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on

TERTIARY AROMATIC AMINE ACCELERATORS WITH MOLECULAR WEIGHTS ABOVE 400

by

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U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

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Synopsis

With the proper ring substituents, tertiary aromatic amines with large substituents on the nitrogen atom can be effective accelerators in free radical polymerization. Resistance to discoloration appears to be primarily a function of the substituents on the aromatic ring of the amine, while the rate of polymerization is dependent on both the alkyl substituents on the ring and the groups attached to the nitrogen atom.

TERTIARY AROMATIC AMINE ACCELERATORS WITH MOLECULAR WEIGHTS ABOVE 400

Most of the presently-available composite restorative materials contain an amine-peroxide initiator system to polymerize their methacrylate monomers. These amine-peroxide systems have certain disadvantages including a tendency to discolor the resin or composite filling material,[1] and in some cases, the working and hardening times[2] of the materials may not be optimum for the dentists' requirements.

The liquids used in these composite materials contain very large proportions of crosslinking dimethacrylate monomers[3,4] and are relatively viscous. These high molecular weight viscous dimethacrylates polymerize much more rapidly than do less-viscous non-crosslinking monomers such as methyl methacrylate. This is due to the Trommsdorff,[5] auto-acceleration, or gel effect,[6] attributed to lessened translational mobility (and concurrent termination reactions) of growing polymer radicals, with increasing viscosity. Therefore, there is less need for rapid-acting initiators.

In other words, a slower release of free radicals may well give a longer working time and still give the hardening time that is desired.

In order to get adequate working time with these quick-hardening resin systems, one alternative has been to decrease the concentration of fast-acting amine accelerators. This low initial concentration of amine may run the risk of what has been called "dead end" polymerization,[7] that is, the depletion of amine accelerator (and initiator free radicals) before the conversion has reached its maximum extent; if so, the ultimate chemical and physical properties would suffer.

Another alternative has been to increase the amount of inhibitor above the minimal amount required for storage stability. This would increase the working time at the cost of increased discoloration, in the case of some inhibitors,[8] and possibly at the cost of increased polymerization inhibition at surfaces that are exposed to air (including bubbles of air that have been entrapped within the material itself during mixing and placement), if it is assumed that the peroxy

radical R-O-O· (formed by addition of O_2 to the growing polymer radical) is capable of initiating polymerization of the methacrylate monomer,[9] and that the peroxy radical is inactivated by interaction with "excess" inhibitor.

The foregoing suggests that steric hindrance of an amine accelerator may be useful in slowing down the release of free radicals, and thus the rate of polymerization, at equal or higher concentrations of amine (peroxide and stabilizers being maintained at optimum concentrations), when compared to the amine accelerators currently being used.

If higher molar concentrations of such slow-acting, but efficient amine accelerators were used, it would give a more prolonged release of free radicals, but would put more demand on the inherent color stability of the amine and other ingredients in the formulation.[8]

There has been convincing evidence of various degrees of pulpal inflammatory response to the use of resin and composite restorative materials.[10,11] It has not yet been

shown which ingredients in these formulations are primarily responsible for the inflammation. Since the lower-molecular-weight aromatic amines are capable of skin penetration[12-14] and are systemically poisonous,[13,14] it is conceivable that the amine accelerators presently used in direct filling resins and composites might be contributing to pulpal irritation.

Accordingly, for the last few years, amine accelerators have been investigated in the Dental Research Section at the National Bureau of Standards with objectives of: increased understanding of the factors that reduce discoloration, improved polymerization-initiating characteristics, and reduced toxicity.[8,15] The extant and innovated hypotheses bearing on these structure-property relationships required the synthesis of a number of aromatic amine compounds, since such compounds were not available. Most of this report involves only the synthesis of certain amine accelerators and a few preliminary results obtained with them. Factors bearing on the tendency to discolor have already been reported.[8]

Although no evaluations of toxicity have yet been made on these compounds, the underlying provisional hypothesis is that the toxicity of amine accelerators (as well as the other ingredients in the formulations) will be inversely related to the molecular weight, other things being equal.[12] Furthermore, increasing the bulkiness of a molecule (as determined by its shape in distinction to its molecular weight) may reduce its permeability.[16]

