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Effects of antioxidants and the solid component on the thermal stability of polyol-ester-based thermal pastes

Yasuhiro Aoyagi · D. D. L. Chung

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Abstract The thermal stability of polyol-ester-based thermal pastes is evaluated by weight loss, viscosity and thermal contact conductance measurements. A high degree of thermal stability has been attained by using a half-hindered phenolic primary antioxidant and a thiopropionate secondary antioxidant. By using either carbon black or boron nitride particles as the solid component, a thermally conductive paste with a high degree of thermal stability has been attained. The antioxidants cause the residual weight (excluding the solid component) after oven aging at 200 °C for 24 h to increase from 36 to 97 wt.%. They cause the viscosity not to increase upon heating and they reduce the thermal cracking tendency. They do not affect the thermal contact conductance measured across mating surfaces that sandwich the paste. The use of a fully-hindered phenolic primary antioxidant is less effective. Both carbon black and boron nitride serve as antioxidants in the presence of either primary antioxidant or secondary antioxidant at 200 °C, though, in most cases, they degrade the thermal stability in the presence of both primary and secondary antioxidants, particularly at 220 °C. Below 180 °C and in the presence of primary and secondary antioxidants, boron nitride is particularly effective in promoting the thermal stability. Boron nitride paste shows an estimated lifetime of 19 years at 100 °C, compared to 1.3 years for the carbon black paste, and 0.10 year for commercial polyol-ester-based Arctic Silver 5. Carbon black paste has a lower tendency for cracking after heating than boron nitride paste, due to the low volume fraction of the solid component.

Introduction

Thermal interface materials (TIMs) are materials that are applied to the interface between a heat source and a heat sink in order to improve the thermal contact. The surface of a heat source or a heat sink is never perfectly smooth, and the air pockets between the mating surfaces decrease the heat flow. Therefore, a good thermal contact is necessary for heat to flow effectively from the heat source to the heat sink. TIMs usually involve pastes, which are known as thermal pastes. A thermal paste contains a liquid component that is known as the vehicle.

Polyol ester [1, 2] and silicone [3, 4] are the main types of vehicle used in thermal interface materials. Silicone is typically more stable thermally than polyol ester, due to the high dissociation energy between silicon and oxygen [5]. However, it suffers from the tendency of the paste to migrate and to separate [6]. Thermal stability is important for long-term usage of a thermal paste. In the case that polyol ester is used as the vehicle, the addition of antioxidant(s) to the vehicle to improve the thermal stability is necessary. Thermal degradation can result in delamination of the paste from a mating surface, thereby lowering the performance of the paste [7]. It can also result in cracking and weight loss of the paste.

Y. Aoyagi · D. D. L. Chung (✉)
Composite Materials Research Laboratory, University at Buffalo State University of New York, Buffalo, NY 14260-4400, USA
e-mail: ddlchung@buffalo.edu
URL: http://alum.mit.edu/www/ddlchung

Polyol ester refers to a neopentyl polyol ester that is made by reacting a monobasic fatty acid with a polyhedric alcohol with a neopentyl structure [8]. Polyol esters are technologically important as lubricants. Compared to other synthetic lubricants, such as diesters and polyalphaolefins, polyol esters are superior in the thermal stability [9]. The superior thermal stability of polyol esters over diesters stems from the larger number of ester groups in a polyol ester and the consequent increased polarity and reduction in volatility. Thermal stability is important for numerous applications, such as jet engine lubrication (which involves temperatures as high as 200 °C), industrial oven chains, high temperature greases, fire resistant hydraulic fluids, fire resistant transformer coolants, tenter frames and textile lubricants.

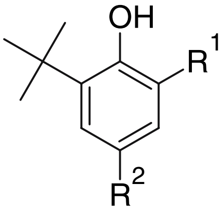
In spite of the relatively high inherent thermal stability of polyol esters [10], antioxidants (organic compounds that inhibit oxidation) are usually used with them in practice in order to improve the thermal stability. The science behind the use of antioxidants is complex, not only because of the variety of antioxidants, but also because of the interactions among the antioxidants, polyol esters and fillers (solid components present to improve the thermal conductivity, increase the viscosity or for other purposes).

Polyol ester degrades and becomes higher in viscosity at elevated temperatures. The thermal degradation in air is mainly due to the oxidation of polyol ester [11]. The oxidation causes chain scission and the formation of radicals. The chain scission results in small molecules, which tend to evaporate easily. The reactivity of the radicals can cause the linking of molecules, thus resulting in large molecules, which increase the viscosity. In the presence of an antioxidant, the radicals are changed to stable ROOR′ and ROOH. As a consequence, the antioxidants enhance the thermal stability [12].

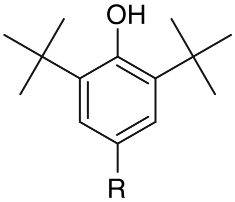
Improvement of the thermal stability of an organic vehicle can be attained by the addition of one or more antioxidants. By reacting with the vehicle molecules, an antioxidant renders improved oxidation resistance to the vehicle. By using more than one antioxidant, multiple mechanisms act synergistically to raise the thermal stability to levels above what can be attained by using a single antioxidant.

Antioxidants are classified into primary and secondary antioxidants. Combined use of a primary antioxidant and a secondary antioxidant provides a synergistic effect.

Primary antioxidants include hindered phenolic and aryl amine compounds. Phenolic compounds have active OH groups, whereas amine compounds have active NH or NR (where R is a side group) groups. An example of a half-hindered phenolic primary antioxidant is



where the bulky *tert*-butyl (or $C(CH_3)_3$) group on the left side of the OH group hinders the approach to the OH group by other molecules, and common R^1 is either hydrogen or methyl group. An example of a fully-hindered phenolic primary antioxidant is



where the bulky *tert*-butyl groups on both sides of the OH group hinder the approach to the OH group more than the case of a half-hindered phenolic compound. The steric hindrance due to this *tert*-butyl group makes the molecular interaction between primary antioxidant and secondary antioxidant that is called synergistic effect, more difficult. On the other hand, the radical stability of a fully-hindered phenolic antioxidant is higher than that of a half-hindered phenolic antioxidant [13].

A peroxy radical reacts with a primary antioxidant (abbreviated as AH), thereby terminating the free radical chain reaction, as shown by Eq. (1).

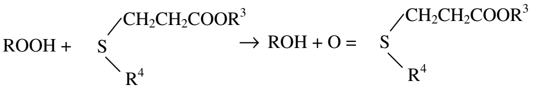
$$ROO^{\bullet} + AH \rightarrow ROOH + A^{\bullet} \quad (1)$$

The $A^{\bullet}$ radical is stable, thus preventing thermal oxidative degradation [13].

A secondary antioxidant reduces an active hydroperoxide, ROOH in Eq. (1), to an inactive alcohol, ROH [13]. Secondary antioxidants include phosphorous and thiopropionates. An example of a thiopropionate type secondary oxidant is

$$S\begin{cases} CH_2CH_2COOR^3 \\ R^4 \end{cases}$$

It functions through the reaction



$$\mathrm{ROOH} + \mathrm{S}\genfrac{}{}{0pt}{}{\diagup \mathrm{CH_2CH_2COOR^3}}{\diagdown \mathrm{R^4}} \rightarrow \mathrm{ROH} + \mathrm{O} = \mathrm{S}\genfrac{}{}{0pt}{}{\diagup \mathrm{CH_2CH_2COOR^3}}{\diagdown \mathrm{R^4}} \qquad (2)$$

Although antioxidants have long been used in organic materials to increase the thermal stability [14–16], the choice of antioxidants in most of the commercial thermal interface materials is proprietary and the scientific reason behind the choice of antioxidants that are not proprietary is often unclear. This paper provides a comparative evaluation of various antioxidants and antioxidant combinations at various concentrations, with and without a solid component (carbon black or boron nitride particles), for the purpose of understanding the relative performance of various antioxidants and developing polyol-ester-based thermal pastes of improved thermal stability. The antioxidants used in this work include primary and secondary antioxidants. The primary antioxidants are hindered phenolic compounds. The secondary antioxidant is a thiopropionate compound.

One of the solid components used in this work is carbon black, due to the ability of carbon black (thermally conductive) to provide polyol-ester-based thermal pastes of outstanding performance [17–19]. Thermal pastes, which constitute the main form of thermal interface material [20], are needed for improving the thermal contact between the microprocessor and heat sink of a computer, as overheating is the most critical problem in the microelectronic industry. In addition, carbon black is widely used as a black pigment in paints, the thermal stability of which is also of concern [21].

The effectiveness of carbon black in thermal pastes is due to the fact that the mating surfaces in a thermal contact are never perfectly smooth and a thermal paste must conform to the surface topography, thereby displacing the interfacial air, which is a thermal insulator. Because of their high conformability, thermal pastes with carbon black as the conductive solid component are exceptionally effective for improving thermal contacts, particularly when the mating surfaces are relatively smooth (0.05 μm roughness) [17–19], or when the paste is used as a coating on a sheet (such as aluminum foil) for functioning as a thermal gap filling material [22]. Under these conditions, the carbon black pastes are more effective than silver thermal paste (Arctic Silver® 5, Arctic Silver Inc.), in spite of the low thermal conductivity of carbon compared to silver. The high conformability of carbon black stems from its microstructure, which consists of porous agglomerates of nanoparticles.

