(12) UK Patent Application (19) GB (11) 2 174 994 A

(43) Application published **19 Nov 1986**

(21) Application No **8609954**

(22) Date of filing **23 Apr 1986**

(30) Priority data

(31) **60/092569** (32) **30 Apr 1985** (33) **JP**

(71) Applicant
Nissan Motor Co Ltd (Japan),
No 2 Takara-cho, Kanagawa-ku, Yokohama City, Japan

(72) Inventors
Tsueno Sakauchi,
Shozo Yamamoto

(74) Agent and/or Address for Service
Marks & Clerk, 57-60 Lincoln's Inn Fields, London WC2A 3LS

(51) INT CL^4
C09K 3/10 C08L 63/00 C09J 3/16

(52) Domestic classification (Edition H):
C3B 1C14A 1C15 1C1 1C22 1C6AX 1C6X 1C8B 1D2C 1D3 1L1B 1L2B 1L6A 1N1A 1N4F 1N6B 1N6X B2 N
U1S 1369 1383 3010 C3B

(56) Documents cited
None

(58) Field of search
C3B

(54) Rust preventive sealant for joints between sheet steel panels

(57) A sealant comprises, by weight, 100 parts of a base resin component which is a nearly 1:1 mixture of bisphenol A type epoxy resin and a bisphenol F type epoxy resin, 40-80 parts of an auxiliary resin component which is at least one kind of dimer acid modified epoxy resin, 25-40 parts of a reactive synthetic rubber, 60-150 parts of flake filler 16, e.g. flaky silica powder, and 60-130 parts of rust preventive pigment 14, e.g. a mixture of zinc oxide and zinc phosphate. This rust preventive sealant is fairly high in the strength of adhesion to oiled steel surfaces, and rupture of a seal structure using this sealant by the action of excessive shearing or peeling force is always in the manner of cohesive rupture within the sealant layer, so that the sealant remains adhered to the panel surfaces even after rupture of the seal structure.

GB 2 174 994 A

2174994

FIG. 1

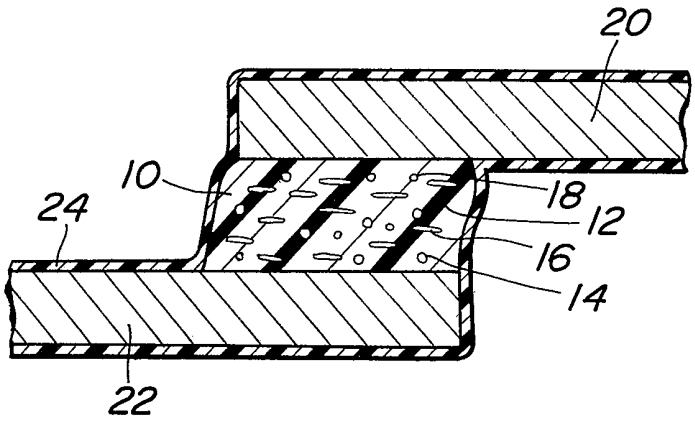


FIG. 2

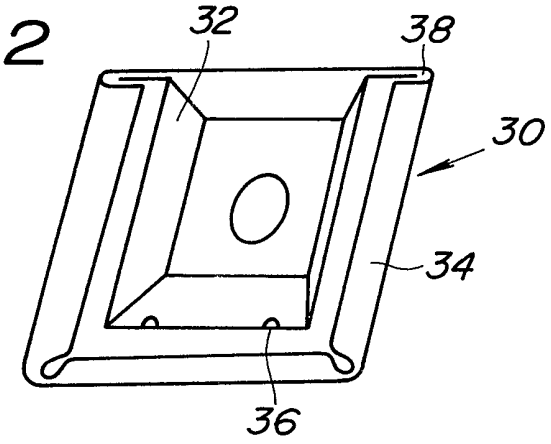
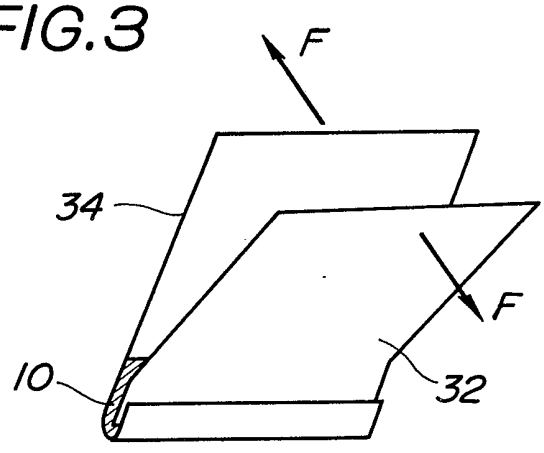


FIG. 3



SPECIFICATION

Rust preventive sealant for joints between sheet steel panels

In the manufacture of automobiles it is usual to apply a rust preventive sealant or adhesive to a joint between two panels made of sheet steel. Currently, chloroprene rubber base sealants and vinyl plastisol base sealants are prevailing for this purpose. In some cases epoxy resin base structural adhesives are used for rust preventive purposes too.