There is evidence that tissue penetration by organic compounds goes through maxima (depending on the nature of the body tissues) as the oil/water partition coefficient is varied between its limits.[12,17] Since the physical properties of highly hydrophilic organic materials might be adversely affected by the aqueous oral environment, the water-insoluble end of this oil/water partition coefficient spectrum would appear to be required. Substituents allowing for biotransformation and excretion by the human body should be considered.[18]

The feasibility of utilizing the foregoing considerations depends on the extent to which bulky substituents on the aromatic

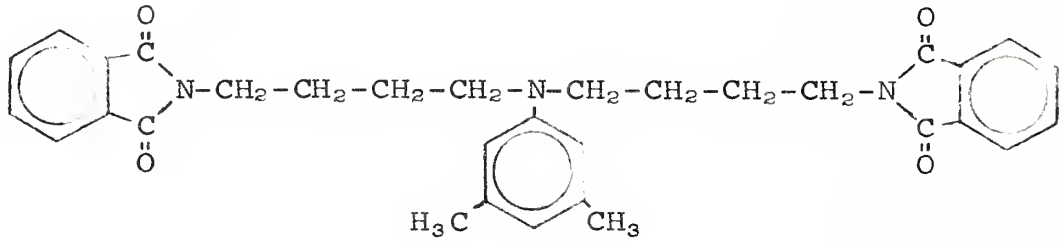
amines sterically hinder and electronically alter their interaction with peroxide initiators. In a previous study it became apparent that steric hindrance of the nitrogen atom of tertiary aromatic amines having suitable ring substituents is not as much a problem as had previously been expected.[15] For example, in one composite formulation in which the dimethacrylate monomer liquid contained one percent of N,N-didodecyl-p-toluidine (DPT), the hardening time at room temperature was about four minutes.

With this encouragement, the present study was undertaken to investigate tertiary aromatic amine accelerators containing effective ring substituents such as methyl groups in the 3 and 5 positions,[8] and also large, bulky nitrogen substituents of such a nature that they would not only raise the molecular weight appreciably but also would yield crystallizable compounds having melting points above room temperature. This latter feature would allow for purification of these compounds by crystallization; consequently, production, product quality control, and storage stability might be facilitated.

Materials and Methods*

Most of the materials that were used are listed in Table 1. They were used as received.

SYNTHESIS OF BPX·-The first such compound synthesized was presumed to be N,N-bis(4-phthalimidobutyl)-3,5-xylidine (BPX):



(BPX)

This compound was prepared by combining 4.3 ml (4.0 gm, 0.033 mol) of 3,5-xylidine, 23.3 gm (0.082 mol) of N-(4-bromobutyl)phthalimide, 6.5 gm (0.077 mol) sodium bicarbonate, and 140 ml of distilled water in a 250 ml round bottom flask, and refluxing for about 18 hours. A

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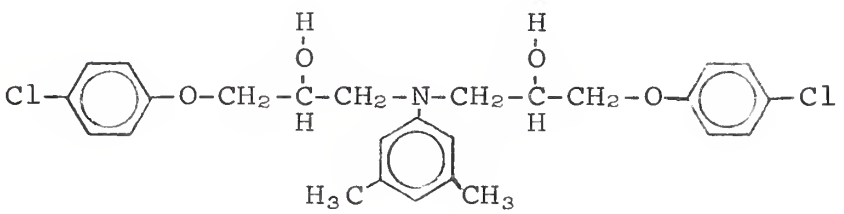
* Certain commercial materials and equipment are identified in this paper to specify adequately the experimental procedure. In no instance does such identification imply recommedation or endorsement by the National Bureau of Standards or that the material or equipment identified is necessarily the best available for the purpose.

yellow precipitate formed, which was recrystallized from ethanol and ethanol-water. The bright yellow crystals had a melting point of 119-120°C. The yield was 86% of theoretical (based on the 3,5-xylidine).