Another solid component used in this work is hexagonal boron nitride, which is thermally conductive, yet electrically insulating. This combination of characteristics makes boron nitride particularly attractive for thermal pastes that are used in electronic packages [19]. In addition, due to its lamellar structure, hexagonal boron nitride is used as a lubricant additive [23].

In the case of polyol ester as the organic material, a single antioxidant, namely Ethanox 330 (a fully hindered phenolic compound from Albemarle Corp., Baton Rouge, LA) in the amount of 1 wt.%, was recommended by Khatri [1]. However, no antioxidant was used in the polyol-ester-based thermal pastes of Ref. [19]. In the case of silicone as the organic material, a single antioxidant of an unspecified type in the amount from 0.001 to 1 wt.% was recommended by Feng et al. [24]. In the case of polyethylene as the organic material, a primary antioxidant that is either a fully hindered or half-hindered phenolic (but preferably fully hindered for greater thermal stability) in the amount from 0 to 0.083 wt.%, a secondary antioxidant that is of the phosphorous type and is in the amount from 0 to 0.083 wt.%, and carbon black in the amount from 0 to 0.83 wt.%, were used by Pena et al. [25].

In order to study the effect of the solid component on the antioxidative function, the thermal stability is evaluated in this work both in the absence and in the presence of a solid component. Evaluation is conducted separately for carbon black and boron nitride as solid components in order to understand better the effect of the solid component on the antioxidative function.

Due to the elevated temperatures encountered by thermal pastes during use, the ability to withstand elevated temperatures is required for thermal pastes. However, the thermal stability of organic vehicles tends to be low, because the organic molecules may evaporate or decompose at the elevated temperature. Although polyol ester is more thermally stable than many other organic compounds, as shown by its wide application as a high temperature lubricant, its thermal stability is not sufficient for the thermal paste application. The thermal paste application is particularly demanding in relation to the thermal stability, because partial loss of the thermal paste after the paste has been installed at the thermal contact causes microscopic voids in the paste. As air is a thermal insulator, voids are detrimental to the effectiveness of a thermal interface material. Therefore, the main objective of this paper is to improve the thermal stability of polyol-ester-based materials in relation to reducing the extent of mass loss upon heating.

Another undesirable thermal effect is the irreversible increase in viscosity of an organic vehicle upon heating. This effect may be due to crosslinking, which occurs upon heating. A high viscosity is not desirable for conformability of a thermal paste, although an increase in viscosity after the paste has already conformed may be acceptable. Nevertheless, the use of a thermal paste during temperature variation will be more reliable and simpler if the paste does not increase its viscosity upon heating. Therefore, the second objective of this paper is to improve the thermal stability of polyol-ester-based materials in relation to reducing the extent of viscosity increase upon heating.

Yet another undesirable thermal effect is cracking of the paste after heating. Therefore, the third objective of this paper is to improve the thermal stability of polyol-ester-based materials in relation to reducing the tendency for cracking after heating.

Additional objectives of this paper are (i) to understand the effect of the solid component (carbon black and boron nitride) on the function of antioxidants, (ii) to provide a comparative evaluation of various antioxidants and various antioxidant combinations in their effectiveness in improving the thermal stability of polyol-ester-based materials, and (iii) to compare the performance of the polyol-ester-based materials with commercial products.

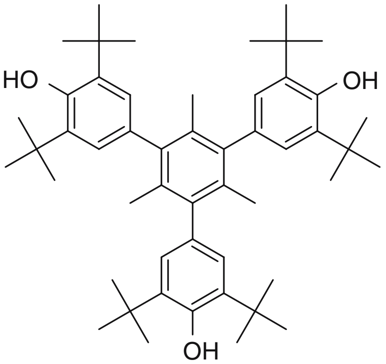
Experimental methods

Materials

The polyol esters in this work are pentaerythritol ester of linear and branched fatty acids and dipentaerythritol ester of linear and branched fatty acids. The polyol ester mixture (HATCOL 2372) is provided by Hatco Corp., Fords, NJ. The specific gravity is 0.97. Evaporation loss is 2 % after heating for 6.5 h at 204 °C.

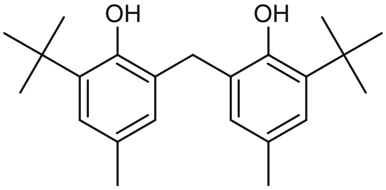
The various antioxidants used in this work are listed in Table 1. They include primary and secondary antioxidants.

A primary antioxidant used in this work is 1,3,5-trimethyl-2,4,6-tris (3,5-di-*tert*-butyl-4-hydroxybenzyl) benzene, i.e.,



It is a fully-hindered phenolic compound and is a commercial product (ETHANOX 330, Albemarle Corp., Baton Rouge, LA) in the form of a powder with melting point 244 °C and molecular weight 775.2 amu.

Another primary antioxidant used is 2,2′-methylenebis(4-methyl-6-*tert*-butylphenol), i.e., $C_{23}H_{32}O_2$, or



It is a fully-hindered phenolic compound and is a commercial product (CYANOX 2246, Cytec Industries Inc., West Paterson, NJ) in the form of a powder with melting point 120–132 °C and molecular weight 340.5 amu.

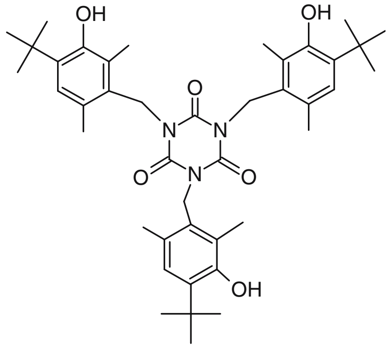
Table 1 Properties of each antioxidant

Name of antioxidant	Weight loss onset temperature (°C) (15%)[b] [27]	Molecular weight (g/mol)	Melting point (°C)	Steric hindrance
ETHANOX 330	/	775	244	Fully-hindered
CYANOX 2246[a]	267	341	120–132	Fully-hindered
SUMILIZER GA-80	401	741	>110	Half-hindered
SUMILIZER WX-R	305	359	>160	Half-hindered
CYANOX 1790	/	699	159–162	Half-hindered
SUMILIZER TP-D	361	1,162	>46	/

[a] CYANOX 2246 has the same molecular structure as SUMILIZER MDP-S, but it is from a different supplier

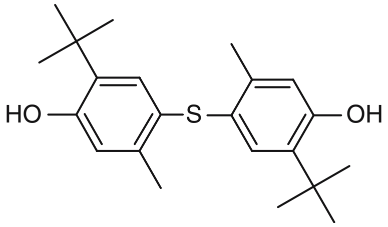
[b] Heating rate is 20 °C/min. The atmosphere is nitrogen

Another primary antioxidant used is 1,3,5-tris(4-*tert*-butyl-3-hydroxy-2,6-dimethyl benzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione, i.e., $C_{42}H_{57}N_3O_6$, or



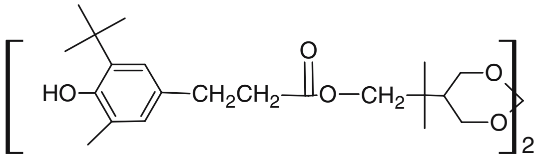
It is a half-hindered phenolic compound and is a commercial product (CYANOX 1790, Cytec Industries Inc.) in the form of a powder with melting point 159–162 °C and molecular weight 699 amu.

Yet another primary antioxidant is 4,4′-thiobis(2-*tert*-butyl-5-methylphenol), i.e.,



It is a half-hindered phenolic compound and is a commercial product (SUMILIZER WX-R, Sumitomo Chemical Corp.) in the form of a powder with melting point >160 °C and molecular weight 359 amu.

Still another primary antioxidant is 3,9-bis[2-[3-(3-*tert*-butyl-4-hydroxy-5-methylphenyl)-propionyloxy]-1,1-dimethylethyl] 2,4,8,10-tetraoxaspiro-[5.5] undecane, i.e.,



It is a half-hindered phenolic compound and is a commercial product (SUMILIZER GA-80, Sumitomo Chemical Corp.) in the form of a powder with melting point >110 °C and molecular weight 741 amu.

A secondary antioxidant is pentaerythrityl tetrakis-(3-dodecylthiopropionate), i.e.

$$(H_{25}C_{12}SCH_2CH_2\overset{O}{\overset{\|}{C}}OCH_2)_4C$$

It is a thiopropionate and is a commercial product (SUMILIZER TP-D, Sumitomo Chemical Corp.) in the form of flakes with melting point >46 °C and molecular weight 1,162 amu.

Thermal stability is necessary, so that the polyester-based material retains its fluidity and remains in a sufficient amount at elevated temperatures. An antioxidant with a low molecular weight tends to have high mobility [26], thereby allowing it to have a greater chance of approaching the radicals that result from the decomposed polyol ester molecules. In addition, an antioxidant that is itself thermally stable is preferred.

