

#### US00RE34066E

# United States Patent [19]

Patent Number: Re. 34,066 [11] E

[45] Reissued Date of Patent: Sep. 15, 1992 Yamamoto et al.

1 (11)	HAIHOLO CI	L &LL.	[75] Reissueu	Date	OI I ALCIIL.	5cp. 15, 1772
[54]	PRIMER (	COMPOSITIONS	4,103,056	7/1978	Baratto et al	428/142
[75]	Inventors:	Shosaku Yamamoto; Kazuo Kakinuma, both of Yokohama, Japan	4,320,170	3/1982	Findlay	
[73]	Assignee:	Nippon Oil & Fats Co., Ltd., Japan	4,448,843	5/1984	Yamada et al.	
	Appl. No.:		4,529,632	7/1985	Fujii et al	524/871
[22]	Filed:	May 2, 1990	4,551,498	11/1985	Yeater et al	
Reiss	Relat sue of:	ed U.S. Patent Documents			Kikukawa et a 'ATENT DOC	1 428/694 CUMENTS
[64]	Patent No Issued: Appl. No. Filed:	May 16, 1989	2030992 1577998 Primary Exam	4/1980 10/1980 miner—I	United Kingdo United Kingdo Herbert J. Lilli	m . m . ng
[30] Jan	Foreig	n Application Priority Data  P] Japan	[57]		rm—Parkhurst ABSTRACT	, Wendel & Rossi
[51]	Int. Cl. <sup>5</sup> U.S. Cl		A primer consherts in vehicles in the consing a glass to	icle bodi sisting es ransition	es consists essessessentially of at temperature	el sheets and plastic entially of a compo- least one resin hav- of not higher than
[58]		arch	elongation at not greater th	break o	of not less than %, at 20° C. an	n -75° C., and an 400%, preferably d a component (B) crosslinking resin,
[56]	U.S. I	References Cited PATENT DOCUMENTS	_	•		of (A) to (B) being
3	3,919,444 11/1	1975 Shayman 428/95		- ~*	J 187 - 188 - 1	

6 Claims, No Drawings

10

#### PRIMER COMPOSITIONS

Matter enclosed in heavy brackets [ ] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

#### **BACKGROUND OF THE INVENTION**

#### 1. Field of the Invention

This invention relates to a primer composition adaptable for both steel sheet and plastic sheet as vehicle bodies.

#### 2. Related Art Statement

Lately, the use of plastic materials for automotive 15 parts has rapidly progressed since it can reduce the weight of the vehicle body, act as a rust-preventing means and increase freedom of design in the automobile industry. Moreover, the vehicle body is typically formed by intricately combining steel sheet with plastic 20 sheet.

In this case, there has hitherto been adopted a method wherein the painting of all the materials is first performed and then the painted materials are assembled in a final step.

The steel sheet is degreased and phosphated to form a phosphate layer thereon. After an under coat is formed by electrodeposition, a chipping primer or a [stoneger] stronger coat is partially applied and then an intermediate coat and a top coat are formed thereon. 30

On the other hand, the plastic sheet is degreased, dried and coated with a primer for the plastic sheet. Then, an exclusive intermediate coat and an exclusive top coat are successively formed thereon. In this case, the formation of the exclusive intermediate coat may be 35 omitted.

Thereafter, the painted plastic sheet is assembled onto the painted steel sheet.

In another painting method, the plastic sheet is degreased, dried, coated with an exclusive primer, baked 40 and then assembled onto the steel sheet which is previously degreased, phosphated and coated with an under coat, and thereafter the common intermediate coat and top coat are formed and baked on the assembly of the plastic sheet and steel sheet.