SYNTHESIS OF BCX.-The next amine accelerator that was synthesized was N,N-bis(3-p-chlorophenoxy-2-hydroxypropyl)--3,5-xylidine, F.W. 490, (BCX):



(BCX)

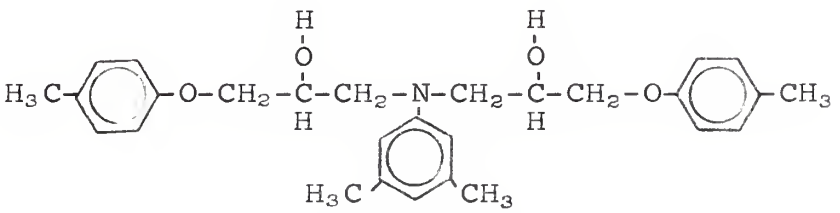
This compound was prepared in a 500 ml 3-necked round-bottom flask equipped with a dropping funnel, reflux condenser and heating source. To 15.4 ml (15 gm, 0.124 mol) of 3,5-xylidine was added 44 ml of methanol in the flask. Water was added to the stirred solution to the cloud point (when 40 ml of water had been added, the solution became slightly turbid). After the xylidine solution had been

heated to refluxing, a solution of 50 gm (0.274 mol) of p-chlorophenyl-2,3-epoxypropyl ether dissolved in 200 ml of methanol (forming what appeared to be a nearly saturated solution) was added dropwise from a dropping funnel over a period of about five hours. The combined solutions were refluxed for an additional six hours with stirring. The solvents were then evaporated under partial vacuum, leaving an off-white solid. Recrystallization from acetone yielded several fractions of white crystals, the total amounting to 62% of the theoretical yield (based on xylidine). Since the reaction product would be expected to consist of three stereoisomers (meso and d,l),[20] the higher melting fraction was recrystallized from acetone yielding 15.9 gm of white, crystalline material having a melting point of 180-181°C. The elemental analysis for the high-melting fraction, $C_{26}H_{29}NCl_2$ was calculated: C, 63.7; H, 6.0; N, 2.9; and Cl, 14.5%; found: C, 63.6; H, 6.0; N, 2.9; and Cl, 14.5%.

The lower-melting fraction was recrystallized several times from 9:1 methanol-water, yielding 6.2 gm of colorless

crystals with a melting point of 126-129°C; its elemental analysis was: C, 64.2; H, 6.2; N, 2.9; and Cl, 14.5%.

SYNTHESIS OF BTX·-As will be seen, the high-melting fraction of the foregoing compound had limited solubility in the dimethacrylate monomer formulation; consequently, this suggested the synthesis of a similar but lower-melting compound, namely N,N-bis(3-p-tolyloxy-2-hydroxypropyl)-3,5-xylidine, F.W. 450, (BTX):

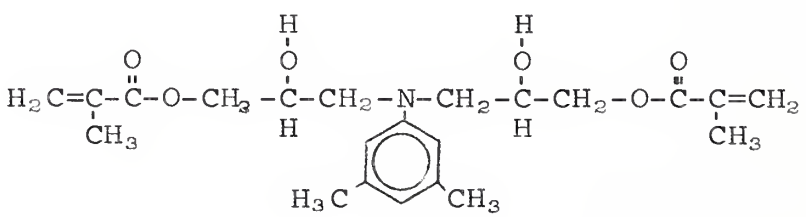


(BTX)

In a 500 ml, 3-necked round-bottom flask equipped with a dropping funnel, reflux condenser and heating equipment, were mixed 15.4 ml (15 gm, 0.124 mol) of 3,5-xylidine, 45 ml methanol and enough water (40 ml) to just bring about a perceptible turbidity. A mixture of 41.3 ml (44.9 gm, 0.274 mol) of 1,2-epoxy-3-(p-methylphenoxy) propane and 200 ml of methanol were placed in the dropping funnel. After the xylidine solution had been heated to reflux temperature, the epoxy solution was added dropwise over a period of 2.5 hours, and reflux was continued for an additional hour.