Table 1 shows the molecular weight and thermal stability of each of the antioxidants mentioned above. The thermal stability is described in terms of the weight loss onset temperature [27]. The combination of low molecular weight and high weight loss onset temperature is desirable. Thus, SUMILIZER WX-R is expected to be particularly effective. In contrast, CYANOX 2246 suffers from a low weight loss onset temperature, in spite of its low molecular weight.

The carbon black is Vulcan XC72R GP-3820 from Cabot Corp., Billerica, MA. It is a powder with particle size 30 nm, a nitrogen specific surface area 254 m^2/g, maximum ash content 0.2%, volatile content 1.07%, and density 1.7–1.9 g/cm^3. The carbon black powder is mixed with the polyol ester vehicle by hand stirring to form a uniform paste containing 2.4 vol.% carbon black [19]. The particle size (30 nm) of the carbon black is much less than those of the metal or ceramic particles used in commercial thermal pastes.

The boron nitride particles were hexagonal boron nitride, equiaxed in shape (as shown by scanning electron microscopy), with size 5–11 μm, surface area 17 m^2/g, oxygen content 0.5%, sulfur content <50 ppm, thermal conductivity 280 W/m K, and specific gravity 2.2, as provided by GE Advanced Ceramics Corporation, Cleveland, OH (Polartherm 180). No functional group is present on the basal plane, but functional groups such as OH, BOH, NH and NH_2 groups are present on the edge plane [GE Advanced Ceramics, Private communication]. The boron nitride powder is mixed with the polyol ester vehicle by hand stirring to form a uniform paste containing 16 vol.% boron nitride [19].

A number of commercial thermal interface materials were also evaluated in terms of the thermal stability for the sake of comparison. These commercial materials are Arctic Silver® 5 (polyol ester filled with micronized silver particles, together with smaller quantities of submicron particles of boron nitride, zinc oxide and aluminum oxide, such that all the conductive solid components together make up 88 wt.% of the paste [2], from Arctic Silver Inc., Visalia, CA), Shin-Etsu X-23-7762 (aluminum particle filled silicone from Shin-Etsu MicroSi, Inc., Phoenix, AZ), Thermagon T-pli 210 and T-gon 210 (silicone pads filled with boron nitride particles, with fiberglass reinforcement and thickness 250 μm), Thermagon T-gon 230 (same as T-gon 210 except for a thickness of 760 μm), Dow Corning 340 Heat Sink Compound (zinc oxide filled polydimethylsiloxane), Thermagon T-pcm HP105 (phase change material with phase change softening temperature 50–60 °C), Thermagon T-pcm FSF 52 (phase change material that melts at 52 °C), and Chomerics T454 (phase change material with phase change temperature 43 °C and thickness 130 μm).

Thermal stability testing

Thermogravimetric analyzer (TGA) under isothermal or constant heating rate conditions is conventionally used [29, 30]. In particular, the isothermal method is attractive for detailed kinetic study [31–33]. Although the constant heating rate condition requires less time than the isothermal condition [30], the isothermal condition is used in this research, due to small range of temperatures involved.

The degree of degradation, α [31], is defined as the fractional loss in weight due to the heating. It is expressed as

$$\alpha = (w_0 - w)/w_0, \tag{3}$$

where w_0 is the initial weight of the specimen before heating and w is the actual weight at a point during the heating.

Cracking is observed when a commercial thermal paste (Arctic Silver® 5) is heated at 200 °C and the remaining weight is 92.3 wt. % (Table 2). This suggests that a weight loss of 7.7% may reduce the performance of a thermal paste. Therefore, the time for 3% weight loss (i.e., a remaining weight of 97%) is used in this work as an indicator of the lifetime of the thermal paste.

The isothermal heating time (τ) for attaining a weight loss of 3% is determined for each of several temperatures, namely 120 ± 2, 140 ± 2, 160 ± 2, 180 ± 2, 200 ± 2 and 220 ± 2 °C. The time of zero is taken as the time at which temperature just reaches the set isothermal temperature. The time τ is considered as a lifetime indicator. It is not the true lifetime of the paste under use condition. Nevertheless, the determination of τ for various thermal pastes allows comparison of the thermal stability of the pastes.

Table 2 Thermal stability of commercial thermal interface materials and polyol-ester-based materials of this work

Material	Residual weight (%)	Cracking tendency
Carbon black paste of this work[a,b]	96.3 ± 0.6	No
Boron nitride paste of this work[a,b]	97.5 ± 0.2	No
Arctic Silver® 5[b]	92.3 ± 0.2	Yes
Shin-Etsumicrosi[b]	94.3 ± 0.2	No
Dow Corning 340[b]	99.6 ± 0.1	No
T-gon 210[c]	99.0 ± 0.0	No
T-gon 230[c]	99.1 ± 0.1	No
Thermagon T-pli 210[c]	99.0 ± 0.1	No
Thermagon T-pcm HP105[d]	73.9 ± 0.4	No
Thermagon T-pcm FSF 52[d]	71.9 ± 0.2	Yes
Chomerics T454[d]	68.4 ± 0.6	No

[a] Paste containing 0.500 wt.% SUMILIZER GA80 and 1.000 wt.% SUMILIZER TP-D (Line 15 of Tables 3 and 4)

[b] Thermal paste

[c] Solid

[d] Phase change material

The rate of degradation, dα/dt (where t is the time), describes the rate of weight loss. It is expressed as:

$$\mathrm{d}\alpha/\mathrm{d}t = k(T)\, f(\alpha), \tag{4}$$

where k is the temperature-dependent rate constant, T is the temperature in K, and $f(\alpha)$ is a function of α The rate constant k increases with temperature, following the Arrhenius form, i.e.,

$$k(T) = A \exp(-E/RT), \tag{5}$$

where E is the activation energy, A is the pre-exponential factor and R is the gas constant.

Substitution of Eq. (5) into Eq. (4) gives

$$\mathrm{d}\alpha/\mathrm{d}t = A\ \exp(-E/RT)\, f(\alpha). \tag{6}$$

Integration of Eq. (6) with respect to time gives

$$g(\alpha) = \int [\mathrm{d}\alpha/\, f(\alpha)] = A\ [\exp(-E/RT)]\ t. \tag{7}$$

Rearrangement of Eq. (7) gives

$$\ln\ t = E/RT + \ln[g(\alpha)/A]. \tag{8}$$

Based on Eq. (8), E can be determined from the slope of the plot of ln t versus 1/T.

The thermal stability is evaluated in this work by two methods, namely (i) oven-aging (weighing before and after isothermal heating in air at 200 °C for 24 h, with the heating and cooling rates being 3.0 °C/min), and (ii) isothermal TGA in air (the heating rate being 3.0 °C/min prior to the isothermal period). The TGA testing is conducted by using a Perkin-Elmer Corp. (Norwalk, CT) TGA 7 system. Both over-aging and TGA specimens are contained in aluminum pans.

A heat sink used in a computer is typically made of aluminum or copper. The heat spreader that is in contact with the chip is made of nickel-plated copper. Thus, the surfaces in contact with a thermal paste are usually metals. When a polyol ester is oxidized, it generates acid substances, which can react with a metal surface, thereby partly dissolving the metal [34] and forming radicals [35], thereby degrading the polyol ester. Although different metals are used in practice, aluminum is one of the most common. The use of aluminum pans in the thermal stability testing of this work means that the results reported here are particularly relevant to applications that involve the thermal paste touching an aluminum surface.

In oven-aging testing, each specimen is contained in an aluminum weighing dish (57 mm in diameter and 10 mm in depth, VWR International) and is heated in air in a box furnace (0.004 m^3 in volume, without forced convection, Isotemp® Programmable Muffle Furnace, Fisher Scientific Co.) at 200 ± 5 °C for 24 h. The maximum operation temperature of thermal pastes used in computers is typically around 100 °C. The testing temperature of 200 °C was chosen for oven-aging testing in this work, in order to compare rapidly the thermal stability of pastes containing various combinations of antioxidants and solid components. The weight is measured before heating and after the heating by using an electronic balance (Mettler MT, Mettler-Toledo, Inc.). The specimen weight (excluding the solid component) is 2,000 ± 1 mg. In addition, each specimen is visually inspected for surface cracks after the heating and subsequent cooling. Two specimens of each type are tested. The same over-aging testing method is used for all types of specimen, including the commercial thermal interface materials.

In both oven-aging and TGA testing, the antioxidant (or antioxidant combination) and the vehicle are placed in an aluminum pan and heated at 190 ± 10 °C for 15 min in order to allow the antioxidant(s) to dissolve in the vehicle. After that, the solid component (either carbon black in the amount of 2.4 vol.%, or boron nitride in the amount of 16 vol.%) is optionally added and the mixture is stirred manually for 10–15 min. These proportions of solid component have been previously used in relation to thermal paste performance evaluation [19]. The specimen weight (excluding the solid component) is 12.0 ± 0.5 mg. Each specimen is contained in an aluminum pan (6.4 mm in diameter and 1.6 mm in depth, Perkin-Elmer Corp.). The aluminum pan used in TGA is much smaller than that used in oven aging. This difference in size contributes to the difference in percentage weight loss between the two cases.