According to these conventional painting methods, however, the structure of the resulting paint coats formed is different between the plastic sheet and the steel sheet and the paint used and the painting step are also different, so that there are caused the following 50 problems:

- (1) Since the painting equipment must be separately arranged for the painting of steel sheet and for the painting of plastic sheet, not only the operation efficiency is poor but also the huge equipment investment is re- 55 quired;
- (2) The difference in appearance such as color tone, gloss and the like is caused between the plastic sheet and the steel sheet to degrade the commercial value of the automobile as a whole;
- (3) The difference in the durability of painted coating is caused between the plastic sheet and the steel sheet to detract from the [apperarance] appearance of the automobile over time; and
- (4) When the plastic sheet is coated with the exclusive 65 primer, assembled into the steel sheet and then the resulting assembly is subjected to a painting together, there problems (1)-(3) above are not caused. In the

selection of paints for intermediate coat and top coat, however, when a soft coating is used in compliance with the plastic sheet, the weather resistance, polishing property, solvent resistance, stain resistance and the like are degraded, and when a hard coating is used in compliance with the steel sheet, the impact resistance, chipping resistance and the like on the plastic sheet are degraded.

#### SUMMARY OF THE INVENTION

The present invention is directed to a primer composition consisting essentially of a component (A) consisting essentially of at least one resin having a glass transition temperature of not higher than  $-20^{\circ}$  C. and an elongation at break of not less than 400% at 20° C. and a component (B) consisting essentially of at least one crosslinking resin. The weight ratio as solid resin content of component (A) to component (B) is 70-99:30-1. The primer composition is applied onto an under coat formed in the case of the steel sheet by electrodeposition and, in the case of the plastic sheet, as a primer for plastic, whereby the simultaneous painting for of the intermediate coat and top coat as a hard coating used for steel sheet is possible and the aforementioned problems can be solved.

That is, the invention provides a primer composition consisting mainly of a component (A) composed of at least one resin having a glass transition temperature of not higher than  $-20^{\circ}$  C. and an elongation at break of not less than 400% at 20° C. and a component (B) composed of at least one crosslinking resin, and having a weight ratio as solid resin content of component (A) to component (B) of 70-99:30-1.

# DESCRIPTION OF THE PREFERRED EMBODIMENTS

The component (A) used in the invention is selected from well-known polyurethane resin, polyvinyl resin, polyolefin resin, polyester resin, polyacrylic resin and linear high molecular weight elastomer composed fundamentally of their modified resin.

On the other hand, the component (B) used in the invention is selected from well-known melamine resin, urea resin, polyisocyanate resin and a modified resin thereof, and may include resins capable of chemically reacting with the crosslinking resin, such as a reactive functional group containing acrylic resin, epoxy resin, polyester resin, polyurethane resin and so on.

When the resin used as the component (A) has a glass transition temperature of higher than  $-20^{\circ}$  C. and an elongation at break of less than 400% at 20° C., the flexibility of the resulting coat is poor, and the impact resistance and chipping resistance on the plastic sheet are not satisfied, and the chipping resistance on the steel sheet is also poor.

Even when the resin satisfies the conditions defined as the component (A), if only the component (A) is used, the ability to withstand heating-cooling cycles is 60 poor when used as an overall coat comprising an under coat, an inter (i.e., intermediate) coat and a top coat and considerable cracks are undesirably caused in the coating. For this reason, the component (A) is used together with the component (B) in a weight ratio as solid resin content of component (A) to component (B) of 70-99:-30-1, whereby satisfactory heating-cooling cycle properties can be obtained. According to the invention, the components (A) and (B) are essential.

Since the component (B) is a crosslinking resin as mentioned above, when the solid content of component (B) in the primer composition exceeds 30% by weight, the flexibility of the resulting coating lowers, and the chipping resistance and impact resistance on the plastic sheet are poor, and the chipping resistance on the steel sheet is not satisfied, while when it is less than 1% by weight, the crosslinking effect is poor, and the heatingcooling cycle property is deteriorated, and cracks are produced in the coating.