A colorless precipitate formed on cooling. The solvents were removed under partial vacuum and mild heating. Two fractions were obtained after several recrystallizations from acetone-water: 12.5 gm melting at 102.5-106°C and 21.8 gm melting at 146-148°C; together, these constituted 61% yield (based on the xylidine). The results of an elemental analysis of the higher-melting fraction were: calculated: C, 74.8; H, 7.9; N, 3.1; found: C, 75.2; H, 7.9; and N, 3.0%. The elemental analysis on the lower melting fraction was: C, 75.1; H, 7.9; and N, 3.2%.

SYNTHESIS OF BMX·-Another somewhat similar compound that had previously been synthesized was N,N-bis(2-hydroxy-3-methacryloxypropyl)-3,5-xylidine, F.W. 405 (BMX):



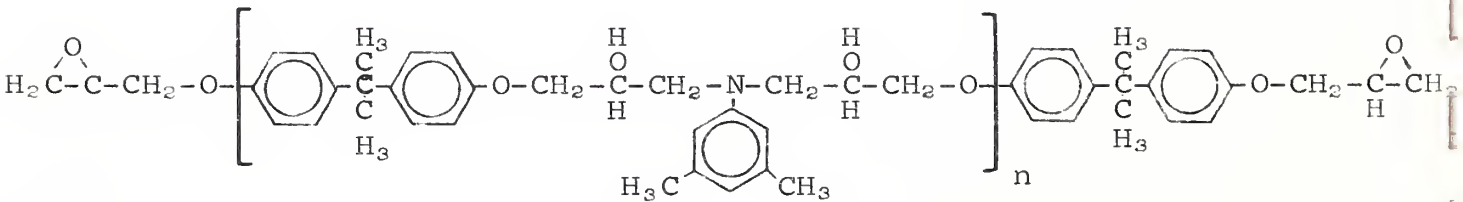
(BMX)

It was prepared in a 2,000 ml, 3-necked round-bottom flask equipped with a stirrer, condenser, thermometer, and hot water

bath. The following were added to the flask: 112 ml (109 gm, 0.90 mol) of 3,5-xylidine, 248 ml (266 gm, 1.87 mol) glycidyl methacrylate, 9.8 ml water, 0.571 gm of an acid-catalyzed condensation product of p-hydroxybenzoic acid and 2-hydroxyethyl methacrylate (MHB),[19] 0.272 gm of di-t-butyl sulfide, and 0.206 gm of butylated hydroxytoluene (BHT). The latter three compounds were added to prevent (premature) polymerization of the methacrylate groups. The mixture was stirred at 70 ± 10°C for about 8 hours until the reaction appeared to be complete as evidenced by a plot of the refractive index against reaction time. When the index of refraction had reached a plateau, a small aliquot was mixed with reinforcing filler containing 0.52% benzoyl peroxide plus 0.85% lauroyl peroxide; the thin mix hardened in 2.0 minutes at room temperature. The rapid hardening gave supportive evidence that there was little if any residual primary or secondary aromatic amine remaining which would act as a free-radical polymerization inhibitor.[2] The water was removed with vacuum, stirring and slight

warming, leaving a clear, viscous (but pourable) yellow liquid having a refractive index n_D^{23} of 1.528. More of the stabilizers (polymerization inhibitors) were added (0.608 gm of MHB; 0.273 gm of di-t-butyl sulfide, and 0.365 gm of butylated hydroxy toluene), and the hardening time of this liquid mixed with the same powder was thus increased to about 9.5 minutes at room temperature. An attempt to obtain a crystalline product by cooling a saturated ethanol-water solution of the product was unsuccessful. An elemental analysis of the product calculated for BMX was: C, 65.2; H, 7.7; N, 3.5%. Found: C, 64.7; H, 7.8; and N, 3.3%.

