



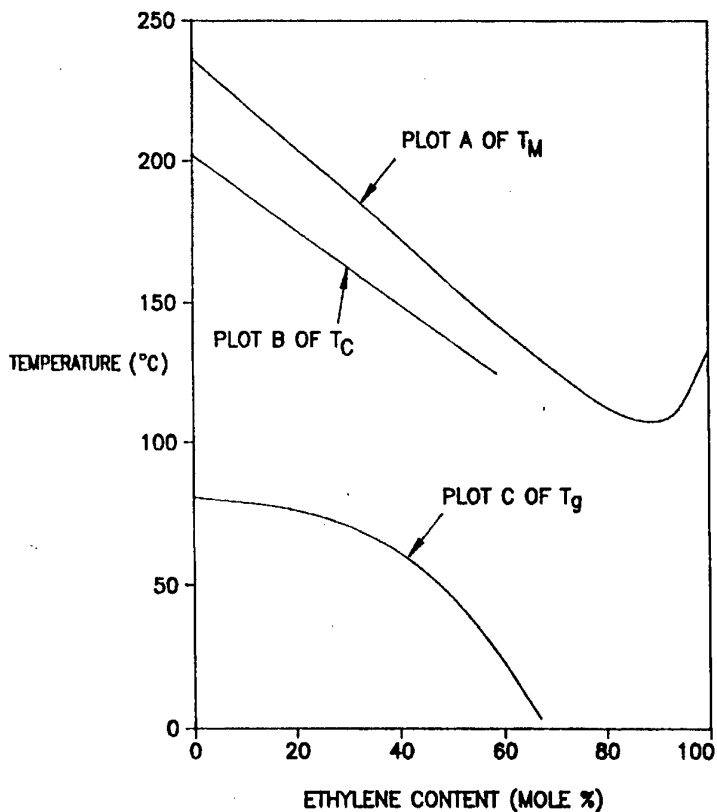
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(54) Title: REWORKABLE POLY(ETHYLENE-VINYL ALCOHOL) ADHESIVE FOR ELECTRONIC APPLICATIONS

(57) Abstract

The present invention provides a reworkable, semi-crystalline thermoplastic adhesive composition, suitable for bonding electronic components. The adhesive composition, preferably provided as an adhesive film, includes one or more poly(ethylene-vinyl alcohol) copolymers.



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**REWORKABLE POLY(ETHYLENE-VINYL ALCOHOL) ADHESIVE
FOR ELECTRONIC APPLICATIONS**

Field of the Invention

5 The present invention relates to adhesive compositions, and particularly to poly(ethylene-vinyl alcohol) adhesive compositions having properties especially suited for use in electronic applications. Specifically, the adhesive compositions are reworkable or
10 repairable in use with an integrated circuit, rigid circuit, or flexible circuit. More specifically, the adhesive compositions are suitable for flip chip direct attachment films for mounting semiconductors on conductive substrates.

15

Background of the Invention

Electronic devices such as pocket calculators, watches, and laptop computers utilize a wide variety of semiconductor based integrated circuit elements.
20 Typically, semiconductors are fabricated on wafers and then cut into individual chips. These chips are typically installed into single-chip packages that are attached to circuit boards via some type of soldering operation. In some instances however, unpackaged chips
25 have been attached directly onto circuit boards in order to achieve reduced product size and increased product performance. The benefits of this "flip-chip" packaging method are expected to increase as I/O counts, clock-rate frequencies, and power densities continue to increase.

30 The most common attachment means used for flip-chip bonding is solder bump interconnection. With this approach, metallurgical solder joints provide both the mechanical and electrical interconnections between the chip and substrate. This method has inherent pitch
35 limitations and also is extremely vulnerable to CTE and elastic modulus mismatches between the chip and substrate. Such mismatches result in high shear stresses in the solder joints that can compromise the reliability of the assembly. See, R.R. Tummalla and E.J.

Rymaszewski, Microelectronics Packaging Handbook, (Van Nostrand Reinhold, 1989) pp. 280-309; 366-391; and K. Nakamura, Nikkei Microdevices, June 1987. Catastrophic failure is the immediate result of any cracking that
5 occurs either in the solder joint or chip as a result of these stresses.

An alternative to solder bump flip-chip bonding is disclosed in U.S. Patent No. 4,749,120 (Hatada) and in U.S. Patent No. 4,942,140 (Dotsvki). These references
10 disclose liquid, curable adhesive systems which maintain pressure engaged electrical connections between a chip and a substrate. The presence of the adhesive at the interface tends to moderate the shear strain which in turn provides an increased capacity to accommodate
15 mismatches in the coefficients of thermal expansion (CTE) and elastic moduli. However, in order to be useful, the adhesive must be capable of sustaining stable contact forces, even in the presence of these stresses and at temperatures of 100°C or higher. The use of a highly
20 crosslinkable adhesive was assumed necessary in the above references to provide this level of stability.

One concern relative to liquid adhesives is that they must be applied in excess to assure that the entire die bonding surface is wet during the die placement, and
25 consequently the excess can flow into undesirable areas. In addition, curable materials such as these can be expected to be difficult, if not impossible to rework.

To solve the problems associated with liquid systems, adhesives can be provided in the form of self-
30 supporting films. A film is capable of being cut to the precise size of the die, which provides the exact amount of adhesive in the precise area necessary for die bonding. In U.S. Patent 4,820,446 (Prud'homme), a thermoplastic adhesive is disclosed for use in electronic
35 applications which is repairable. However, a deficiency of this and other related adhesives is that they tend to display high deformation at elevated stress and

temperature which leads to poor contact stability. Accordingly, such adhesives are useful only in applications involving limited stress. Thus, such adhesives are almost exclusively used for the bonding of
5 lightweight, flexible circuits to other components in which thermal stresses are minimal.

While certain highly crosslinkable, thermosetting adhesive films perform adequately in high stress applications, these adhesives are deficient in that they
10 are not reworkable. An example of such a non-reworkable adhesive composition, exhibiting superior shear-strengths at high temperatures, is disclosed in U.S. Patent No. 4,769,399 (Schenz).

Pujol et al., U.S. Patent No. 5,143,785 and
15 copending application Serial Number 07 816 854 (Hall et al.) disclosed reworkable, crosslinkable systems for use in electronic applications. These systems provide the very desirable reworkable property, but a non-reactive reworkable adhesive would provide further advantages such
20 as, for example, increased shelf-life.