The primer composition consisting of the components (A) and (B) according to the invention may contain a pigment. As the pigment, mention may be made of inorganic and organic pigments usually used in the paint, such as titanium dioxide, carbon black, talc, kaolin, calcium carbonate, magnesium carbonate, barium sulfate, iron oxide, cyanine blue, quinacridone red and so on. In order to form the inter coat and top coat by electrostatic painting, it is favorable if the resulting coating has electrical conductivity. In this case, a conductive pigment, particularly conductive carbon black can be used, wherein the surface resistivity is usually suitable to be not more than  $10^{10} \Omega$ .cm.

In the primer composition according to the invention, it is desirable that a ratio of pigment to components (A)+(B) is 0-2.0. When this ratio exceeds 2.0, the flexibility of the coating is poor, and the chipping resistance on the steel sheet and the chipping resistance and impact resistance at low temperature on the plastic sheet 30 are poor.

[Or-ganic] Organic solvent is provided to uniformly dissolve the components (A) and (B) and stably store them for a long time. Suitable solvents includes organic solvents for usual paint, such as ketones, esters, aromat- 35 ics, alcohols, aliphatics and the like.

If necessary, the primer composition according to the invention may be compounded with additives for paint such as surface regulating agent, antisettle agent, heat degradation preventing agent, light degradation pre- 40 venting agent, pigment dispersing agent and the like as well as a reaction catalyst for promoting the reaction.

The primer composition according to the invention may be produced by the usual paint manufacturing process or pigment dispersing process. When the primer 45 composition does not contain a pigment, it can be produced by mixing the components (A) and (B) with, if necessary, additives for paint and organic solvent in the well-known agitating device such as dissolver to form a uniform resin solution. On the other hand, when the 50 primer composition contains a pigment, it can be produced by dispersing the pigment into a part or whole of the resin in the well-known pigment dispersing machine such as attritor, sand mill or the like and then adding the remaining resin, organic solvent and additives for paint 55 thereto so as to adjust the viscosity to a given value.

As a means for applying the primer composition according to the invention, use may be made of wellknown painting manners such as air spraying, electrostatic air spraying, electrostatic spray painting and the 60 tion of xylene and butyl acetate so as to adjust a spraylike.

The primer composition according to the invention is simultaneously applicable to the steel sheet for vehicle bodies after the painting of under coat and the plastic sheet after degreasing and drying. After the application 65 of the primer composition, the primer coating is left to stand at room temperature for 1-10 minutes, or the forced drying is carried out at 80° C. for about 30 min-

utes. Then, inter and top coats usually used can be formed thereon.

Even when the primer composition is applied to both the steel sheet and plastic sheet, the painting of inter coat can be omitted, if necessary. As a paint for inter coat and top coat, there may be used paints usually used for the steel sheet for a vehicle body and the plastic sheet.

As the plastic material applicable to the primer composition according to the invention, mention may be made of ones used as a plastic for vehicle body, such as polyamide resin, polybutylene terephthalate resin, polyurethane resin, polycarbonate resin, unsaturated polyester resin, polypropylene resin, a mixture thereof, a reinforced resin thereof and the like. However, the invention is not restricted to these resins as a plastic material.

As mentioned above, the primer composition according to the invention can simultaneously be applied to the steel sheet for a vehicle body and the plastic sheet for a vehicle body owing to the presence of the components (A) and (B) at a particular weight ratio, so that it is possible to simultaneously paint the same hard inter coat and hard top coat to both the sheets with the same painting equipment and to effect the baking in the same baking furnace. Therefore, the uniformity of qualities in the painted coats on both the sheets, for example, appearance qualities such as color tone, gloss and the like and durability qualities such as weather resistance, chemical resistance and the like can be made complete.

Further, when the primer composition according to the invention is applied to the undercoated steel sheet, the chipping resistance, heating-cooling cycle property and the like are improved, and when it is applied to the plastic sheet for vehicle body, the chipping resistance, heating-cooling cycle property, impact resistance and the like are improved.

The following examples are given in illustration of the invention and are not intended as limitations thereof. In the examples, all percentages are by weight, unless otherwise stated.