Viscosity testing

The viscosities of thermal pastes are measured by using a rotational viscometer (Brookfield Engineering Laboratories, Inc., Middleboro, MA, Model LVT Dial-Reading Viscometer, equipped with a Model SSA-18/13R small sample adaptor). The measurement is conducted at room temperature (19.8 ± 0.5 °C) after heating at 200 °C for various lengths of time up to 48 h.

Thermal contact conductance testing

Various thermal interface materials are sandwiched between the 1×1 $inch^2$ (25×25 mm^2) surfaces of two copper blocks (both 1×1 $inch^2$ surfaces of each block having a 12 μm or 800 grit roughness, prepared by mechanical polishing by Hardric laboratories, Inc., MA). Each copper block has a height of 35 mm.

The thermal contact conductance between two 1×1 $inch^2$ (25×25 mm^2) copper blocks with a thermal interface material between them is measured using the guarded hot plate method, which is a steady-state method of heat flux measurement (ASTM Method D5470). The heat in this test is provided by a 3×3 $inch^2$ (76×76 mm^2) copper block that has two embedded heating coils (top block in Fig. 1). During the period of temperature rise, the heating rate is controlled at 3.2 °C/min by using a temperature controller. This copper block is in contact with one of the 1×1 $inch^2$ copper blocks that sandwich the thermal interface material. The cooling in this test is provided by a second 3×3 $inch^2$ copper block, which is cooled by running water that flows in and out of the block (bottom block in Fig. 1). This block is in contact with the other two 1×1 $inch^2$ copper blocks that sandwich the thermal interface material. A RTD probe (connected to Digi-Sense ThermoLogR RTD Thermometer from Fisher Scientific Co., with accuracy ±0.03 °C) is inserted in four holes (T_1, T_2, T_3 and T_4 in Fig. 1, each hole of diameter 3.3 mm) one after the other. Two of the four holes are in each of the 1×1 $inch^2$ copper blocks. The temperature gradient is determined from T_1–T_2 and T_3–T_4. These two quantities should be equal at equilibrium, which is attained after holding the temperature of the heater at the desired value for 30 min. Equilibrium is assumed when the temperature

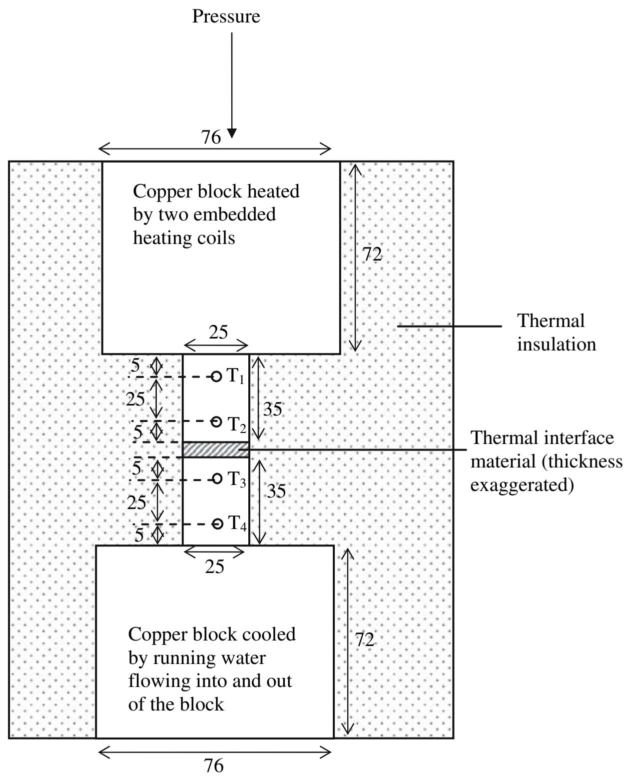


Fig. 1 Experimental set-up for the guarded hot plate method of thermal contact conductance measurement. T_1, T_2, T_3 and T_4 are holes of diameter 2.4 mm. A thermocouple (Type T) is inserted in each hole. All dimensions are in mm

variation is within ±0.1 °C in a period of 15 min. At equilibrium, the temperature of the hot block is 100 °C, that of the cold block is in the range 12–25 °C, while that of the thermal interface material is in the range 50–63 °C. The pressure in the direction perpendicular to the plane of the thermal interface is controlled by using a hydraulic press at a pressure of 0.46, 0.69 or 0.92 MPa. The system is thermally insulated by wrapping laterally all the copper blocks with glass fiber cloth.

In accordance with ASTM Method D5470, the heat flow Q is given by

$$Q = \frac{\lambda A}{d_A} \Delta T \tag{9}$$

where $\Delta T = T_1 - T_2 = T_3 - T_4$, λ is the thermal conductivity of copper, A is the area of the 1×1 inch^2 copper block, and d_A is the distance between thermocouples T_1 and T_2 (i.e., 25 mm).

The temperature at the top surface of the thermal interface material is T_A, which is given by

$$T_A = T_2 - \frac{d_B}{d_A}(T_1 - T_2), \tag{10}$$

where d_B is the distance between thermocouple T_2 and the top surface of the thermal interface material (i.e., 5 mm). The temperature at the bottom surface of the thermal interface material is T_D, which is given by

$$T_D = T_3 + \frac{d_D}{d_C}(T_3 - T_4), \tag{11}$$

where d_D is the distance between thermocouple T_3 and the bottom surface of the thermal interface material (i.e., 5 mm) and d_C is the distance between thermocouples T_3 and T_4 (i.e., 25 mm).

The thermal impedance θ is given by

$$\theta = (T_A - T_D)\frac{A}{Q} \tag{12}$$

Note that insertion of Eq. (9) into Eq. (12) causes cancellation of the term A, so that θ is independent of A. The thermal contact conductance is the reciprocal of θ.

Each type of thermal interface material is tested in terms of the thermal contact conductance for at least twice. Each time involves measurement at three pressures (0.46, 0.69 and 0.92 MPa) in the order listed.

Results and discussion

Thermal stability evaluation by oven-aging testing

Tables 3–5 show the oven-aging results of the thermal stability evaluation for various combinations of antioxidant(s) and solid component. Table 3 is for the case without any solid component. Table 4 is for the case with carbon black as the solid component. Table 5 is for the case with boron nitride as the solid component. Each of these tables includes the following categories of antioxidant use: (i) use of a primary antioxidant alone at 0.500 wt.%, (ii) use of a secondary antioxidant alone at 0.500 wt.%, (iii) combined use of a primary antioxidant and a secondary antioxidant at a total of 0.500 wt.% (0.167 wt.% of a primary antioxidant and 0.333 wt.% of a secondary antioxidant), and (iv) combined use of a primary antioxidant and a secondary antioxidant at a total of 1.500 wt.% (0.500 wt.% of a primary antioxidant and 1.000 wt.% of a secondary antioxidant). These categories allow comparative evaluation of the effectiveness of various antioxidant species and their proportions.

Table 3 Thermal stability of polyol-ester-based materials in the absence of a solid component, as indicated by weight loss measurement

Line no.	Total antioxidant content (wt.%)	Primary antioxidant	Secondary antioxidant SUMILIZER TP-D (wt.%)	Residual weight (%)	Calculated residual weight (%)[a]
1	0	/	/	35.9 ± 2.5	/
2	0.500	0.500 wt.% ETHANOX 330	/	40.3 ± 0.8	/
3	0.500	0.500 wt.% CYANOX 2246	/	41.7 ± 2.3	/
4	0.500	0.500 wt.% SUMILIZER GA80	/	40.9 ± 2.5	/
5	0.500	0.500 wt.% SUMILIZER WX-R	/	58.0 ± 0.5	/
6	0.500	0.500 wt.% CYANOX 1790	/	46.7 ± 1.8	/
7	0.500	/	0.500	47.6 ± 0.3	/
8	0.500	0.167 wt.% ETHANOX 330	0.333	51.1 ± 4.6	45.2
9	0.500	0.167 wt.% CYANOX 2246	0.333	47.5 ± 1.5	45.6
10	0.500	0.167 wt.% SUMILIZER GA80	0.333	97.6 ± 0.1	45.4
11	0.500	0.167 wt.% SUMILIZER WX-R	0.333	96.3 ± 0.9	51.1
12	0.500	0.167 wt.% CYANOX 1790	0.333	97.5 ± 0.1	47.3
13	1.500	0.500 wt.% ETHANOX 330	1.000	97.0 ± 0.2	/
14	1.500	0.500 wt.% CYANOX 2246	1.000	69.5 ± 3.7	/
15	1.500	0.500 wt.% SUMILIZER GA80	1.000	97.7 ± 0.2	/
16	1.500	0.500 wt.% SUMILIZER WX-R	1.000	97.2 ± 0.0	/
17	1.500	0.500 wt.% CYANOX 1790	1.000	97.4 ± 0.2	/

[a] Calculated residual weight (wt.%) using measured values in Lines 2–7 and the antioxidant proportions in Lines 8–12

Effect of antioxidant in the absence of a solid component

Comparison of Line 1 and Lines 2–17 of Table 3 shows that all the antioxidants and antioxidant combinations used are effective for improving the thermal stability. Comparison of Lines 2–7 shows that SUMILIZER WX-R is more effective than the other four primary antioxidants or the one secondary antioxidant, all at 0.500 wt.%.