U.S. Patent No. 5,061,549 (Shores) describes heat activated adhesive films suitable for electronic applications. The adhesive's main constituent is a thermoplastic polymer having a Vicat softening
25 temperature of from 70 to 280°C. Shores exemplifies a number of thermoplastic polymers (column 3, lines 14-48), but fails to recognize the beneficial effects of semi-crystalline polymers. While amorphous thermoplastic polymers do provide short bonding times and
30 repairability/reworkability for bonded circuit components, they do not have the strength above glass transition temperature (T_g) to provide a high level of dimensional stability or the steep viscosity/temperature gradient in the vicinity of the melt temperature (T_m)
35 that produces excellent wetting during bonding.

Crosslinkable hot-melt adhesives based on poly(ethylene-vinyl alcohol) in combination with an

isocyanate and a tackifier are disclosed in European Patent Application No. 302,620 A2 (Exxon Chemical, Inc.). Like thermoset adhesive systems, these adhesives are not reworkable once they are crosslinked. Furthermore, the curing time for these adhesives is longer than 15 minutes, which is not desirable for efficient mass production of consumer electronics products. The use of poly(ethylene-vinyl alcohol) as an adhesive coating for steel is briefly described in H. Kempe and M. Kempe, Plaste Kautsch, 34, 210-211 (1987).

In addition to the thermoplastic and thermoset adhesive systems, thermoplastic/thermoset blends are of possible interest for electrical interconnections. Such mixtures have been designed to improve high temperature performance of the thermoset materials, and/or to improve the fracture toughness of the thermoset material. See, U.S. Patent No. 3,530,087 (Hayes et al.); and R.S. Bauer, Toughened High Performance Epoxy Resins: Modifications with Thermoplastics, 34th International SAMPE Symposium, May 8-11, 1989.

However, despite the prior uses of thermoplastic adhesives, thermoset adhesives, and mixtures thereof, most presently known interconnect means for demanding applications, such as FDCA, have failed to adequately solve the problems set forth above. Accordingly, there remains a need for a non-reactive, reworkable adhesive that permits rapid bonding at a modest temperature and that also has a modulus sufficient to withstand significant stress and/or high temperatures, at least through the range of use temperatures. The adhesive should also be reworkable at a processing temperature, that is sufficiently low so that the substrate is not damaged during removal of a chip. There is also a need for such an adhesive that has an extended shelf life at room temperature (i.e., is storage-stable); has a low viscosity at the intended bonding temperature to provide good flow properties; is resistant to conditions of up to

85°C and 85% relative humidity; and may be provided as a film that is substantially tackfree at the intended handling temperature for repositioning.

5 Summary of the Invention

The present invention provides a reworkable thermoplastic adhesive composition comprising one or more semi-crystalline polymers suitable for bonding electronic components. The adhesive composition, preferably provides a nontacky or slightly tacky adhesive film, includes poly(ethylene-vinyl alcohol) copolymers having a glass transition temperature, T_g , of from 30° to 70°C, preferably from 40° to 60°C; a crystallization temperature, T_c , of from 115° to 155°C, preferably from 125° to 145°C. The T_m will typically be 130° to 170°C, preferably 140° to 160°C. Figure 2 shows that T_g , T_c and T_m are functions of the relative amounts of ethylene and vinyl alcohol in the semi-crystalline, thermoplastic copolymer.

20 The adhesive composition of the present invention preferably includes a silane coupling agent, and may also contain electrically conductive particles and other additives, especially additives selected to control the room temperature "tack" of the adhesive film.

25 The adhesive composition of the present invention has a modulus of greater than 50 MPa, preferably greater than 100 MPa, at a temperature of 20°C below the T_c of the cured adhesive composition.

The present invention also provides a method for forming a reworkable adhesive bond between two conductive surfaces to form a conductive bonded composite. The method comprises the steps of: providing a reworkable adhesive film of the present invention; providing a conductive substrate having one or more conductive bonding sites; providing one or more conductive devices, each having a conductive bonding surface; positioning the reworkable adhesive between each of the conductive

bonding sites and each of the conductive devices; and applying sufficient heat and/or pressure, for a sufficient time, to form a reworkable adhesive bond between each conductive bonding site and each conductive
5 device. The reworkable adhesive has a modulus of greater than 50 MPa at a temperature of 20°C below the T_g of the adhesive film. The conductive substrates are typically printed circuit boards having conductive bonding sites adapted to be bonded to integrated circuits, flexible
10 circuits, rigid circuits, or the like.

The bonding time required for adhesives of the present invention are typically fewer than 30 seconds, and preferably fewer than 20 seconds, at 200°C or less, preferably 185°C or less.

15 Semi-crystalline polymers, as used herein, are defined as, polymers that show crystalline behavior. Semi-crystalline polymer exhibit both a crystalline melting and glass transition temperature. See, e.g. Odian, *Principles of Polymerization (Second Edition)*,
20 John Wiley & Sons, New York, (1981), page 25 and 30.

"Melt temperature," as used herein, is the temperature at which the solid-to-liquid phase transition occurs in semi-crystalline polymers.

"Crystalline temperature" or "re-crystallization
25 temperature," as used herein, is the temperature at which the liquid-to-solid phase transition occurs in semi-crystalline polymers, since in semi-crystalline polymers there is a hysteresis in the solid-liquid phase transition depending on the temperatures through which it
30 is approached, i.e., heating the solid-to-liquid transition, or cooling the liquid-to-solid transition.

Reworkable adhesives of the present invention are typically entirely removable from the substrate at a temperature of less than 200°C, preferably less than
35 170°C. The reworkable adhesive of the invention will typically be entirely removable at T_m , because the use of excessively high temperatures may degrade the substrate

or conductive devices thereon. The use of a suitable solvent may also be necessary to remove remaining residue. It is preferred that the reworkable adhesive film be removable from a substrate selected from the group consisting of: conductive materials such as copper, gold, silver, aluminum, nickel, and solder; dielectrics such as ceramic, glass, silicon and epoxy/glass laminates; and polymer films such as polyimide and PET.

10 **Brief Description of the Drawings**

Fig. 1 is a schematic plan view of integrated circuits, printed circuit boards, and the like on which the adhesive composition of the present invention can be used;

15 Fig. 2 depicts a plot of temperature (T_c , T_m , T_g) as a function of ethylene content; and

Fig. 3 depicts elastic modulus as a function of temperature for an adhesive of the invention.