SYNTHESIS OF PBX·--The polymeric adduct (addition reaction product) of the diglycidyl ether of bisphenol A and 3,5-xylidine was prepared:



(PBX) n = 1 to ∞, with an average of 2; where n = 2, F.W. = 1262. In a 1,000 ml round-bottom flask equipped with a reflux

condenser and heating equipment, 104.4 gm (0.31 mol) of the diepoxide D.E.R.® 332, 24.8 ml (24.2 gm, 0.20 mol) of 3,5-xylidine, and 500 ml of methanol were mixed, and two poly-(tetrafluoroethylene) pellets were added to prevent bumping. The mixture was refluxed for 12 hours, during which time the clear solution became turbid. After cooling and settling, the supernatant was decanted off and methanol was removed from the residue under partial vacuum, yielding a clear yellow amorphous product. This product (PBX) was soluble in acetone and in the dimethacrylate liquid (Table 2).

SPECIMEN PREPARATION.--The various aromatic amines were formulated with a liquid dimethacrylate monomer as given in Table 2. These liquids were then mixed with a powder containing 0.85% benzoyl peroxide dispersed in an inorganic siliceous filler treated with 3-methacryloxypropyl-trimethoxysilane, as described previously.[8,15] The filler made up about 70% of the mixed material. The methods of mixing, measurement of hardening times, comparisons of relative color formation and discoloration under the sun lamp for 24 hours were also the same as described in a prior report.[15]

Results and discussion

HARDENING TIMES.--The hardening times were determined at room temperature (22.5 ± 1.0°C) three times for each amine-containing formulation; the results are given in Tables 3 and 4.

Useful hardening times of about 3 to 4 minutes can be obtained by the use of each of these aromatic amine accelerators providing that the proper concentration of amine, inhibitor (BHT or other stabilizer) and peroxide are utilized. However, the limited solubility of the high-melting fraction of BCX in this particular monomer formulation restricted the concentration to low values giving hardening times that were too long for practical purposes. High-melting compounds tend to be less soluble in a given solvent, and higher-molecular-weight solvents tend to dissolve less of a given solute than do low-molecular-weight solvents, other factors being similar. The monomers,[4] which are the solvents in these cases, have formula weights of 390.

In agreement with evidence previously reported,[15] the hardening times appeared to be somewhat longer for formulations containing amines having bulky nitrogen substituents in contrast to those having small methyl groups attached to the nitrogen atom. However, it is important to note that hardening times are only moderately increased (at equimolar concentrations). If the bulky groups (e.g., rings) had been connected to the nitrogen atom by linear chains of less than four atoms, the effects of steric hindrance might have been greater.

It may well be that the efficiency (number of free radicals produced per mole) of the amine accelerator is not reduced, but that only the rate of interaction with benzoyl peroxide is reduced (due to moderate steric hindrance). Such slower-acting but efficient amines, used at higher concentrations, might result in a lower ratio of hardening time to working time and in a more rapid increase in desirable physical properties following hardening because of a

higher concentration of amine accelerator in the later stages of polymerization. In other words, such amines might provide for "snap-hardening" characteristics desired by dentists.

In a plot of rotational (T_R) versus linear (T_L) hardening times, there was a nearly linear relation such that, as a first approximation: $T_R = 1.1\ T_L + 0.1$. Plots of T_R versus T_L might be useful in evaluating the so-called "snap-hardening" characteristics of direct filling resins and composites.

There was some evidence that certain liquid formulations that had aged resulted in mixes with slightly longer hardening times than the same solutions used immediately after they had been prepared. The reason for this is not presently understood, but should be determined.

The effect of BHT on hardening times is shown in Figure 1.

DISCOLORATION--In the previous study,[15] an ultraviolet absorber was included in the liquid formulation. This resulted in no

color change for DMSX (referred to as: N,N-dimethyl-sym-m-xylidine; N,N-dimethyl-3,5-xylidine; N,N-dimethyl-3,5-dimethylaniline, or N,N,3,5-tetramethylaniline by various sources) on exposure to the sun lamp. In the present study, the ultraviolet absorbers were not included so as to enable a more critical comparison of the amine accelerators with respect to discoloration by exposure to the sun lamp.