During practical use of an automobile it is not seldom that immoderate or excessive force attributed to an external cause, such as collision of the car body with something, acts on a joint between two steel panels in the car body to result in peeling of the rust preventive sealant from either of the two panels. It is likely that the peeling is undetected or overlooked even if a repair action is taken. Then a steel panel surface remains exposed in the damaged joint, and rusting of the steel panel begins in the joint region as rainwater or washing water intrudes into the joint.

It would therefore be desirable to be able provide a rust preventive sealant, which is suitable for application to joints between sheet steel panels and adheres strongly to steel surfaces, including oiled steel surfaces, such that the covering and rust inhibiting effects of the sealant last even a sealing structure provided between two panels by application of this sealant is broken by the action of immoderate shearing or peeling force.

The present invention provides a rust preventive sealant, comprising 100 parts by weight of a base resin component which is a mixture of 40–60 parts by weight of a bisphenol A type epoxy resin and 60–40 parts by weight of a bisphenol F type epoxy resin, 40–80 parts by weight of an auxiliary resin component which is at least one kind of dimer acid modified epoxy resin, 25–40 parts by weight of a reactive synthetic rubber, 60–150 parts by weight of a flake filler, and 60–130 parts by weight of a rust preventive pigment.

A rust preventive sealant according to the invention possesses an adhesive property and can be called a sealant or adhesive of cohesive rupture type. That is, in case of rupture of a seal layer formed between two steel sheets by using this rust preventive sealant by the action of excessive shearing or peeling force, cohesive rupture occurs within the seal layer before peeling of the seal layer from either of the two steel sheets takes place. As a result, the rust preventive sealant remains adhering to both of the two steel sheets in sufficient and nearly equal thicknesses. Therefore, the covering and rust preventive effects of the sealant lasts even after rupture of the seal structure. This rust preventive sealant is very suitable for application to joints between sheet steel panels used as automobile body parts.

It is usual that sheet steel panels as automobile body parts are assembled in a state coated with a rust inhibiting oil which is applied at the stage of press operations to form the panels. In the present invention a blend of a bisphenol A type epoxy resin and a bisphenol F type epoxy resin is used as a base resin component of the rust preventive sealant in view of good compatibility of these two types of epoxy resins with naphthene oil which is widely used as rust inhibiting oil for steel parts. These two types of epoxy resins are almost equivalent in many items of physical and chemical properties. The main purpose of jointly using these two types of epoxy resins is to facilitate to desirably adjust the liquid properties, and particularly viscosity of the resin component of the sealant.

The auxiliary resin component, which is at least one kind of dimer acid modified epoxy resin, and the reactive synthetic rubber are incorporated in the sealant composition mainly for the purpose of affording flexibility and elasticity to the sealant so that the sealant applied to a joint between two panels can follow deformation of the panels in the joint regions.

It is essential for a rust preventive sealant according to the invention to contain a specified amount of a flake filler besides a usually used rust preventive pigment. Primarily by reason of the presence of a flake filler this sealant becomes of a cohesive rupture type.

In the accompanying drawings:

Figure 1 is an explanatory and sectional illustration of a seal structure provided by applying a rust preventive sealant according to the invention to a joint between two panels;

Figure 2 is a perspective view of an assembly of two small steel panels used as specimens to test the rust preventive capabilities of sealants prepared as examples of the invention; and

Figure 3 shows the manner of causing forced rupture of a rust preventive seal structure in the specimen to be subjected to corrosion test.

As to the base resin component of a rust preventive sealant according to the invention, the use of a blend of a bisphenol A type epoxy resin and a bisphenol F type epoxy resin is described hereinbefore. In general bisphenol A type epoxy resins are better than bisphenol F type epoxy resins in resistance to showering but are rather inferior in deliverability. Therefore, it is desirable to use these two types of epoxy resins in nearly the same quantities.

At least one kind of dimer acid modified epoxy resin is incorporated to render the rust preventive sealant sufficiently flexible and to thereby enhance the flexibility, impact resistance and peel strength of the sealant. It is preferred to jointly use a dimer acid modified epoxy resin which has a relatively high molecular weight and is semi-solid at normal temperature and another dimer acid modified epoxy resin which has a relatively low molecular weight and is liquid at normal temperature. In such a case, it is suitable to use a blend of up to 40 wt% of the former (semi-solid) resin and the balance of the latter (liquid) resin.