20 **Detailed Description**

A reworkable adhesive composition of the present invention may be produced using one or more semi-crystalline thermoplastic poly(ethylene-vinyl alcohol) polymer having a T_g of 30°C to 70°C, a T_c of from 115°C to 155°C, and a T_m of 130°C to 170°C. The adhesive film has a sufficiently high shear strength throughout the desired range of use temperatures, but demonstrates a sufficiently rapid drop in shear strength above its T_c so that at the melt temperature T_m , the adhesive is reworkable. "Shear strength" as used herein refers to the force needed to shear a chip off a glass substrate.

One of ordinary skill in the art would not be motivated to select copolymers of ethylene and vinyl alcohol as the polymeric component in adhesive compositions because these copolymers are inherently "non-tacky." These copolymers are noted for their low permeability to atmospheric oxygen and therefore have

utility as packaging materials for food, e.g. a component in the resins used to make plastic catsup bottles.

Adhesives used in electronic die attach applications are subjected to unusually high levels of stress due to

- 5 "mismatches" in the coefficients of thermal expansion (CTE) between microelectronic circuit chips, adhesive, and substrate to which the chips are bonded. When amorphous thermoplastic polymers are used in such highly stressed adhesive applications, it is normally required
10 that the T_g of the polymer exceeds the maximum temperature encountered in the use environment (T_{max}) in order to assure sufficient creep resistance to maintain electrical contact between chip and substrate. It is for this reason that many electronic die attach adhesives are
15 "cured" (chemically crosslinked) to raise T_g above T_{max} .

- In the semi-crystalline polymers used in the adhesives of the present invention, the detrimental creep associated with stress relaxation occurs at temperatures above the recrystallization temperature (T_c) which is
20 higher than T_g . Therefore semi-crystalline polymers generally provide adhesives with higher values of T_{max} than those derived from amorphous thermoplastic polymers. Semi-crystalline polymers preferred for reworkable adhesive applications are those having a sharp decline in
25 modulus between the recrystallization temperature (T_c) and the melt temperature (T_m), as shown in Figure 3.

- The adhesives of the present invention are film-type materials, typically coated on release liners. Due to the thermoplastic nature of the polymer in the
30 formulations, the compositions are fast bonding adhesives and they are repairable. Despite the relatively low T_g , high dimensional stability is maintained at high temperature due to the semi-crystallinity of poly(ethylene-vinyl alcohol). The polymers have a
35 crystallization temperature (115°C to 155°C) which insures high cohesion of the bond after recrystallization. The semi-crystallinity also provides

a steep viscosity/temperature gradient near T_m which leads to an excellent wetting during the bonding operations (see Fig. 3).

The reworkable adhesive film of the present invention is also preferably storage stable for at least one month at room temperature, has a sufficiently low viscosity at the bonding temperature to provide good flow properties, is rapidly bondable at a modest temperature e.g. 145°C to 225°C, more preferably 150°C to 215°C and most preferably 160°C to 200°C, and is not substantially affected by conditions of up to 85°C at 85% relative humidity.

The reworkable adhesive of the present invention is particularly useful in electronic applications. Many types of electronic components include one or more silicon chips. These chips are normally rectangular or square in shape and are of small dimension, e.g., a few millimeters (mm) on a side. Each chip has at least one, and often many, conductive terminals that must be electrically connected to conductive pathways on a substrate in order to complete the desired circuit. The pathways may comprise thin films or strips of metal, e.g., silver, gold, copper, etc., bonded to the substrate, or may consist of strips of an adhesive or ink which is electrically conductive or rendered electrically conductive by the presence of conductive particles therein.

The reworkable adhesive of the present invention is particularly useful as an attachment means in the FDCA bonding method. The FDCA bonding method bonds a bare chip directly to a conductive substrate. Certain chips have bumps (bumped chips) adapted to bridge the adhesive layer and connect directly to the substrate. An unbumped chip is typically bonded using an adhesive having an array of conductive particles that will form a conductive pathway between the substrate and the chip. FDCA bonding is discussed in Investigations Into The Use Of Adhesives

For Level-1 Microelectronic Interconnections, P.B. Hogerton et al., Electronic Packaging Materials Science, Symposia Proceedings, April 24-29, 1989.

Typical commercial bonding temperatures are in the
5 range of 145°C to 225°C, and more typically 160°C to
200°C. Bonding times can range from several minutes to a
few hours in the use of prior art adhesives, however,
for a commercially feasible, mass production assembly of
an electronic component, adhesives of the present
10 invention have preferred bonding times of 30 seconds or
fewer, preferably fewer than 20 seconds.

The reworkable adhesive composition of the present
invention is preferably provided as a film that is
nontacky or slightly tacky at the intended handling
15 temperature. The advantages of such an adhesive film
over a liquid or paste adhesive include ease of handling,
accurate alignment of the chip, and the ability to place
the exact amount of adhesive onto the chip to be bonded
with minimal waste.

20 The processing temperature is the temperature at
which the adhesive will be used to bond the chip to a
substrate. This temperature must be sufficiently low so
that the chips or substrates are not damaged during
processing, and must be sufficiently high so that the
25 adhesive will adequately bond the chip to the substrate.

Fig. 1 is a schematic plan view of integrated
circuits, printed circuit boards, and the like, on which
the adhesive composition of the present invention is
particularly suitable for use. A printed circuit board
30 10 is shown having flexible circuit terminals 20, printed
circuit board terminals 30, and printed circuit board
terminals 40. An adhesive of the present invention may
be utilized, for example, to bond flexible circuit 50 to
the flexible circuit terminals 20; a printed circuit
35 board 60 to the printed circuit board terminals 30; and a
TAB, i.e., tape automated bonding, lead frame 70 to the
printed circuit board terminals 40.

A TAB lead frame 72 is shown bonded to the printed circuit board 10. The printed circuit board 60 has flip chips 61-66. Flip chip 66 is shown prior to bonding to the printed circuit board 60. An adhesive of the present invention could be used to bond flip chips 61-66 to printed circuit board 60. Also shown in Fig. 1 is a liquid crystal display 80. The liquid crystal display 80 has the flexible circuit 50 bonded thereto. A flip chip 90 and a TAB lead frame 100 are also shown bonded to the liquid crystal display 80.