In a careful comparison of the colors of the hardened specimens and their color change when exposed to the sun lamp for 24 hours, there was no perceptible difference between formulations containing 0.275% DMSX and those containing equimolar concentrations of the high-melting fraction of BTX, the low-melting fraction of BCX or BMX, each containing 0.159% of BHT.

There was little if any variation in color or susceptibility to discoloration under the sun lamp with varying amounts of BHT, DMSX, BCX, and BTX, within the small range of concentrations used in this study.

The specimens prepared with the amorphous, polymeric PBX had very slightly more coloration (a barely perceptible pinkish tint) and discoloration when exposed to the sun lamp than did specimens with equimolar concentrations of the

other amines. Since it was used without re-precipitation or other purification, impurities may have contributed to specimen discoloration.

Although the bright yellow crystalline BPX was sufficiently soluble in the monomer liquid and was an effective polymerization accelerator, it imparted a yellow coloration to the solutions and specimens in which it was used. The yellow color of the composites produced with BPX was darker than the typical yellow of natural teeth, although no darker than some teeth. The color change induced by exposure to the sun lamp appeared to be no greater than the color change of specimens utilizing any of the other amines (described here) in equimolar proportions.

The bright yellow color of BPX was assumed to be the result of charge transfer complex formation between the electron-rich aromatic amine moiety and the electron-deficient phthalimide groups. This hypothesis was supported by the

observation that when clear, colorless 95% ethanol solutions of DMSX

or of N,N-dimethyl-p-t-butyl-aniline (DMBA) were mixed with a colorless solution of N-(4-bromobutyl)phthalimide, a yellow solution formed; when a solution of DMBA was mixed with one of p-chlorophenyl glycidyl ether, the mixture remained colorless.

Conclusions

Relatively high-molecular-weight polymerization accelerators can be prepared by the addition reaction of certain ring-substituted anilines and glycidyl ethers or esters. Some of these have melting points above room temperature and can be purified readily by crystallization. Although it has not been demonstrated, there are theoretical reasons for expecting such high-molecular-weight accelerators to be less able to penetrate body tissues and thus be less toxic than the tertiary aromatic amine accelerators that are being used in commercial dental composites and direct filling resins. There may also be advantages in polymerization kinetics.

Although certain limitations were noted, [for example, the aniline derivative having phthalimide substituents (BPX) appeared to give a colored charge-transfer complex, and the highest-melting amine (the BCX melting at 180-181°C) was not sufficiently soluble in the monomer formulation being investigated to be effective] practical, useful hardening times of about 3 to 4 minutes can be obtained by the use of most of these aromatic amine accelerators providing that the proper concentration of amine, inhibitor (BHT or other stabilizer) and peroxide are used.

TABLE 1

MATERIALS USED

Material	Grade	Source
3,5-Xylidine;(3,5-dimethylaniline; sym-m-xylidine)	Undesignated	Naftone, Inc.
N-(4-Bromobutyl)phthalimide	Practical	J. T. Baker Chem. Co.
Methanol	A.C.S.	Fisher Scientific Co.
p-Chlorophenyl-2,3-epoxypropyl ether	97-100%	Aldrich Chem. Co., Inc.
1,2-Epoxy-3-(p-methylphenoxy)propane	Lot # 0316; product # 01-60170-01; undesignated	PCR, Calgon Corp.
Acetone	Reagent	Allied Chemical
Glycidyl methacrylate	Commercial	American Aniline & Extract Co., Inc.
MHB (nominally, 2-Methacryloxyethyl-p--hydroxybenzoate)	Undetermined	Synthesized[19]
Di-t-butyl sulfide	95-99%	K & K Laboratories, Inc.
BHT (Butylated hydroxytoluene)	Food grade	Eastman Kodak Co.
Diglycidyl ether of bisphenol A	D.E.R.® 332	Dow Chemical Co.