#### EXAMPLE 1

#### (Production of primer)

100 g of mixture having a compounding recipe as shown in Table 1 was mixed in a dissolver and added with an equal mixed solution of xylene and butyl acetate so as to adjust a spraying viscosity to 13 seconds (20° C.) as Ford cup No. 4, whereby a primer composition was produced.

# EXAMPLES 2-17, COMPARATIVE EXAMPLES

# (Production of primer)

100 g of a mixture having a compounding recipe as shown in Table 1 was thoroughly kneaded in a dissolver and then mixed in a paint shaker for 1 hour. The resulting composition was added with an equal mixed soluing viscosity to 13 seconds (20° C.) as Ford cup No. 4.

The details of components shown in Table 1 are as follows.

Polyurethane resin varnish I:

Resin solution prepared by adding an equal mixed solution of xylene and methyl isobutyl ketone (MIBK) to Sanprene LQ-377 (trade name, made by Sanyo Chemical Industries, Ltd., elongation at break: 610%, 5

glass transition temperature — 35° C.) and having a solid content of 20%.

Polyurethane resin varnish II:

Resin solution prepared by adding an equal mixed solution of xylene and MIBK to Sanprene LQ-X35B 5 (trade name, made by Sanyo Chemical Industries, Ltd., elongation at break: 440%, glass transition temperature: -20° C.) and having a solid content of 20%.

Polyurethane resin varnish III:

Resin solution prepared by adding an equal mixed 10 solution of xylene and MIBK to Nipporan 2301 (trade name, made by Nippon Polyurethane Industry Co., Ltd., elongation at break: 600%, glass transition temperature: -20° C.) and having a solid content of 15%.

Polyurethane resin varnish IV:

Resin solution prepared by adding an equal mixed solution of Cellosolve acetate (trade name) and MIBK to Desmorac 2100 (trade name, made by Sumitomo Bayer Urethane Co., Ltd. elongation at break: 350%, glass transition temperature: -15° C.) and having a 20 solid content of 15%.

Ethylene-vinyl acetate copolymer resin varnish I:

Resin solution prepared by adding a mixed solution of xylene and MIBK with a mixing ratio of 2:1 to Evaflex ® 150 (trade name, made by Mitsui Polychemical 25 Company, Ltd., elongation at break: 900%, glass transition temperature: -30° C.) and having a solid content of 20%.

[Ethylne] Ethylene-vinyl acetate copolymer resinvarnish II:

Resin solution prepared by adding a mixed solution of xylene and MIBK with a mixing ratio of 2:1 to Evaflex ® 410 (trade name, made by Mitsui Polychemical Company, Ltd., elongation at break: 300%, glass transition temperature: -20° C.) and having a solid content 35 of 15%.

Ethylene-vinyl acetate copolymer resin varnish III:

Resin solution prepared by adding an equal mixed solution of toluene and xylene to MB-600 (trade name, made by Nippon Unicar Co., Ltd., elongation at break: 40 880%, glass transition temperature: -75° C.) and having a solid content of 10%.

Ethylene-ethyl acrylate copolymer resin varnish:

Resin solution prepared by adding an equal mixed solution of toluene and xylene to MB-870 (trade name, 45 made by Nippon Unicar Co., Ltd., elongation at break: 800%, glass transition temperature: -75° C.) and having a solid content of 10%.

Polyolefin resin varnish:

Resin solution prepared by adding toluene to Unistol 50 P (trade name, made by Mitsui Petrochemical Industries, Ltd., elongation at break: 500%, glass transition temperature: -40° C.) and having a solid content of 7%.

Chlorinated ethylene - vinyl acetate copolymer resin 55 varnish:

Resin solution prepared by adding an equal mixed solution of toluene and xylene to Superchlon BX (trade name, made by Sanyo-Kokusaku Pulp Co., Ltd., elongation at break: 600%, glass transition temperature: 60 - 50° C.) and having a solid content of 15%.