The reactive synthetic rubber incorporated in a sealant according to the invention affords viscoelasticity to the sealant and therefore contributes to enhancement of the flexibility and impact resistance of the sealant. Furthermore, the rubber enters the epoxy molecules of the resin cmponents with the effects of preventing permeation of moisture through the sealant and enhancing the rust preventive capability of the sealant.

The importance of using a flake filler is described above. The material of the flake filler is not strictly limited. For example, a selection can be made from inorganic flaky powder materials such as silica powder, vermiculite powder, graphite powder, aluminium powder, and talc.

Examples of rust preventive pigments useful in the present invention are iron oxide powder, zinc powder, zinc oxide powder, zinc phosphate powder, trizinc phosphate powder, and zinc carbonate powder.

Besides these essential ingredients, rust preventive sealants according to the invention may contain an electroconductive filler such as carbon black because one often performs spot welding of the steel panels after application of a rust preventive sealant.

Furthermore, rust preventive sealants of the invention may contain a conventional curing agent for curing the resin components. For example, selection is made from dicyandiamide or modified dicyandiamide, acid anhydrides, hydrazines, carbamates and thiazoles.

Figure 1 illustrates a simplified model of a seal structure provided by applying a rust preventive sealant 10 of the invention to a joint between a steel panel 20 and another steel panel 22. In the seal layer formed of the sealant 10, rust preventive pigments 14, flake filler 16, and optional conductive filler 18 are uniformly dispersed in the matrix 12 of epoxy resins and synthetic rubber. After completion of the rust preventive seal structure the outer surfaces of the panel assembly is coated with a covering film 24 by an electrodeposition coating process. If excessive peeling force acts on the panel(s) 20 and/or 22, the seal layer 10 undergoes cohesive rupture without separating from the two panels 20, 22. That is, the panel surfaces in the joint region are still closely covered with the rust preventive sealant. Therefore, the rupture of the seal structure does not lead to rusting of the steel panels 20, 22.

The invention will further be illustrated by the following nonlimitative examples.

Examples 1–4

As Examples 1–4 of the present invention, four differently composed rust preventive sealants were prepared by blending the ingredients shown in Table 1. The quantities of the ingredients are given in percent by weight. The curing agent was a 1:2 mixture of a low-temperature working type curing agent and a high-temperature working type curing agent. These sealants were tested as described hereinafter.

TABLE 1

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Comp. Ex. 1	Comp. Ex. 2
Epoxy Resin						
Bisphenol A type	18	18	18	25	12	23
Bisphenol F Type	5	5	5	3	7	—
Dimer Acid Modified Epoxy Resin						
High Molecular Weight	3	3	3	3	2	3
Low Molecular Weight	15	15	15	10	20	15
Reactive Synthetic Rubber	8	8	8	8	8	8
Carbon Black	2	4	4	4	4	9
Curing Agent	3	3	3	3	3	3
Flake Pigment (silica)	20	25	30	30	10	10
Rust Preventive Pigment						
Zinc Powder	—	—	—	—	10	24
Zinc Phosphate	5	5	5	5	5	5
Zinc Oxide	19	14	9	19	19	—

Comparative examples

As Comparative Examples 1 and 2, two kinds of rust preventive sealants not in accordance with the invention were prepared by modifying the compositions of Examples 1–4 in the manners as shown in Table 1. In Comparative Example 1, the acid modified epoxy resin component and the rust preventive pigment component were excessively increased whereas the flake filler was decreased. In Comparative Examples 2 the bisphenol F type epoxy resin was omitted, and the flake filler was decreased. These rust preventive sealants were tested along with the rust preventive sealants of Examples 1–4.

Evaluation tests

1. Basic Tests

The rust preventive sealants shown in Table 1 were each subjected to peeling test (generally according to

JIS K 6854), shearing test (at room temperature and at 100°C, generally according to JIS K 6850), heat ageing test (generally according to JIS K 6829, item 17), low-temperature resistance test (generally according to JIS K 6829, item 15) and moisture resistance test (generally according to JIS K 6830, item 21). The results are shown in Table 2.

2. Corrosion Test

Figure 2 shows the outline of specimens used in this test. Each specimen 30 was an assembly of an inner panel 32 and an outer panel 34 which was hemmed along its three edges so as to couple with the corresponding edges of the inner panel 32. The inner and outer panels 32, 34 were made of an oiled steel sheet. The inner panel 32 was formed with drain holes 36. Each specimen 30 was 150 mm long and 150 mm wide. Preparatory to the hemming operation, a rust preventive sealant to be tested was applied to the outer panel 34, as indicated at 38 in Figure 2, along the edges to be fold back at a distance of about 5 mm from the bend line. The bead of the applied sealant had a diameter of about 3 mm. After the hemming operation the specimens 30 were left standing at room temperature for more than 1 h and then were entirely coated with a polyamide base paint by an electrodeposition coating process.