Table 1 (continued)

MATERIALS USED

Material	Grade	Source
Benzoyl peroxide	96% (min)	Wallace & Tiernan, Inc.
Lauroyl peroxide	95% (min)	Wallace & Tiernan, Inc.
3-Methacryloxypropyl-trimethoxysilane	A-174	Union Carbide Corp.
DMSX (N,N,3,5-tetramethylaniline)	Reagent	Eastman Kodak Co.
DMBA (N,N-dimethyl-p-t-butylaniline)	Undetermined	Synthesized[15]

TABLE 2

LIQUID DIMETHACRYLATE RESIN FORMULATIONS USED FOR ASSESSING POLYMERIZATION ACCELERATORS

%	Compound	Source
47	Bis(2-methacryloxyethyl)isophthalate	The Epoxylite Corp.*
38	Bis(2-methacryloxyethyl)phthalate	The Epoxylite Corp.*
15	Bis(2-methacryloxyethyl)terephthalate	The Epoxylite Corp.*
As given in Tables 3 and 4	DMSX or equimolar weight of one of the other aromatic amines for comparison	Given in Table 1
As given in Tables 3 and 4	Butylated hydroxytoluene (Tenox® BHT; food grade)	Eastman Kodak Co.

* Custom syntheses[4]

TABLE 3

HARDENING TIMES, AS AN INDICATION OF

POLYMERIZATION-ACCELERATING EFFECTIVENESS

% BHT	Equimolar Concentrations of Amines	Linear Hardening Times*	Rotational Hardening Times*
		minutes	minutes
0.004	1.81% BCX (low-melting fraction)	<1.0†	1.25†
0.004	2.23% PBX	0.92(0.14)‡	1.42(0.14)‡
0.004	1.66% BTX (high-melting fraction; almost all dissolved)	2.00(0.00)	2.25(0.00)
0.142	1.81% BCX (low-melting fraction)	2.17(0.14)	2.58(0.14)
0.220	0.55% DMSX	2.58(0.14)	3.00(0.00)
0.159	1.81% BCX (low-melting fraction)	2.83(0.14)	3.08(0.14)
0.220	1.93% BPX	3.42(0.14)	3.83(0.14)
0.220	1.81% BCX (low-melting fraction)	3.67(0.29)	4.25(0.43)
0.129	2.23% PBX	3.83(0.14)	4.42(0.14)
0.129	2.23% PBX (aged solution)	4.58(0.14)	5.00(0.24)

* Each hardening time (as described and defined previously[15]) is the average of 3 measurements, each to the nearest 0.25 minutes, determined at room temperature; the times in parentheses are the standard deviations as estimated by

$$s = \sqrt{\frac{n\Sigma x^2 - (\Sigma x)^2}{n(n-1)}}$$

where x is the measured value and n equals 3, the number of measurements.

† Hardening time of a single measurement made with an extra-thin mix.

‡ Thin mix.

TABLE 4

HARDENING TIMES, AS AN INDICATION OF

POLYMERIZATION-ACCELERATING EFFECTIVENESS

% BHT	Equimolar Concentrations of Amines	Linear Hardening Times*	Rotational Hardening Times*
		minutes	minutes
0.159	0.275% DMSX (fresh solution)	2.67(0.14)	3.00(0.00)
0.159	0.275% DMSX (solution aged 11 weeks)	3.42(0.29)	3.92(0.14)
0.159	0.905% BCX (low-melting fraction)	3.92(0.52)	4.33(0.63)
0.159	0.83% BTX (low-melting fraction)	4.92(0.29)	5.42(0.29)
0.004	0.905% BCX (high-melting fraction partly dissolved)	5.08(0.14)	5.92(0.14)
0.159	0.83% BTX (high-melting fraction)	5.83(0.38)	6.42(0.29)
0.159	0.747% BMX	6.00(0.43)	6.58(0.29)
0.220	0.275% DMSX	6.83(0.29)	7.58(0.29)
0.159	0.83% BTX (high-melting fraction; aged solution)	7.50(0.25)	8.33(0.38)

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Figure 1: Semi-logarithmic graph of the relationship between linear O---, and rotational ●—— hardening times in minutes (test method described in ref. 15) of composites (each containing 1.81% of the low-melting fraction of BCX) and varying amounts of the stabilizer butylated hydroxytoluene (BHT) as the sole compositional variable. The starred point is a single determination; the other points represent averages of three measurements each.