Polyisocyanate resin varnish:

Coronate HL (trade name, made by Nippon Polyure-thane Industry Co., Ltd., solid content: 75%).

Block isocyanate resin varnish:

TPKL-5-2544 (trade name, made by Sumitomo Bayer Urethane Co., Ltd., solid content: 75%).

n-Butylated urea resin varnish:

6

Super Bekamin P-138 (trade name, made by Dainipon Ink and Chemicals, Inc., solid content: 60%).

Isobutylated melamine resin varnish:

Yuban 60R (trade name, made by Mitsui Toatsu Chemicals, Inc., solid content: 50%).

Titanium dioxide:

JR-602 (trade name, made by Teikoku Kako Co., Ltd.).

Carbon black:

Rarben 420 (trade name, made by Columbian Carbon, Japan).

Conductive carbon black:

Vulcan XC-72 (trade name, made by Cabot Corp.). Calcium carbonate:

Homokal D (trade name, made by Shiraishi Kogyo K.K.).

#### (Painting of steel sheet)

A cold rolled steel sheet of  $0.8 \text{ mm} \times 70 \text{ mm} \times 150 \text{ mm}$  was subjected to a phosphating treatment with Bonderite #3004 (trade name, made by Nihon Parkerizing Co., Ltd.), coated with a cation electropaint of Aqua No. 4100 (trade name, made by Nippon Oil and Fats Co., Ltd.) as an under coat, and then dried by baking at 175° C. for 20 minutes. The dried thickness of the resulting electrocoating was 20  $\mu$ m.

Then, each of the aforementioned primer compositions was applied by an air spray painting process, and thereafter Epico No. 1500 Sealer TX-100 (trade name, made by Nippon Oil and Fats Co., Ltd.) was applied as an amino/oil-free polyester resin series inter coat of wet-on-wet system by an air spray painting process and dried by baking at 140° C. for 30 minutes. The dried thickness of the primer was 5-8 µm, and that of the inter coat was 30-35 µm.

Next, an amino/alkyd resin series solid color of Melami No. 1 Red (trade name, made by Nippon Oil and Fats Co., Ltd.) was applied as a top coat by an air spray painting process and dried by baking at 140° C. for 30 minutes. The dried thickness of the top coat was 40  $\mu$ m.

#### (Painting of plastic sheet)

I. Plastic sheet

(A) Polyamide resin sheet (PA)

1014RX-109 (trade name, made by Ube Industries, Ltd.).

(B) Polybutylene terephthalate resin sheet (PBT) 5201X11 (trade name, made by Toray Industries, Inc.).

(C) Unsaturated polyester resin sheet (SMC)

N12 (trade name, made by Takeda Chemical Industries, Ltd.).

(D) Polyurethane resin sheet (PU)

C1056/FA720 (trade name, made by Nippon Polyurethane Industry Co., Ltd.).

(E) Polycarbonate resin sheet (PC)

Yupiron MB-2201 (trade name, made by Mitsubishi Gas Chemical Company, Inc.).

II. Painting process

Each of the above plastic sheets having a size of 3 mm×70 mm×150 mm was degreased with a vapor of 1,1,1-trichloroethane (74° C.) for 60 seconds, dried, coated with the aforementioned primer by an air spray painting process, and then coated with Epico No. 1500 Sealer TX-100 as an amino/oil free polyester resin series inter coat of wet-on-wet system by an air spray painting process, which was then dried by baking at 140° C. for 30 minutes. The dried thickness of the primer was 5-8

 $\mu$ m, and that of the inter coat was 30-35  $\mu$ m. Thereafter, the amino/alkyd resin paint of Melami No. 1 Red was applied as a top coat by an air spray painting process and dried by baking at 140° C. for 30 minutes. The dried thickness of the top coat was 40  $\mu$ m.