The comparison of the effectiveness of various antioxidant combinations should consider the difference in proportions of the antioxidants in the various combinations. Without any synergistic effect, the remaining weight of Hatcol including two antioxidants and the calculated remaining weight from two remaining weights of Hatcol including different type of single antioxidant in each solution should be equal. However, due to the synergistic effect, the remaining weight of Hatcol including two antioxidants increased the remaining weight.

The proportion of the primary antioxidant in Lines 8–12 is 1/3 of that in Lines 2–7; the proportion of the secondary antioxidant in Lines 8–12 is 2/3 of that in Line 7. If the effectiveness of an antioxidant is proportional to its use proportion, the residual weight for Line 8 is expected to be the sum of 1/3 of that of Line 2 and 2/3 of that of line 7. Hence, the residual weight for Line 8 is expected to be 45.2 wt.%, which is lower than the measured value of 51.1 wt.%. This indicates a synergistic effect of the combined use of ETHANOX 330 and SUMILIZER TP-D. Similar comparison of the calculated and measured residual weights for Lines 8–12 shows similar synergistic effect for each of these antioxidant combinations. The synergistic effect is particularly strong for Lines 10–12, due to the half-hindered structure and high thermal stability (Table 1) of the primary antioxidants for these Lines. In contrast,

Table 4 Thermal stability of polyol-ester-based materials in the presence of carbon black (the solid component), as indicated by weight loss measurement

Line no.	Total antioxidant content in vehicle (wt.%)	Primary antioxidant	Secondary antioxidant SUMILIZER TP-D (wt.%)	Residual weight (%)		Calculated residual weight (%)[a]	Cracking after heating
				Excluding the solid component	Including the solid component		
1	0	/	/	44.5 ± 0.8	47.0 ± 0.7	/	Yes
2	0.500	0.500 wt.% ETHANOX 330	/	55.4 ± 0.3	57.3 ± 0.3	/	Yes
3	0.500	0.500 wt.% CYANOX 2246	/	52.4 ± 2.1	54.5 ± 2.0	/	Yes
4	0.500	0.500 wt.% SUMILIZER GA80	/	56.9 ± 1.0	58.8 ± 0.9	/	Yes
5	0.500	0.500 wt.% SUMILIZER WX-R	/	70.3 ± 2.0	71.6 ± 1.9	/	No
6	0.500	0.500 wt.% CYANOX 1790	/	58.6 ± 0.7	60.4 ± 0.7	/	No
7	0.500	/	0.500	60.1 ± 2.9	61.8 ± 2.8	/	No
8	0.500	0.167 wt.% ETHANOX 330	0.333	53.0 ± 4.1	55.1 ± 3.9	58.5	Yes
9	0.500	0.167 wt.% CYANOX 2246	0.333	53.0 ± 4.2	55.1 ± 4.0	57.5	Yes
10	0.500	0.167 wt.% SUMILIZER GA80	0.333	54.8 ± 5.7	56.8 ± 5.4	59.0	Yes
11	0.500	0.167 wt.% SUMILIZER WX-R	0.333	66.6 ± 6.5	68.0 ± 6.2	63.5	No
12	0.500	0.167 wt.% CYANOX 1790	0.333	55.7 ± 0.6	57.7 ± 0.6	59.6	Yes
13	1.500	0.500 wt.% ETHANOX 330	1.000	92.3 ± 1.4	92.6 ± 1.3	/	No
14	1.500	0.500 wt.% CYANOX 2246	1.000	71.9 ± 1.8	73.1 ± 1.7	/	No
15	1.500	0.500 wt.% SUMILIZER GA80	1.000	96.1 ± 0.6	96.3 ± 0.6	/	No
16	1.500	0.500 wt.% SUMILIZER WX-R	1.000	95.5 ± 0.3	95.7 ± 0.3	/	No
17	1.500	0.500 wt.% CYANOX 1790	1.000	90.2 ± 3.1	90.6 ± 3.0	/	No

[a] Calculated residual weight (wt.%) using measured values in Lines 2–7 and the antioxidant proportions in Lines 8–12

Lines 8 and 9 involve a primary antioxidant that is fully-hindered and Line 9 involves a primary antioxidant that is relatively low in thermal stability. Therefore, Lines 8 and 9 show less synergistic effect than Lines 10–12.

The superior effectiveness of a half-hindered primary oxidant (SUMILIZER GA-80, SUMILIZER WX-R or CYANOX 1790) in combination with a secondary antioxidant (SUMILIZER TP-D) (i.e., Lines 10–12) means that a half-hindered phenolic

Table 5 Thermal stability of polyol-ester-based materials in the presence of boron nitride (the solid component), as indicated by weight loss measurement

Line no.	Total antioxidant content in vehicle (wt.%)	Primary antioxidant	Secondary antioxidant SUMILIZER TP-D (wt.%)	Residual weight (%)		Calculated residual weight (%)[a]	Cracking after heating
				Excluding the solid component	Including the solid component		
1	0	/	/	34.0 ± 0.9	51.0 ± 0.6	/	Yes
2	0.500	0.500 wt.% ETHANOX 330	/	47.3 ± 1.0	63.3 ± 0.7	/	Yes
3	0.500	0.500 wt.% CYANOX 2246	/	47.4 ± 0.6	63.3 ± 0.4	/	Yes
4	0.500	0.500 wt.% SUMILIZER GA80	/	48.8 ± 2.9	64.3 ± 2.0	/	Yes
5	0.500	0.500 wt.% SUMILIZER WX-R	/	60.6 ± 1.6	72.5 ± 1.1	/	No
6	0.500	0.500 wt.% CYANOX 1790	/	48.0 ± 0.5	63.8 ± 0.4	/	Yes
7	0.500	/	0.500	51.0 ± 0.1	65.9 ± 0.1	/	Yes
8	0.500	0.167 wt.% ETHANOX 330	0.333	40.6 ± 7.3	58.6 ± 5.0	49.8	Yes
9	0.500	0.167 wt.% CYANOX 2246	0.333	43.3 ± 4.9	60.6 ± 3.3	49.8	Yes
10	0.500	0.167 wt.% SUMILIZER GA80	0.333	41.2 ± 8.1	59.1 ± 5.6	50.3	Yes
11	0.500	0.167 wt.% SUMILIZER WX-R	0.333	52.6 ± 1.9	67.0 ± 1.3	54.2	Yes
12	0.500	0.167 wt.% CYANOX 1790	0.333	39.4 ± 1.7	59.6 ± 0.9	50.0	Yes
13	1.500	0.500 wt.% ETHANOX 330	1.000	87.6 ± 2.7	91.4 ± 1.9	/	No
14	1.500	0.500 wt.% CYANOX 2246	1.000	63.7 ± 5.6	74.8 ± 3.9	/	No
15	1.500	0.500 wt.% SUMILIZER GA80	1.000	96.3 ± 0.3	97.5 ± 0.2	/	No
16	1.500	0.500 wt.% SUMILIZER WX-R	1.000	95.0 ± 0.2	96.5 ± 0.2	/	No
17	1.500	0.500 wt.% CYANOX 1790	1.000	95.6 ± 0.6	97.0 ± 0.4	/	No

[a] Calculated residual weight (wt.%) using measured values in Lines 2–7 and the antioxidant proportions in Lines 8–12

primary antioxidant in combination with a thiopropionate type secondary antioxidant is particularly effective for improving the thermal stability. This effectiveness is because of the association between the hydrogen end of the OH group in these three primary antioxidants with the oxygen end of the C=O group in SUMILIZER TP-D [13, 26, 36, 37]. Such intermolecular association will be more difficult if a fully-hindered phenolic compound is used in place of the half-hindered phenolic compound. Due to this association, a primary antioxidant molecule can be very close to a secondary antioxidant molecule. Thus, SUMILIZER TP-D is positioned to decompose the hydroperoxide to the alcohol, as described in Eq. (2), once the hydroperoxide is generated by Eq. (1). In case of a fully-hindered phenolic compound, the intermolecular association is more difficult, thus resulting in a time lag between Eqs. (1) and (2) [13, 26, 36, 37].

Comparison of Lines 8–12 with Lines 13–17 of Table 3 shows that increase of the total antioxidant proportion from 0.500 to 1.500 wt.% (such that the ratio of primary antioxidant to secondary antioxidant is fixed at 1:2) improves the thermal stability, except for Lines 15–17, where the increase in total antioxidant proportion does not affect the residual weight. That the increase in total antioxidant proportion does not affect the thermal stability for Lines 15–17 is because of the high level of thermal stability already attained at the lower proportion in Lines 10–12 and the inherent volatile content in the vehicle.