The corrosion test was a repetition of a sequence of (i) salt spraying (for 4 h, at 35°C, 5% sodium chloride solution), (ii) hot air drying (60°C, for 2 h), and (iii) moistening (for 2 h, at 50°C, at relative humidity of 95% or above). This sequence was cycled 200 times. The tested specimens were visually examined to judge the degree of rusting. The results are shown in Table 2.

3. Corrosion Test after Rupture of Seal Layer

As indicated by arrows F in Figure 3, peeling force was exerted on the inner and outer panels 32, 34 of the specimens assigned to this test, until rupture of the seal layer 10 either within the seal layer 10 or at the interface between the seal layer 10 and either of the two panels 32, 34.

The thus treated specimens were subjected to the above described corrosion test. In this case the sequence of (i) salt spraying, (ii) drying, and (iii) moistening was cycled 100 times. The tested specimens were visually examined to judge the degree of rusting. The results are shown in Table 2.

In Table 2, "A" in parentheses means cohesive rupture of the seal layer 10, and "B" means rupture or peel at the interface between the seal layer 10 and either of the two panels 32, 34. Each fractional number before "B" indicates the proportion of samples in which the rupture was interfacial in the total samples: cohesive rupture of the seal layer occurred in the remaining samples.

TABLE 2

Sealant	*Peel Strength* (kg/25mm)	*Shear Strength* (kg/cm^2)	*High Temp. Shear Strength* (kg/cm^2)	*Heat Aging (peel strength)* (kg/25mm)	*Low Temp. Resistance (peel strength)* (kg/25mm)	*Moisture Resistance (peel strength)* (kg/25mm)	*Corrosion Test* (rusting)	*Corrosion Test after Peeling* (rusting)
Ex. 1	14.5 (A)	151 (A)	86 (A)	15 (A)	17 (A)	17 (A)	no	no
Ex. 2	12 (A)	136 (A)	75 (A)	11 (A)	15 (A)	10 (A)	no	no
Ex. 3	9(A)	115 (A)	70 (A)	10(A)	13 (A)	7 (A)	no	no
Ex. 4	12(A)	195 (A)	106 (A)	9 (A)	4 (A)	7 (A)	no	no
Comp. Ex. 1	18 (1/2B)	135 (1/2B)	72 (1/2B)	19 (1/2B)	21 (1/2B)	17 (1/2B)	no	heavy
Comp. Ex. 2	9 (1/2B)	123 (1/2B)	70 (1/2B)	10 (1/2B)	12 (1/2B)	9 (all B)	no	heavy

As can be seen in Table 2, the rust preventive sealants as examples of the invention were fairly high in adhesion strength and exhibited very good rust preventive effects even after forced rupture of the seal structure by the action of excessively great input force in the peeling directions. Such excellence in the rust preventive performance is attributed to the fact that the applied sealant remained nearly uniformly on both of the opposite two panel surfaces even after forced rupture of the seal structure, since the rupture was always in the manner of cohesive rupture of the rust preventive sealant layer itself.

CLAIMS

1. A rust preventive sealant for application to joints betwen sheet steel panels, comprising:
100 parts by weight of a base resin component which is a mixture of 40–60 parts by weight of a bisphenol A type epoxy resin and 60–40 parts by weight of a bisphenol F type epoxy resin;
40–80 parts by weight of an auxiliary resin component which is at least one kind of dimer acid modified epoxy resin;
25–40 parts by weight of a reactive synthetic rubber;
60–150 parts by weight of a flake filler; and
60–130 parts by weight of a rust preventive pigment.

2. A sealant as claimed in claim 1, in which the auxiliary resin component is a mixture of up to 40 wt% of a first dimer acid modified epoxy resin which is relatively high in molecular weight and is semi-solid at room temperature and the balance of a second dimer acid modified epoxy resin which is relatively low in molecular weight and is liquid at room temperature.

3. A sealant as claimed in claim 1 or 2, in which the material of the flake filler is selected from the group consisting of silica, vermiculite, graphite, aluminium, and talc.

4. A sealant as claimed in claim 1, 2, or 3, in which the rust preventive pigment comprises a pigment selected from the group consisting of iron oxide powder, zinc powder, zinc oxide powder, zinc phosphate powder, trizinc phosphate powder, and zinc carbonate powder.

5. A sealant as claimed in any preceding claim, further comprising an electroconductive filler.

6. A sealant as claimed in claim 5, in which the electroconductive filler is carbon black.

7. A sealant as claimed in any preceding claim, further comprising a curing agent for epoxy resins.

8. A sealant substantially as described in any of Examples 1 to 4.

Printed in the UK for HMSO, D8818935, 9/86, 7102.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.