Fig. 2 shows a plot A of melting point (T_m), a plot B of crystallization temperature (T_c), and a plot C of glass transition point (T_g) as a function of ethylene content for an adhesive of the invention. This plot is only a generalized example of a typical adhesive of the invention and is not meant to limit the types of co-polymers or adhesives that can be used. The adhesive shown in Fig. 2 at 56% ethylene had a T_g of 55°C, a T_c of 142°C, and a 10-30 second bonding time at 180-230°C. The molecular weight of the co-polymers used correlates to the melt viscosity such as that exemplified in Fig. 2.

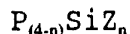
Fig. 3 shows a plot of elastic modulus (E') as a function of temperature (°C) for an adhesive of the invention. The upper modulus figure M corresponds to 100 MPa, and the lower modulus line N corresponds to 50 MPa. Adhesives of the present invention will have a modulus of greater than 50 MPa at a temperature of 20°C below the T_c . The temperature line B corresponds to 20°C below the T_c of the adhesive depicted in Fig. 3. The line A represents the T_c of the adhesive depicted in Fig. 3. The plot of modulus versus temperature 200 in Fig. 3 shows that the adhesive has a modulus of greater than 100 MPa at a temperature of 20°C below T_c .

35 Coupling Agents

The adhesive composition of the present invention may also include a coupling agent to aid in adhesion of

the adhesive to a given substrate. A silane coupling agent is preferred, and is preferably provided in an amount of 0.1 to 5 percent by weight of the composition, more preferably 1 percent by weight.

- 5 Preferred silane coupling agents have the formula:



in which:

- P represents an organic substituent of up to 12 carbon atoms, e.g., propyl, which should possess
10 functional substituents such as mercapto, epoxy, glycidoxy, acrylyl, methacrylyl and amino;

Z represents a hydrolyzable group, e.g., alkoxy, preferably methoxy or ethoxy, and

n is 1, 2, or 3, preferably 3.

- 15 In addition to silane coupling agents, titanate and zirconate coupling agents may be utilized. See, e.g., the chapter on coupling agents by J. Cromyn in Structural Adhesives edited by A.J. Kinloch, published by Elsevier Applied Science Publishers, 1986, pp 269-312. Page 270
20 provides examples of epoxy and amine silane coupling agents. Pages 306-308 discuss the use of titanate and zirconate coupling agents.

Additional Additives

- 25 Conductive particles, including, for example, those described in U.S. Patent No. 4,606,962 (Reylek et al.) and 4,740,657 (Tsukagoski et al.), may be added to the adhesive composition as desired. Reylek describes electrically and thermally conductive particles that at
30 the bonding temperature of the adhesive are at least as deformable as are substantially pure silver spherical particles. The thickness of the particles exceeds the thickness of the adhesive between the particles. The particles described in Reylek are preferably
35 substantially spherical and made of a metal such as silver or gold or of more than one material, such as "a solder surface layer and either a higher melting metal

core such as copper or a nonmetallic core" (column 4, lines 20-21). These and other conductive particles (e.g., non-spherical and/or having a thickness of less than the thickness of the adhesive) are suitable for use in the adhesive composition of the present invention.

Conductive particles contained in adhesive compositions of the invention may be randomly dispersed therein or may be arranged in a uniform array of desired configuration. To economize the use of electrically conductive particles, they may be located only in segments of the adhesive film which are to contact individual electrical conductors.

Other fillers can be added to the adhesive composition. The use of a filler can provide benefits of increased adhesion, higher modulus, and decreased coefficient of thermal expansion. Useful fillers include, but are not limited to, the following: silica particles, silicate particles, quartz particles, ceramic particles, glass bubbles, inert fibers, and mica particles. Preferably, the filler is microcrystalline silica particles.

It is important that the adhesive composition have a low ionic impurity level. The electronics industry specifies low extractable ion content of the adhesives. Specifications include Cl^- , Na^+ , K^+ , and NH_4^+ of less than 10 ppm. Such extremely low ionic contents are important to prevent corrosion of the metals and to keep the conductivity of the adhesive as low as possible except through any conductive metal particles present.

In the following examples, which are intended to be merely illustrative and nonlimiting, all percentages are by weight.

Examples 1-6

Adhesive compositions of the present invention were made as follows using components in the amounts shown in Table 1. The polymer was initially dissolved in methanol

and water at 60°C. The silica and conductive particles were added when the solution was still warm. The adhesive composition was cast onto a Teflon™ film using a knife coater. The thickness of the adhesive was set
5 between 20 and 40 μm by adjusting the distance between the knife and the backing. The adhesive film was dried at 50°C for one hour and stored in a desiccator.

Table 1
Formulations of Examples 1 through 6

<u>Component</u>	<u>Ex. 1</u>	<u>Ex. 2</u>	<u>Ex. 3</u>	<u>Ex. 4</u>	<u>Ex. 5</u>	<u>Ex. 6</u>
poly(ethylene-vinyl alcohol) SCE 105 ¹	14.92		15.25	15.17		12.42
poly(ethylene-vinyl alcohol) EPG 115 ¹					11.09	
poly(ethylene-vinyl alcohol) 4408M3 ²		19.28				
silica L207A ³	23.30		23.79	23.67	19.28	37.27
glycidoxypopyltrimethoxy- silane (3-GPMS)	0.45	0.60		0.46	0.39	0.62
methanol	54.31	72.17	55.47	55.24	69.24	45.22
water	5.37	7.95	5.49	5.46		4.47
gold/nickel/polystyrene conductive particles ⁴	1.65					

¹ from Eval Company of America, Lisle, Illinois

² Sellar OH from Du Pont De Nemours Company

³ Novacite from Malvern Minerals Company

⁴ Fine Pearl from Sumitomo Chemical

Example 7

The adhesion was evaluated for each of Examples 1, 2, 4, 5, 6 by measuring the die shear strength. The purpose of the test was to determine the applied force needed to shear the chip from the substrate. The bond strength was measured by using a shear tester on glass chips of 2 mm x 2 mm x 1 mm bonded to glass slides of 25 mm x 25 mm x 1 mm.

The following method was used to bond the chip on the slide. The adhesive was transferred to the glass chip by applying the chip onto the film and using heat activation and pressure to make the adhesive tacky. When the chip was removed from the release backing it was covered with a uniform layer of adhesive. Then it was applied to the slide. The bonding was accomplished with a die bonder for several seconds at 180°C under 2.5 MPa of pressure.