Figure 2 shows the effect of heating time up to 1,500 min at a fixed temperature (120, 160 or 200 °C) on the remaining weight of polyol ester in the absence of antioxidants, as obtained by TGA. At 200 °C, the fractional weight loss is large, but levels off after about 600 min. This leveling suggests the occurrence of cross-linking at 200 °C.

Figure 3 shows the corresponding results in the presence of antioxidants (0.500 wt.% SUMILIZER GA 80 and 1.000 wt.% SUMILIZER TP-D) for heating at 160, 180 and 199 °C. Note the difference in scales between Figs. 2 and 3. At 160 °C, the weight loss is small, even after heating for 4,000 min. At 199 °C, the weight loss abruptly increases after heating at 1,000 min, due to the reaction and consequent loss of function of the antioxidants.

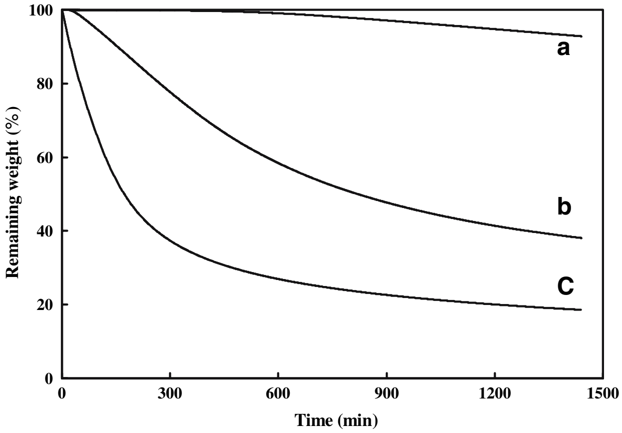


Fig. 2 Remaining weight of polyol ester excluding antioxidants (a: 393 K, b: 433 K, c: 473 K)

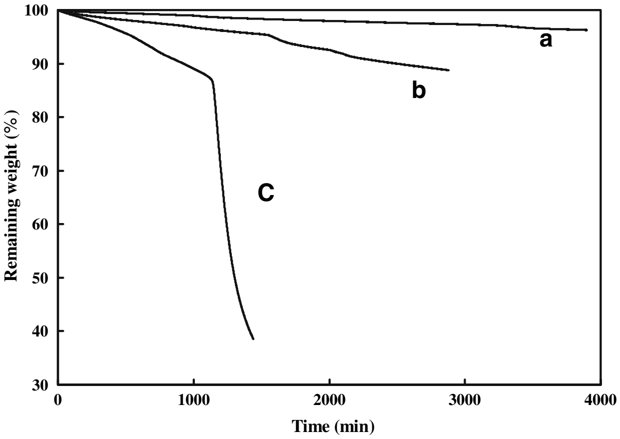


Fig. 3 Remaining weight of polyol ester including 0.500 wt.% of SUMILIZER GA 80 and 1.000 wt.% of SUMILIZER TP-D (a: 433 K, b: 454 K, c: 472 K)

Comparison of Figs. 2 and 3 shows the effect of antioxidants on the thermal stability. For the essentially same temperature and the same heating time, the weight loss is much lower in the presence of antioxidants. Thus, as expected, the antioxidants enhance the thermal stability.

Comparison of the results from TGA (Figs. 2 and 3, where 1,440 min is equal to 24 h, which is the time for the oven-aging heating) and those from oven-aging shows similar effect of antioxidants. However, for the same composition, the weight loss is lower for the TGA results than the corresponding oven-aging results. Specifically, in the absence of antioxidant, the remaining weight is 19% from TGA (Fig. 2), but is (35.9 ± 2.5)% from oven-aging (Table 3). In the presence of antioxidants, the remaining weight is 39% from TGA (Fig. 3), but is (97.7 ± 0.2)% from oven aging (Table 3). This difference between TGA and -aging results is attributed to the presence of forced convection in TGA and the absence of forced convection in the furnace.

Effect of antioxidant(s) in the presence of carbon black

Comparison of Line 1 with Lines 2–17 of Table 4 shows that any of the antioxidant combinations is effective in the presence of carbon black. This is consistent with the effectiveness in the absence of carbon black, as shown in Table 3.

Comparison of Line 1 of Table 3 with Line 1 of Table 4 shows that carbon black improves the thermal stability in the absence of an antioxidant. This is because of the surface functional groups such as phenolic groups on the carbon serving as a primary antioxidant, and quinone [38] and lactone on the carbon

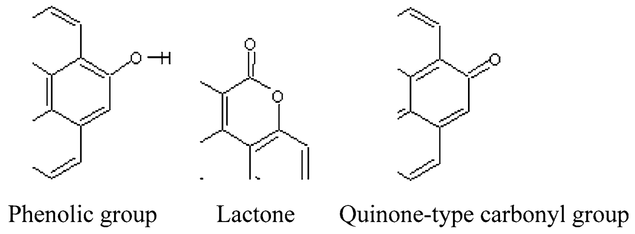


Fig. 4 Functional groups that may work as an antioxidant on the edge sites of carbon black

serving as a scavenger of alkyl free radicals (Fig. 4). The primary phenolic antioxidant (AH in Eq. (1)) reacts with the peroxy radical ($ROO^{\bullet}$ in Eq. (1)) according to Eq. (1). This reaction rate constant is 3–4 times higher than that of Eq. (13) [39] below. This is due to the stabilization of the antioxidant radical ($A^{\bullet}$ in Eq. (1)) by the resonance effect in the phenolic structure.

$$RH + ROO^{\bullet} \rightarrow R^{\bullet} + ROOH \qquad (13)$$

Since carbon black has more aromatic rings than the phenolic antioxidant, the radical on the carbon black is even more stable than that on the antioxidant. Thus, carbon black can act as an antioxidant, the radical of which is even more stable than that of a phenolic antioxidant (Fig. 5). As a consequence, carbon black used as an antioxidant can cause the reaction in Eq. (1) to be even faster than the use of a phenolic antioxidant. Oxidation of organic compounds starts from the generation of alkyl free radicals. Therefore, scavenging alkyl free radicals reduces the amount of peroxide radicals. It has been previously reported that carbon black inhibits oxidation [36, 40] due to the functional groups on the carbon black, as mentioned above, but carbon black can also promote oxidation [25, 41] due to the adsorption of antioxidants on the carbon black surface [25, 42].

Comparison of Lines 1–7 of Table 3 with Line 1 of Table 4 shows that carbon black serves as an antioxidants that is superior to the primary antioxidants in Lines 2–4 of Table 3, inferior to the primary antioxidant in Line 5 of Table 3, and similar in effectiveness to the primary antioxidants in Lines 6 and 7 of Table 3.

Comparison of Lines 2–7 of Table 3 with Lines 2–7 of Table 4 shows that carbon black improves the thermal stability in the presence of a single antioxidant. Comparison of Lines 8–17 of Table 3 with Lines 8–17 of Table 4 shows that the addition of carbon black hinders the interaction between primary antioxidant and secondary antioxidant. Since comparison of Lines 2–7 of Table 3 with Lines 2–7 of Table 4 shows that the addition of carbon black improves the thermal stability in the presence of either primary or secondary antioxidant, carbon black does not have antagonistic effect with either antioxidant. However, the fact that the addition of carbon black in the presence of both primary and secondary antioxidants lowers the thermal stability implies that carbon black hinders the synergistic interaction between the primary and secondary antioxidants. This negative effect of carbon black is most severe for Lines 10–12 of Table 4. The most effective antioxidant combination when carbon black is present corresponds to Lines 15 of Table 4.

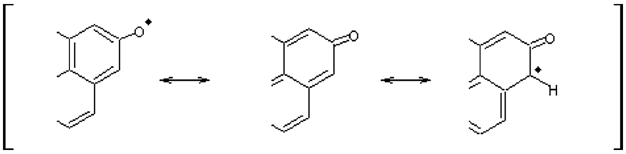


Fig. 5 A possible example of the resonance effect at the edge site of carbon black

Effect of antioxidant(s) in the presence of boron nitride

Comparison of Line 1 of Table 5 with Lines 2–17 of Table 5 shows that any of the antioxidant combinations is effective in the presence of boron nitride. This is consistence with the effectiveness in the absence of boron nitride, as shown in Tables 3 and 4.

Comparison of Line 1 of Table 3 with Line 1 of Table 5 shows essentially the same residual weight (excluding the solid component). This means that the presence of boron nitride does not improve the thermal stability, in contrast to the improvement in the presence of carbon black (Table 4).

Comparison of Lines 2–7 of Table 3 with Lines 2–7 of Table 5 shows that boron nitride improves the thermal stability for the case of a single antioxidant being used. This means that there is a slight synergetic effect between boron nitride and an antioxidant (primary or secondary). This effect may be due to the NH functional groups at the edge of the basal plane of hexagonal boron nitride (Fig. 6). The radical on the oxygen atom in boron nitride is not stabilized, due to the absence of resonance. Due to the poor stability of the radical, the addition of boron nitride did not show enhancement of the thermal stability (Line 1 of Tables 3 and 5). In other words, boron nitride does not act as a primary antioxidant. However, the NH group on boron nitride may work as an antioxidant.