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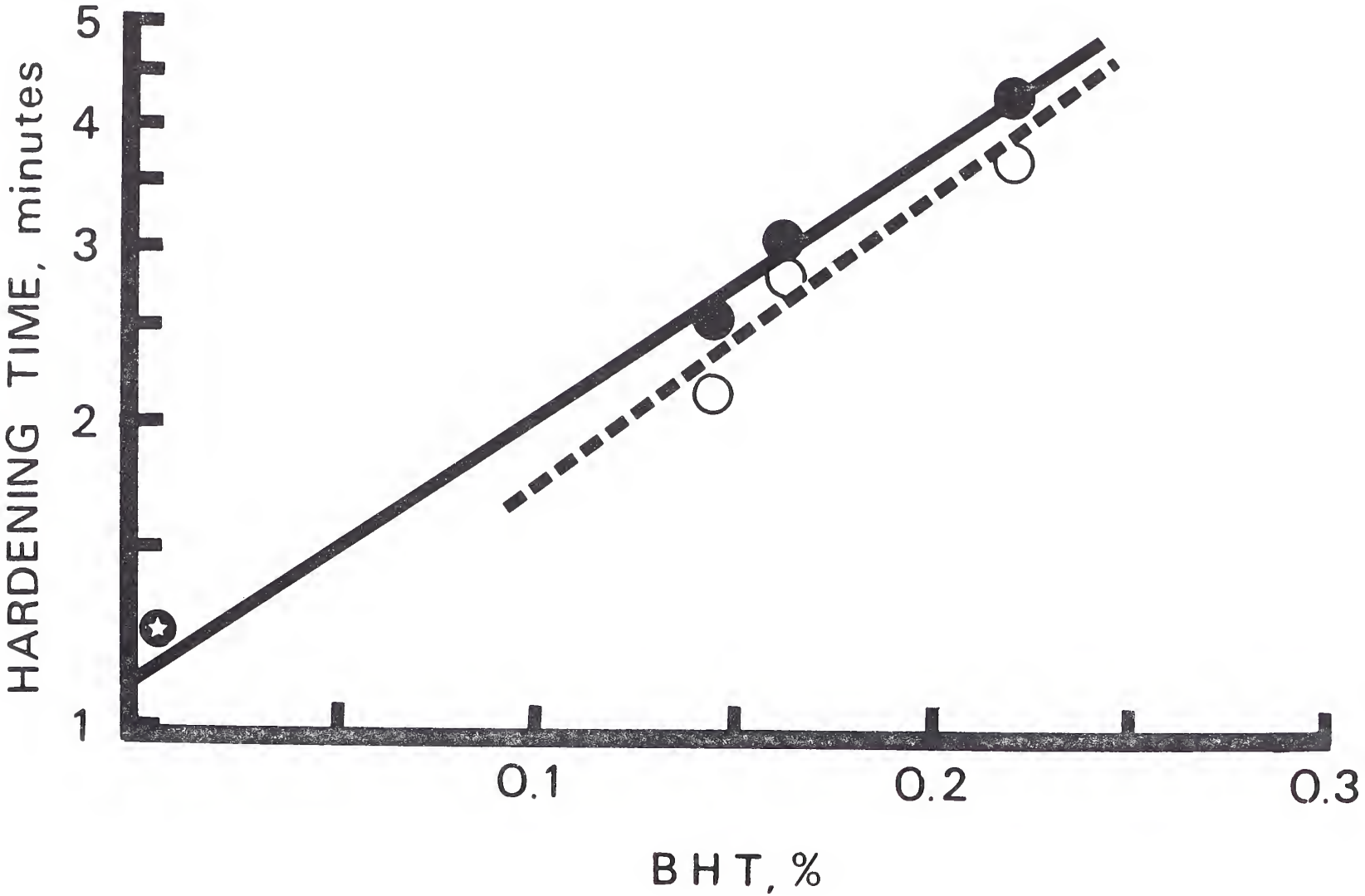

fig 1

Pendaflex

Esselte

R152 1/3 RED 10% P4