The specification for the selection and use of adhesives in microelectronic applications requires a minimum bond strength of 6 MPa (MIL STD 883C, method 5011). The results shown in Table 2 indicate that high adhesion is obtained with poly(ethylene-vinyl alcohol) adhesive compositions.

Table 2

**Adhesion of Poly(ethylene-vinyl alcohol)
Adhesive Compositions**

<u>Adhesive from Example #</u>	<u>Shear Strength (MPa)</u>
1	16.5
2	11.7
4	16.3
5	12.8
6	18.0

Example 8

The adhesive compositions of Examples 1-6 were used to bond silicon chips to circuits on glass substrates using a flip chip direct attachment method. The test
5 chips (0.5 mm x 7 mm x 7 mm) were bearing 120 gold bumped pads (pad pitch: 0.2 mm) to make the electrical connections. The circuits were indium tin oxide configured to permit a four probe resistance measurement. The indium tin oxide was 0.1 μm thick and had a sheet
10 resistance of 20 Ω per square.

The adhesive film was transferred to the active face of the chip by heating the film to 150-180°C on a hot plate surface and applying light pressure to laminate the film on the chip. The laminated structure was removed
15 from the hot plate after a few seconds.

The final flip chip on glass attachment was done after alignment of the chip with the conductive electrodes on the substrate. The bonding was done at 200°C by applying pressure (around 10 MPa) for 30
20 seconds.

Interconnection resistances were measured using a four probe method. Average resistance, minimum and maximum resistances were determined. The data shown in Table 3 are the measured resistances. They represent
25 twice the true interconnection resistance since two contacts are involved during the measurement; they include also the resistance of the indium tin oxide circuit on the glass substrate and the resistance of the aluminum strap connecting the gold bumps on the silicon
30 chip. From these observations, it is considered that a value lower than 2 Ω indicates a good interconnection.

Table 3Flip Chip on Glass Interconnection Resistances

<u>Adhesive From Example #</u>	<u>R Ave. (Ω)</u>	<u>R Min. (Ω)</u>	<u>R Max. (Ω)</u>
3	1.0	0.6	2.1
4	1.4	0.8	2.5
5	1.8	0.6	3.4

The data of Table 3 indicate that good electrical connections are obtained when using poly(ethylene-vinyl alcohol) compositions to bond flip chips on glass.

5

Example 9

Environmental testing of the test samples (Examples 3 and 4) from Example 8, were conducted under thermal aging and humidity aging.

During 1000 hours of thermal aging at 100°C, the
10 adhesive composition of Example 3 maintained the electrical connections without open circuits.

During 1000 hours of humidity aging at 60°C, 95% relative humidity (RH), the adhesive composition of Example 4 maintained the electrical connections without
15 open circuits.

Example 10

The adhesive composition of Example 1 was used to bond flexible circuits to printed circuit boards. The
20 flexible circuits were made of polyimide tape 10 mm wide x 50 μ m thick, metallized with copper and protected with a layer of lead-tin solder 12 μ m thick. The tape had 17 conductor lines spaced at a 0.4 mm pitch. The printed circuit boards were FR-4 epoxy glass laminates metallized
25 with copper and lead-tin solder 12 μ m thick with a similar pitch.

A piece of adhesive film 3 mm x 8 mm was transferred on the flexible circuit using heat activation and slight pressure. The final bonding to the board was done by

placing the tape on the board, aligning the stripes, applying pressure of 2 MPa on the tape and simultaneously heating the adhesive to 200°C for 30 seconds using a hot bar type bonder.

- 5 Interconnection resistances were measured using a four probe method. Average resistance, minimum resistance, and maximum resistance were determined. The data shown in Tables 4 and 5 are the measured resistances. They represent twice the true
- 10 interconnection resistance since two bonds are made on each test sample; they include also the resistance of the circuit board and the resistance of the flexible circuit. From these observations, it is considered that a value lower than 0.5 Ω indicates a good interconnection.

15

Table 4

Flexible Circuit on Board Interconnection Resistances

<u>Adhesive From</u> <u>Example No.</u>	<u>R Avg.</u> <u>(Ω)</u>	<u>R Min.</u> <u>(Ω)</u>	<u>R Max.</u> <u>(Ω)</u>
1	0.21	0.19	0.24

The data in Table 4 indicate that good electrical connections are obtained when using poly(ethylene-vinyl alcohol) compositions to bond flexible circuits on boards.

5

Example 11

- The following method was used to test the repairability of the adhesive. A test sample was prepared as described in Example 10. The epoxy glass
- 10 laminate substrate from the test sample was heated to 150°C at which temperature the flexible circuit was easily peeled off. The residues of the adhesive on the board were wiped away. A new flexible circuit was bonded to the board at 200°C for 30 seconds with a new piece of
- 15 adhesive using the bonding procedure described in Example

10. Connections obtained before and after rework are reported in Table 5.

Table 5

Interconnection Resistances Before and After Rework

<u>Adhesive From</u> <u>Example #</u>	<u>R Before Rework</u>			<u>R After Rework</u>		
	R Avg. (Ω)	R Min. (Ω)	R Max. (Ω)	R Avg. (Ω)	R Min. (Ω)	R Max. (Ω)
1	0.23	0.19	0.26	0.23	0.21	0.25

No significant difference was observed after rework of the adhesive. Good electrical connections were again achieved. The poly(ethylene-vinyl alcohol) compositions are repairable adhesives.

5

Example 12

Environmental testing of the test samples from Example 10 was conducted under humidity aging, thermal aging, and thermal cycling. Interconnection resistances were measured 10 after 1000 hours of testing.

Table 6
Flexible Circuit on Board Interconnection Resistances
After Environmental Testing

Adhesive From <u>Example #</u>	<u>Test</u>	<u>R Ave.</u> <u>(Ω)</u>	<u>R Min.</u> <u>(Ω)</u>	<u>R Max.</u> <u>(Ω)</u>
1	Thermal cycling -40, +105°C*	0.24	0.21	0.26
1	Thermal cycling -55, +125°C*	0.26	0.23	0.29
1	Thermal aging 100°C	0.22	0.20	0.25
1	Thermal aging 125°C	0.28	0.24	0.31
1	Humidity aging 60°C, 95% RH	0.23	0.21	0.26
1	Humidity aging 85°C, 85% RH	0.26	0.21	0.35
1	Humidity aging 60°C, 95% RH, 15V biased	0.26	0.24	0.29

*6 hour cycle

The results shown in Table 6 indicate that no significant degradation of contact resistances occurred. The poly(ethylene-vinyl alcohol) compositions show high stability under environmental testing.