The hindered amine light stabilizer (HALS) [13, 39, 43] is an additive that is used for enhancing the stability of a polymer against sunlight. HALS has NH group in its structure. Although the reaction rate constant of the NH group with the peroxy radical is smaller than that of the phenolic antioxidant with the peroxy radical, the NH group can trap an alkyl radical [39]. Therefore,

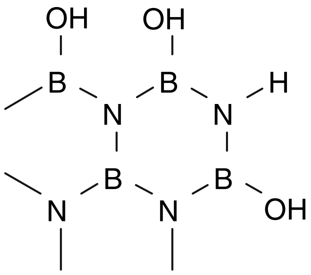


Fig. 6 A functional group (NH) that may work as an antioxidant on the edge plane of boron nitride

although the antioxidant ability of boron nitride itself is not high at 200 °C, the combination of boron nitride and a single antioxidant can give rise to a synergistic effect, as shown in Lines 1–7 of Tables 3 and 4, and the combination of boron nitride and two antioxidants can also have a synergistic effect below 180 °C, as shown in section "Lifetime evaluation based on TGA."

However, comparison of Lines 8–17 of Table 3 with Lines 8–17 of Table 5 shows that the presence of boron nitride diminishes the thermal stability when both primary and secondary antioxidants are used. This means that boron nitride hinders the interaction between primary and secondary antioxidants. Since Lines 1–7 of Table 5 in comparison with those of Table 3 indicates that boron nitride has a slight synergistic effect with either primary or secondary antioxidant, boron nitride does not chemically degrade the vehicle. Nevertheless it hinders the interaction between the primary and the secondary antioxidant. This negative effect due to boron nitride is most severe for Lines 10–12 of Table 5. This negative effect is similar, but less severe, when carbon black is present in place of boron nitride, as shown in Table 4, because of the antioxidant function of carbon black (as shown by comparing Line 1 of Tables 3–5). Due to the polarity of the boron nitride surface, the OH group of the primary antioxidant is attracted to the surface of the boron nitride, thereby reducing the amount of primary antioxidant that is available for interacting with the secondary antioxidant. The interaction between the primary and secondary antioxidants is necessary for these antioxidants to be most effective. Although carbon black has a non-polar nature, it has quinone and lactone groups at the edge sites of the carbon layers. These quinone and lactone groups provide electronegative oxygen atoms, which can interact with the OH group of the primary antioxidant, thereby reducing the amount of primary antioxidant that is available for interacting with the secondary antioxidant. However, the amount of quinone and lactone groups on the carbon black is low compared to that of the lone pairs on the nitrogen atoms of boron nitride. As a result, carbon black has a less negative effect on the thermal stability than boron nitride at 200 °C. The most effective antioxidant combination when boron nitride is present corresponds to Lines 15–17 of Table 5.

Comparison of Tables 4 and 5 shows that carbon black gives better thermal stability than boron nitride, with the exception of Lines 15–17, for which carbon black and boron nitride give similar performance. The superiority of carbon black may be attributed to the higher stability of radicals on the carbon black (due to the resonance associated with the π electrons).

Comparison with commercial thermal interface materials

Table 2 shows that commercial thermal interface materials in the form of silicone-based materials (Shin-Etsumicrosi, Dow Corning 340, T-gon 210, T-gon 230 and Thermagon T-pli 210) are among the most thermally stable thermal interface materials tested in this work, with residual weight of 99 wt.% or more. Among these silicone-based materials, Shin-Etsumicrosi is the least stable thermally. The highest residual weight among pastes developed in this work is 96 and 97 wt.% for carbon black and boron nitride pastes respectively (Line 15 of Tables 4 and 5), so the thermal stability attained in this work is almost as high as that of the most thermally stable commercial pastes. In addition, it is superior to Arctic Silver® 5, which also uses polyol esters as its vehicle, and is also superior to Shin-Etsumicrosi, which is based on silicone.

Although the thermal stability of the silicone-based thermal interface materials is higher than those based on polyol esters, the effectiveness as a thermal interface material is inferior, at least for the case of 340 silicone heat sink compound from Dow Corning Corp [44]. Furthermore, polyol ester is typically less expensive than silicone. The phase change materials (the last three rows in Table 2) are among those that are least stable.

Lifetime evaluation based on TGA

Lifetime evaluation by weight loss measurement in isothermal TGA is conducted for the polyol ester with and without antioxidants (0.500 wt.% of GA80 and 1.000 wt.% of TP-D). For the case with antioxidants, the effect of the solid component (boron nitride or carbon black) is also studied. In addition, similar evaluation is conducted for Arctic Silver® 5.

Figures 7 and 8 show the Arrhenius plots of $\ln \tau$ versus $1/T$, where τ is the lifetime indicator. Extrapolation of the plot to a temperature of 100 °C ($1/T = 2.7 \times 10^{-3}\ \mathrm{K}^{-1}$) gives the lifetime indicator for 100 °C, which is a typical maximum operation temperature of a thermal paste used in computers. As shown in Fig. 7, for the same temperature, τ is much increased by the presence of the antioxidants. All data points essentially fall on a straight line in Figs. 7 and 8, except for one data point at the highest temperature for the carbon black paste in Fig. 7. In case of the carbon black paste, the exceptional data point is not taken into consideration in determining the activation energy and the lifetime indicator.

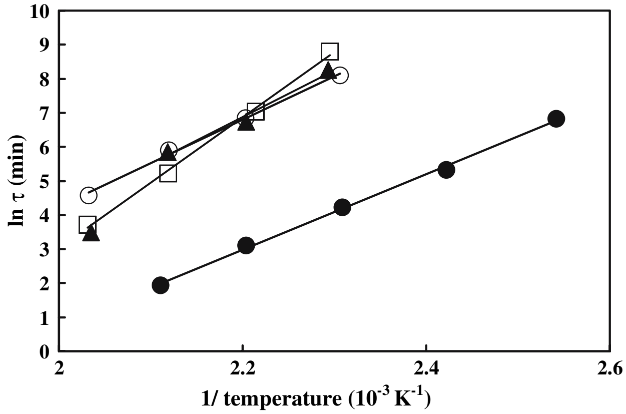


Fig. 7 Plot of $\ln \tau$ versus the reciprocal temperature, where τ is the time for 3% weight loss. The curve is extrapolated to a temperature of 100 °C in order to determine the 100°C lifetime indicator. •: No additive (HATCOL 2372), ○: With antioxidants (HATCOL 2372 with 0.500 wt.% of SUMILIZER GA80 and 1.000 wt.% of SUMILIZER TP-D), □: Boron nitride paste including 0.500 wt.% of SUMILIZER GA 80 and 1.000 wt.% of SUMILIZER TP-D, ▲: Carbon black paste including 0.500 wt.% of SUMILIZER GA 80 and 1.000 wt.% of SUMILIZER TP-D

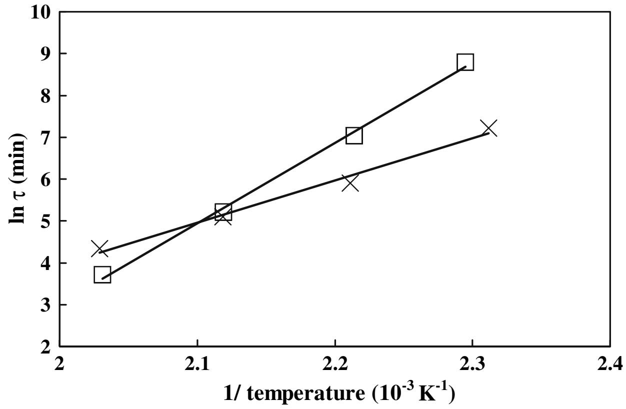


Fig. 8 Plot of $\ln \tau$ versus the reciprocal temperature, where τ is the time for 3% weight loss. The curve is extrapolated to a temperature of 100 °C in order to determine the 100 °C lifetime indicator. □: Boron nitride paste including 0.500 wt.% of SUMILIZER GA 80 and 1.000 wt.% of SUMILIZER TP-D, ×: commercial polyol-ester-based Arctic Silver 5

The effect of the solid component on τ is small compared to the effect of the antioxidants. Nevertheless, the effect of the solid component is still substantial, due to the logarithmic nature of the vertical scale. In the presence of antioxidants (GA80 and TP-D), the addition of boron nitride reduces the thermal stability above 180 °C ($1/T$ around $2.2 \times 10^{-3}\ \mathrm{K}^{-1}$), but increases the thermal stability below 180 °C (Fig. 7). In the presence of antioxidants, the addition of carbon black reduces the thermal stability at 220 °C ($1/T$ around $2.0 \times 10^{-3}\ \mathrm{K}^{-1}$), but increases the thermal stability below 200 °C ($1/T$ around $2.1 \times 10^{-3}\ \mathrm{K}^{-1}$). At 220 °C, both carbon black and boron nitride hinder the synergistic interaction between the two antioxidants. A similar negative effect between the solid component and antioxidants is observed in the 200 °C oven-aging condition (section "Thermal stability evaluation by oven-aging testing"). Comparison of the boron nitride paste and the carbon black paste, both containing antioxidants, shows that the boron nitride paste is more thermally stable than the carbon black paste below 180 °C ($1/T$ around $2.2 \times 10^{-3}\ \mathrm{K}^{-1}$). This means that, at a typical operating temperature of 100 °C, the boron nitride paste is more stable thermally than the carbon black paste.