### **COMPARATIVE EXAMPLE 6**

The same procedure as described in Example 1 was repeated except that the application of the primer com-

#### **COMPARATIVE EXAMPLE 7**

The same procedure as described in Example 2 was repeated except that Plagloss No. 3000 Red (trade name, made by Nippon Oil and Fats Co., Ltd.) as a top coat grade for bumper was applied as a top coat by an air spray painting process instead of Melami No. 1 Red and dried by baking at  $120^{\circ}$  C. for 30 minutes. The dried thickness of the top coat was  $40 \mu m$ .

TABLE 1(a)

		1 📉	DLE I(a)				· · · · · · · · · · · · · · · · · · ·						
Primer	Elongation at break	Glass transition	Example										
composition	20° C.	temperature	1	2	3	4	5	6					
Component (A)													
polyurethane resin varnish I	660%	−35° C.	95.5	78.0	65.9	71.4	83.0	<b>78.0</b>					
polyurethane resin varnish II	440%	−20° C.											
polyurethane resin varnish III	600%	−20° C.											
polyurethane resin varnish IV	350%	−15° C.											
ethylene-vinyl acetate	900%	−30° C.											
copolymer resin varnish I													
ethylene-vinyl acetate	300%	−20° C.											
copolymer resin varnish II													
ethylene-vinyl acetate	880%	−75° C.											
copolymer resin varnish III													
ethylene-ethyl acrylate	800%	−75° C.											
copolymer resin varnish													
polyolefin resin varnish	500%	40° €.											
chlorinated ethylene-vinyl	600%	50° C.											
acetate copolymer resin varnish													
Component (B)													
polyisocyanate resin varnish								3.7					
block isocyanate resin varnish			4.5	3.7	3.1	8.2	0.2						
n-butylated urea resin varnish													
isobutylated melamine resin varnish													
Pigment													
<del></del>				18.2	15.8	20.4	15.8	18.2					
titanium dioxide				0.1	0.2		•	0.1					
carbon black				0.1	V · Pr		1.0	-					
conductive carbon black					15.0								
calcium carbonate			85/15	85/15	85/15	70/30	99/1	85/15					
component (A)/component (B)			0	1.0	2.0	1.0	1.0	1.0					
pigment/components (A) + (B)			Melami	Melami	Melami	Melami	Melami	Melami					
Paint for top coat			No. 1	No. 1	No. 1	No. 1	No. 1	No. 1					
			Red	Red	Red	Red	Red	Red					

# position was omitted.

TABLE 1(b)

			IADLE	1(0)				<u></u>	
Primer					Example				<u></u>
composition	7	8	9	10	11	12	13	14	15
Component (A)		-							
polyurethane resin varnish l	77.3	76.6	39.0	77.0					
polyurethane resin varnish Il			39.0		78	03.5			
polyurethane resin varnish III						82.5			
polyurethane resin varnish IV							78.0		
ethylene-vinyl acetate							70.0		
copolymer resin varnish I									
ethylene-vinyl acetate copolymer resin varnish II									•
ethylene-vinyl acetate						•		87.6	
copolymer resin varnish III									
ethylene-ethyl acrylate									87.6
copolymer resin varnish									
polyolefin resin varnish									
chlorinated ethylene-vinyl									
acetate copolymer resin varnish									
Component (B)									
polyisocyanate resin varnish			3.7		3.7	2.9	3.7	2.1	2.1
block isocyanate resin varnish n-butylated urea resin varnish	4.5		5.7	3.0	•••	_,,			
isobutylated melamine resin varnish	4.5	5.4		1.8					
Pigment									
titanium dioxide	18.2	17.5	18.2	18.1	18.2	14.6	18.3	9.3	10.3
carbon black		0.5	0.1	0.1	0.1				
conductive carbon black								1.0	
calcium carbonate					A 2 11 =	00 (30	05/15	0£ /1£	95/15
component (A)/component (B)	85/15	85/15	85/15	85/15	85/15	85/15	85/15	85/15	85/15