5 The following comparative examples show that film adhesives using only amorphous, thermoplastic polymers as the high molecular weight resin component are not capable of maintaining suitably low contact resistances under the temperature-humidity extremes found in a typical use
 10 environment.

Comparative Amorphous Polymer A

A 30 micrometer thick, film-adhesive was prepared from a thermoplastic poly(vinyl butyral) resin designated B76.

B76 has a weight average molecular weight of about 50,000, a T_g of 50°C, and is available from Monsanto Chemical Corp. Saint Louis, MO. The film adhesive was cast from a 70% solids solution prepared by first dissolving B76 polymer in xylene followed by a sequential addition of isopropanol and water to produce a solution in which the solvent phase was 95% by weight (60:40 xylene:isopropanol) and 5% by weight water. The film adhesive was prepared by knife coating the polymer solution on a Teflon™ film substrate. The thickness of the adhesive was adjusted to between 20 and 40 micrometers by adjusting the distance between the knife and the backing. The adhesive was dried at 80°C for one hour and stored in a desiccator prior to bonding and testing.

This film adhesive was used to bond silicone test chips to an indium-tin oxide coated glass substrate and was tested using the procedure of Example 8. The following bonding conditions were used: temperature = 185°C, pressure = 140 KPa, a bond time = 30 seconds. The results are set forth in Table 7.

Table 7

Flip Chip on Glass Interconnection Resistances

Room Temp. Aging (HOURS)	R. Ave. (Ω)	R. Min. (Ω)	R. Max (Ω)
Sample 1 - 0 Hours	5.1	2.0	15.4
Sample 1 - 15 Hours	6.9	2.4	33.9
Sample 2 - 0 Hours	8.0	2.3	53.8
Sample 2 - 15 Hours	10.0	3.0	2.0E+16 (3 open)

Since the room temperature contact resistance was not stable, B76 thermoplastic adhesive was judged to be unsuitable for use in electronic die attach adhesive applications; therefore, more rigorous environmental testing similar to that of Example 9 was not performed.

Comparative Amorphous Polymer B

A 28 micrometer thick, film-adhesive was prepared from a thermoplastic poly(vinyl butyral) resin designated B98. B98 has a weight average molecular weight of 37,000, a T_g of 65°C, and is available from Monsanto Chemical Corp., Saint Louis, MO. The film adhesive was cast from a 85% solids solution prepared by first dissolving B98 polymer in xylene followed by the sequential addition of isopropanol and water to produce a solution in which the solvent phase was 95% by weight (60:40 xylene:isopropanol) and 5% by weight water. The adhesive film was prepared by knife coating the polymer solution on a Teflon™ film substrate. The thickness of the adhesive was adjusted to between 20 and 40 micrometers by adjusting the distance between the knife and the backing. The adhesive was dried at 80°C for one hour and stored in a desiccator prior to bonding and testing.

This adhesive film was used to bond silicone test chips to an indium-tin oxide coated glass substrate and was tested using the procedure of Example 8. The following bonding conditions were used: temperature = 275°C, pressure = 70KPa, bond time = 10 seconds. The test bonds were allowed to cool to 35°C, before releasing the bonding pressure. The results are set forth in Table 8.

Table 8Flip Chip on Glass Interconnection Resistances

Room Temp. Aging (HOURS)	R. Ave. (Ω)	R. Min. (Ω)	R. Max (Ω)
Sample 1 - 0 Hours	1.6	0.6	7.2
Sample 1 - 22 Hours	1.8	0.6	8.2

The B98 film adhesive was judged to have passed the room temperature aging test and was subjected to environmental testing similar to that of Example 9. The following environmental conditions were used: temperature = 60°C, relative humidity = 95%, time = 73 hours. At the

conclusion of the environmental aging test only 3 of the original 60 pairs of contacts had contact resistances less than 100,000 ohms, and B98 thermoplastic polymer was judged to be unsuitable for electronic die-attach adhesive

5 applications.

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention.

CLAIMS:

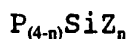
1. A reworkable thermoplastic adhesive composition comprising one or more semi-crystalline poly(ethylene-vinyl alcohol) copolymers having a T_g of from 30° to 70°C, a T_c of from 115° to 155°C, and at least one additive selected from the group consisting of conductive particles, coupling agent, and filler, such that said adhesive composition has a modulus of greater than 50 MPa at a temperature of 20°C below the T_c of the adhesive composition and provides a bond strength greater than 10 MPa as measured by MIL STD 883C, method 5011.

2. The reworkable thermoplastic adhesive composition of claim 1 wherein said composition has a T_g of 40°C to 60°C and a T_c of 125° to 145°C.

3. The reworkable adhesive composition of claim 1 wherein said adhesive film has a modulus of greater than 100 MPa at a temperature of 20°C below the T_c of the cured adhesive composition.

4. The reworkable thermoplastic adhesive composition of claim 1 comprising 0.1 to 5 percent by weight of a silane coupling agent.

5. The adhesive composition of claim 4 wherein said silane coupling agent has the following formula:



in which:

P represents an organic substituent of up to 12 carbon atoms; e.g., propyl, which should possess functional substituents selected from the group consisting of mercapto, epoxy, glycidoxy, acrylyl, methacrylyl and amino;

Z represents a hydrolyzable group, and

n is 1, 2, or 3.

6. A method for forming a reworkable adhesive bond between two conductive surfaces to form a conductive bonded composite comprising the steps of:

- (a) providing a reworkable adhesive film according to claim 1;
- (b) providing a conductive substrate having one or more conductive bonding sites;
- (c) providing one or more conductive devices each having a conductive bonding surface;
- (d) positioning said reworkable adhesive between each of said one or more conductive bonding sites and each of said conductive bonding surfaces of said one or more conductive devices; and
- (e) applying sufficient heat and/or pressure for a sufficient time to form a reworkable adhesive bond between each conductive bonding site and each conductive bonding surface;

wherein each of said one or more reworkable adhesive bonds has a modulus of greater than 50 MPa at a temperature of 20°C below the T_g of the adhesive film.