Table 6 shows the activation energy for each paste, as obtained from the slope of the curves in Figs. 7 and 8.

Table 6 The 100 °C lifetime indicator and the activation energy for each paste

Line no.		E (kJ/mol)	100 °C lifetime indicator (year)
1	Polyol ester	92	0.01
2	Polyol ester with antioxidants[a]	106	0.77
3	Polyol ester with antioxidants[a] and boron nitride	160	19
4	Polyol ester with antioxidants[a] and boron nitride (excluding the weight of boron nitride in the calculation)	138	3.4
5	Polyol ester with antioxidants[a] and carbon black	114	1.3
6	Polyol ester with antioxidants[a] and carbon black (excluding the weight of carbon black in the calculation)	114	1.3
7	Arctic Silver® 5	84	0.10

[a] Antioxidants: 0.500 wt.% of GA 80 and 1.000 wt.% of TP-D

The addition of antioxidants (0.500 wt.% of SUMILIZER GA 80 and 1.000 wt.% of TP-D) increases activation energy (Lines 1 and 2). The addition of a solid component (carbon black or boron nitride) further increases the activation energy (Lines 2, 3 and 5). When the weight of the solid component is excluded in the activation energy calculation, the activation energy is decreased for the case of boron nitride (Lines 3 and 4), but is not affected for the case of carbon black (Lines 5 and 6). Comparison of Lines 2, 4, and 6 gives the effect of the solid components in the presence of the antioxidants; addition of either boron nitride or carbon black increases the activation energy, though the increase is more significant for boron nitride than carbon black. Arctic silver, on the other hand, shows the lowest activation energy—even lower than that of the polyol ester in the absence of antioxidants.

Table 6 also shows the 100 °C lifetime indicator, as obtained by extrapolation of the curves in Figs. 7 and 8. In all cases with antioxidants, the longer lifetime is associated with the higher activation energy. The longest lifetime of 19 years is obtained for the boron nitride paste. In the absence of antioxidants, the lifetime is only 0.01 year—even shorter than that for Arctic Silver® 5.

Cracking tendency

Cracking tendency is reduced by the use of antioxidants, as shown for carbon black pastes (Table 4) as well as boron nitride pastes (Table 5). Cracking occurs only for pastes that contain a solid component. Among pastes that contain a solid component, cracking tends to occur when the weight loss after the heating is high, corresponding to the remaining weight less than about 60% (Tables 4 and 5). This suggests that the cracking is due to the loss of vehicle during heating.

Carbon black pastes do not show any crack after the heating, which was conducted at 200 °C for 24 h, except for those with the residual weight (excluding solid component) less than 57 wt.%. The boron nitride pastes also do not show cracking, except for those with the residual weight (excluding solid component) less than 53 wt.%. Among pastes that show cracking, the degree of cracking is less for carbon black pastes than boron nitride pastes. The lower tendency for cracking for the carbon black pastes compared to the boron nitride pastes is due to the lower solid component volume fraction. All of the commercial pastes also do not show cracking, except for Arctic Silver® 5 and Thermagon T-pcm FSF 52. The cracking tendency of Arctic Silver® 5 relates to the high solid content and the limited thermal stability of the vehicle.

Effect of heating on the viscosity of thermal pastes

Figure 9 shows the effect of prior heating on the room temperature viscosity of thermal pastes without solid components. In the absence of an antioxidant, the viscosity of polyol ester increases significantly after heating at 200 °C for times as short as 2 h. In the presence of antioxidants GA 80 and TP-D, the viscosity essentially does not change, even after heating at 200 °C for 48 h.

The increase in viscosity in the absence of antioxidants suggests the occurrence of crosslinking during heating. This is consistent with the leveling off of the weight loss after 600 min of heating at 200 °C, as shown in Fig. 2. The cross-linking reduces further evaporation of small decomposed molecules, thereby diminishing further weight loss.

Thermal contact conductance

Thermal contact conductance of thermal pastes is shown in Table 7. The presence of antioxidants has negligible effect on the conductance.

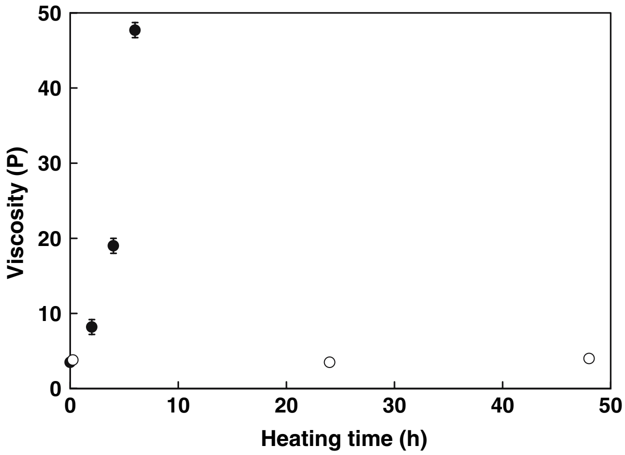


Fig. 9 Variation of the viscosity with the heating time at 200 °C for polyol ester excluding (•) or including (○) the antioxidants 0.500 wt.% of SUMILIZER GA80 and 1.000 wt.%

Table 7 Thermal contact conductance of polyol ester with and without an antioxidant, in the absence of a solid component

Antioxidant	Thermal contact conductance (10^4 W/ m^2 °C)		
	0.46 MPa	0.69 MPa	0.92 MPa
–	10.5 ± 0.6	10.7 ± 0.1	11.3 ± 0.2
0.500 wt.% TPD	11.0 ± 0.1	11.0 ± 0.1	11.9 ± 0.2
0.500 wt.% GA 80	11.1 ± 0.6	11.7 ± 0.3	11.0 ± 0.1

Conclusion

This paper provides polyol-ester-based pastes of high stability at temperatures up to 220 °C. The high thermal stability is associated with a low percentage loss in mass at elevated temperatures, the essential absence of viscosity increase as the temperature increases, and the essential absence of tendency for cracking at elevated temperatures. These attributes are valuable for the use of the pastes as thermal pastes for improving thermal contacts.

The high thermal stability mentioned in the last paragraph is attained by synergistic use of a primary antioxidant, a secondary antioxidant and a solid component in a polyol-ester-based paste. The antioxidants are dissolved in the polyol ester, but the solid component does not dissolve in the polyol ester.

All the antioxidants and antioxidant combinations used are effective for improving the thermal stability, whether a solid component is present or not. In the 200 °C over-aging condition, a synergistic effect occurs when a half-hindered primary antioxidant that has a high thermal stability is used along with a thiopropionate secondary antioxidant. A fully-hindered primary antioxidant is less effective than a half-hindered one. The increment of the total antioxidant proportion from 0.500 to 1.500 wt.% improves the thermal stability, unless a high degree of thermal stability is already attained at 0.500 wt.%. Carbon black and boron nitride as solid components improve the thermal stability for the case of a single antioxidant being used. However, when a primary antioxidant is used along with a secondary antioxidant, the addition of carbon black or boron nitride hinders the synergistic interaction between primary and secondary antioxidants.

In the TGA condition below 180 °C and in the presence of primary and secondary antioxidants, boron nitride enhances the thermal stability, while carbon black has little effect. However, at 220 °C and in the presence of primary and secondary antioxidants, both boron nitride and carbon black hinders the synergistic interaction between the antioxidants and hence degrades the thermal stability. Boron nitride paste shows a 100 °C lifetime indicator of 19 years, compared to 1.3 years for the carbon black paste, and 0.10 year for Arctic Silver 5.

In consideration of both the oven-aging and TGA results, the following general conclusions can be made. The antioxidants cause the residual weight (excluding the solid component) after heating at 200 °C for 24 h to increase substantially (from 36 to 97 wt.% for the case of oven aging and from 19 to 39 wt.% for the case of TGA). The antioxidants cause the viscosity to not increase upon heating and reduce the thermal cracking tendency. They do not affect the thermal contact conductance measured across mating surfaces that sandwich the paste. The use of a fully-hindered phenolic primary antioxidant is less effective. Both carbon black and boron nitride serve as antioxidants in the presence of either primary antioxidant or secondary antioxidant at 200 °C, though, in most cases, they degrade the thermal stability in the presence of both primary and secondary antioxidants, particularly at 220 °C. Below 180 °C and in the presence of primary and secondary antioxidants, boron nitride is particularly effective in promoting the thermal stability.

The thermal stability attained in this work is almost as high as that of the most thermally stable commercial pastes and is superior to Arctic Silver® 5, which also uses polyol esters as its vehicle. Arctic Silver® 5 also suffers from cracking after heating. Cracking after heating was not observed for the carbon black pastes corresponding to the residual weight above 57 wt.%, but it was observed for the boron nitride pastes corresponding to the residual weight above 53 wt.%.

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