA, after correcting the color change for variations in the content of amine and peroxide. As can be seen, the color

Table 1. Content of BISGMA, DEPT and BPO in the monomer of proprietary resins after mixing. In the column to the right the color change is given

	BISGMA (mol %)	DEPT (% w/w)	BPO (% w/w)	ΔE 60°C, 1 month
Adaptic	65	0.91	0.66	2.2
Concise	64	1.23	0.44	3.7
Concise Cap	53	0.56	1.19	4.0
Cosmic	25	0.80	1.33	7.4
Estic	40	0.42	1.23	2.9
Estic Microfill	22	0.86	0.88	5.9
Isopast	0	0.39	0.37	7.2
Isopast Variant	0	0.86	0.47	12.5
Prestige	42	1.16	0.16	9.1
Silar	39	1.99	0.63	6.8

change decreases with increasing amount of BISGMA in the monomer. This finding is contrary to the suggestion that color stability should be reduced with increasing amounts of BISGMA because of the reduction in the degree of polymerization (13, 14). Only tentative explanations of the relationship in Fig. 9 can be proposed.

Fig. 6 demonstrates the oxidizing nature of the color forming process. It is not known to which extent the oxygen concentration on the surface of a restoration may be reduced by the presence of the pellicle or by plaque.

The results depicted in Fig. 7 show that the color change resulting from UV-light irradiation is not correlated with the color change induced by water storage. As mentioned in the introduction, this is no doubt due to the presence of UV-absorbers in commercial resins. The results of Fig. 7 imply that tests for color stability using UV-light are not reliable with commercial resins.

In conclusion, attention should be given to the fact that the present investigation was commenced in 1979. As a consequence the composition of the commercial composites may well have been altered since the measurements of this study were conducted. This means that the values obtained may not be representative for today's brands.

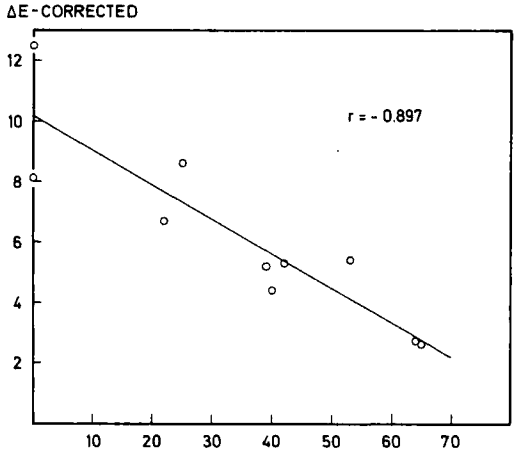

Fig. 9. Color change of DEPT-polymerized proprietary resins (ordinate) in relation to the content of BISGMA (mol %) in the monomer of the mixed materials. The color change was corrected for variations in the amounts of DEPT and BPO.

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Received for publication 9 September 1981