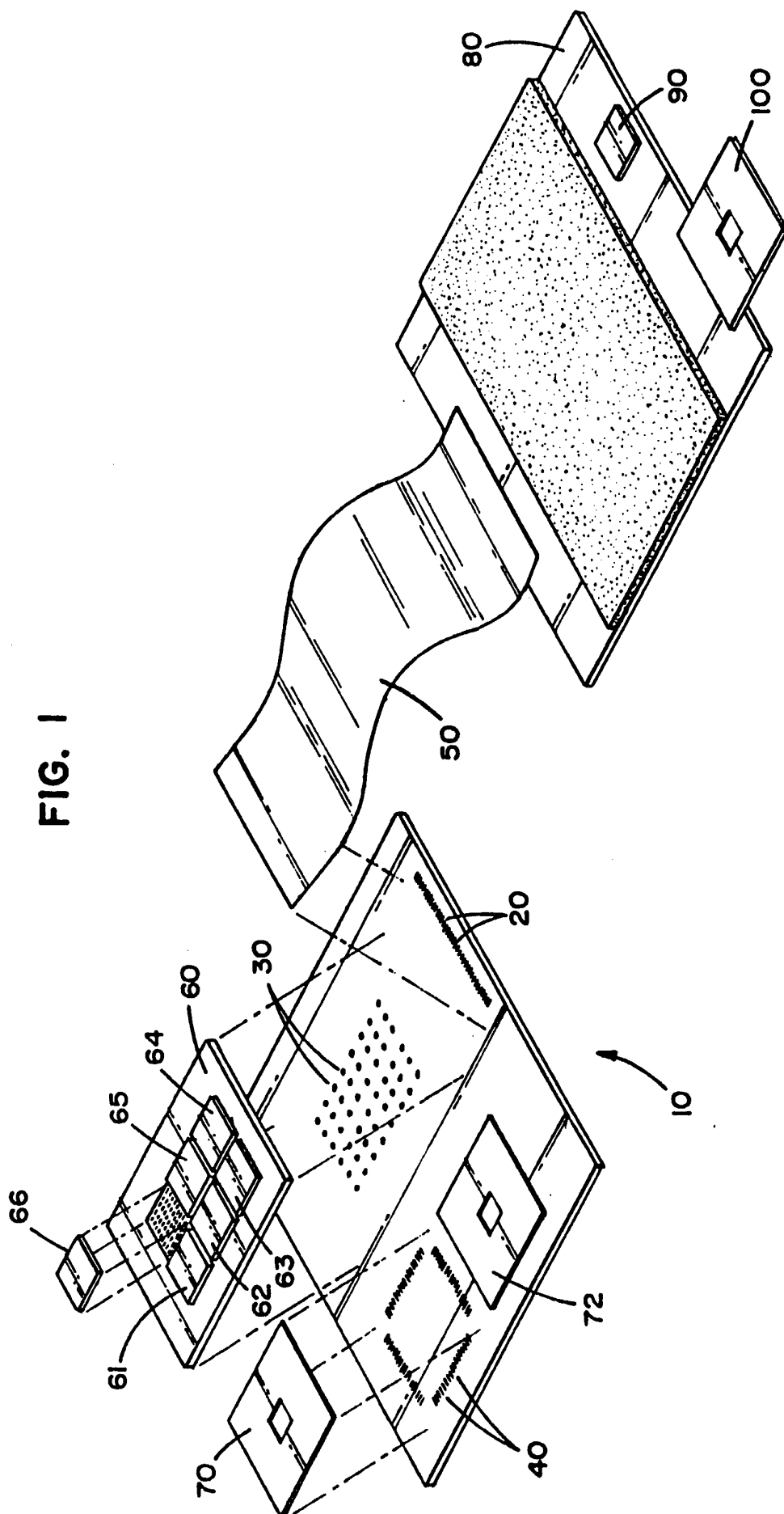
7. The method of claim 6 wherein said conductive substrate is a printed circuit board.

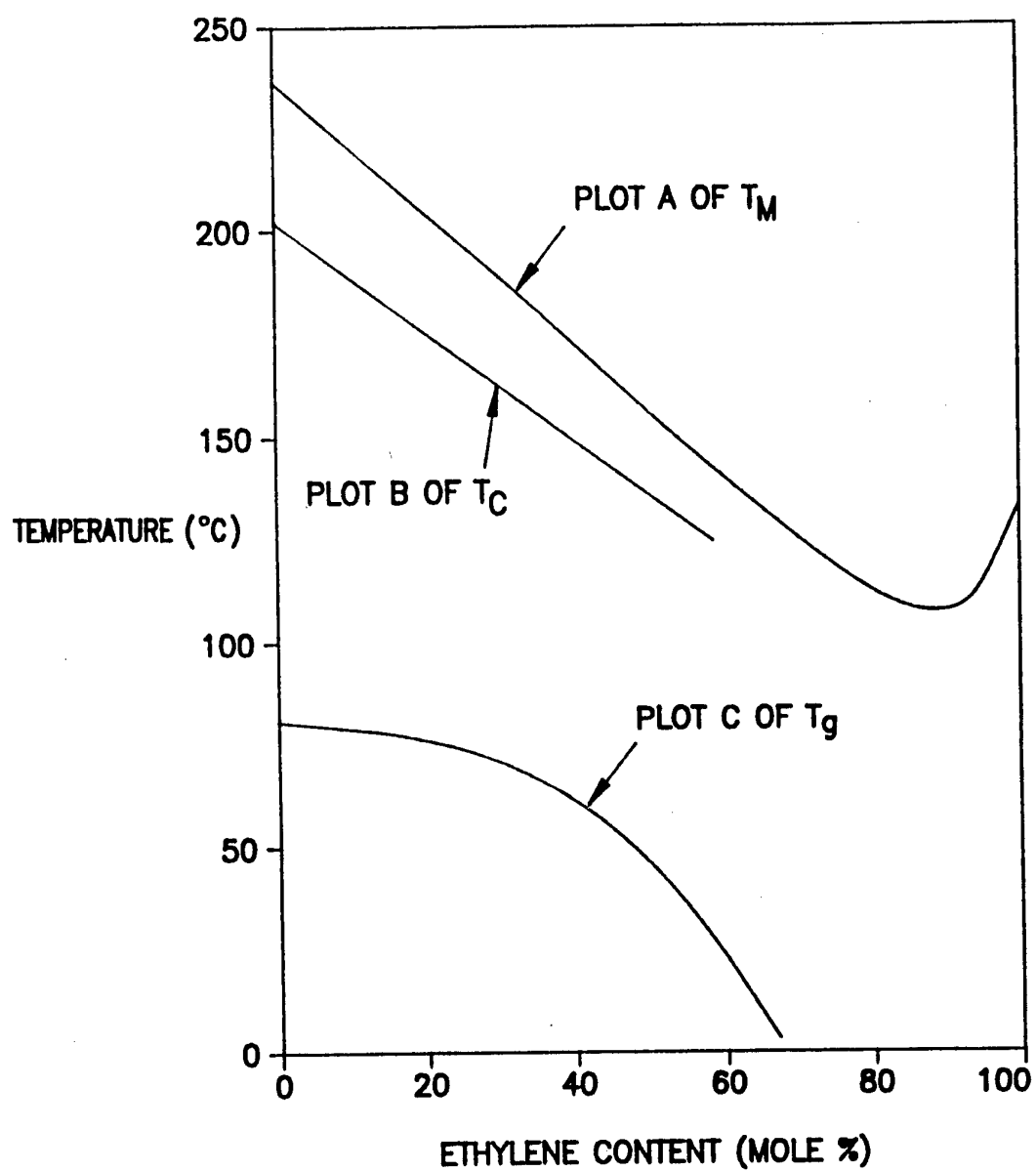
8. The method of claim 7 wherein one or more of said conductive devices are selected from integrated circuits and flexible circuits.

9. The method of claim 6 wherein said conductive bonding surface comprises a material selected from the group consisting of gold, silver, copper, aluminum, nickel, and solder.

10. The method of claim 6 wherein said reworkable adhesive film is heated to a temperature of between 145°C and 225°C to form said reworkable adhesive bond, said heat being applied for fewer than 30 seconds.

FIG. 1



**FIG. 2**

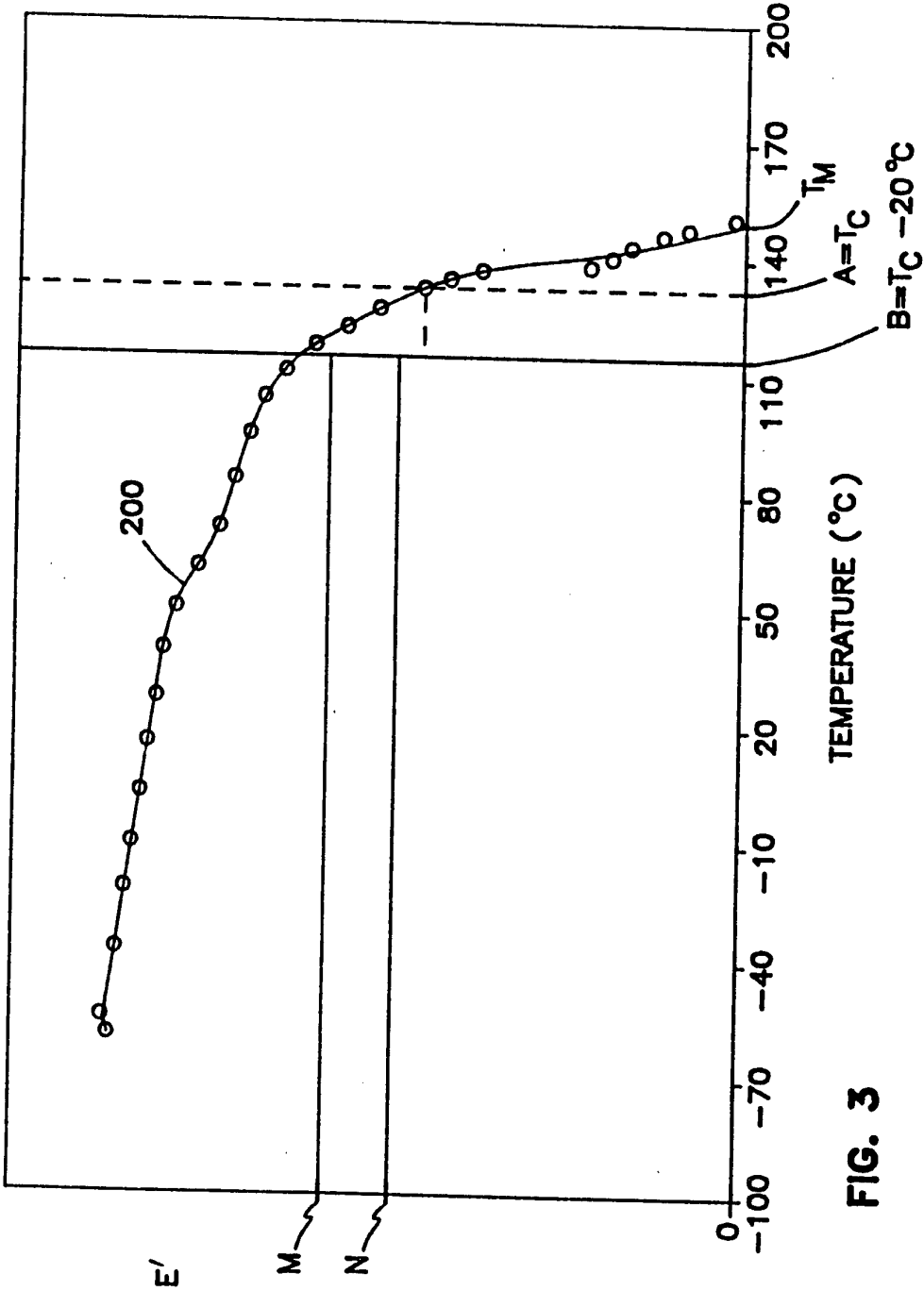


FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/02143

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 5 C09J123/28 C09J5/10 H01L21/58

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CHEMICAL ABSTRACTS, vol. 85, no. 12, 20 September 1976, Columbus, Ohio, US; abstract no. 79289n, 'heat- and water-resistant adhesives' see abstract & JP,A,76 053 541 (MITSUI POLYCHEMICALS CO LTD) 12 May 1976 -----	1



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

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T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search

31 May 1994

Date of mailing of the international search report

17.06.94

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Schueler, D

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP-A-76053541		NONE	