TABLE 1(b)-continued

Primer					Example				
composition	7	8	9	10	11	12	13	14	15
pigment/components (A) + (B)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Paint for top coat	Melami	Melami	Melami	Melami	Melami	Melami	Melami	Melami	Melami
	No. 1	No. 1	No. 1	No. 1	<b>N</b> o. 1	No. 1	No. 1	No. 1	No. 1
	Red	Red	Red	Red	Red	Red	Red	Red	Red

Tr 🛦	DI	T	4	
TA	.DL	Æ	1	(C)

			IADLE	, 1(C)						
Primer	Exa	mple			Con	nparative E	xample			
composition	16	17	1	2	3	4	5	6	7	
Component (A)										
polyurethane resin varnish I			68.9	83.3	63.9				78.0	
polyurethane resin varnish II										
polyurethane resin varnish III										
polyurethane resin varnish IV						82.5				
ethylene-vinyl acetate										
copolymer resin varnish I										
ethylene-vinyl acetate							82.5			
copolymer resin varnish II										
ethylene-vinyl acetate										
copolymer resin varnish III										
ethylene-ethyl acrylate										
copolymer resin varnish										
polyolefin resin varnish	91.0									
chlorinated ethylene-vinyl		82.5								
acetate copolymer resin varnish										
Component (B)										
polyisocyanate resin varnish										
block isocyanate resin varnish	1.5	2.9	9.9		3.0	2.9	2.9		3.7	
n-butylated urea resin varnish										
isobutylated melamine resin varnish										
Pigment										
titanium dioxide	7.5	14.0	<b>20</b> .0	16.7	30.0	14.6	14.5		18.2	
carbon black		0.6	1.2				0.1		0.1	
conductive carbon black					3.1					
calcium carbonate										
component (A)/component (B)	85/15	85/15	65/35	100/0	85/15	85/15	85/15		85/15	
pigment/components (A) + (B)	1.0	1.0	1.0	1.0	2.2	1.0	1.0		1.0	
Paint for top coat	Melami	Melami	Melami	Melami	Melami	Melami	Melami	Melami	Plagloss	
	<b>N</b> o. 1	No. 1	No. 1	No. 1	No. 1	No. 1	No. 1	No. 1	No. 3000	
	Red	Red	Red	Red	Red	Red	Red	Red	Red	

50

The following tests were made with respect to the coatings on the steel sheet and plastic sheet to obtain results as shown in the following Table 2.

#### (Test and evaluation methods)

## 1. Chipping resistance

Testing machine: gravelometer made by Suga Shikenki K.K.

Testing stone: No. 7 hard pulverized sand (diameter:

## 2-3 mm) 100 g/test

Air pressure blown: 4 kg/cm<sup>2</sup>

Blowing angle: 90°

Sheet temperature: 20° C.

The test was made under the above conditions to evaluate the peeling state of the coating (CP-I) and the 55 evaluate color change, swelling, peeling and the like of number of rusting points generated (CP-II).

Evaluation standard of CP-I:

Peeling diameter of less than 0.5 mm, (excellent) Peeling diameter of not less than 0.5 mm but less than 1.0 mm,  $\Delta$  (acceptable)

Peeling diameter of not less than 1.0 mm,  $\times$  (bad).

The evaluation of CP-II was made by the number of rusting points generated after 72 hours by spraying salt (5% salt water, temperature: 35° C.) to the test sheet.

Rust number of less than 20, (excellent)

Rust number of not less than 20 but less than 50,  $\Delta$ (acceptable)

Rust number of not less than 50,  $\times$  (bad).

# 2. Heating-cooling cycle property

A cross cut of 50 mm  $\times$  50 mm was formed on the test sheet, which was subjected to a cycle of heating at 50° 45 C. and 95% RH for 16 hours→cooling at 20° C. for 0.5 hour→cooling at -40° C. for 3 hours—cooling at 20° C. for 1 hour—heating at 80° C. for 3 hours—cooling at 20° C. for 0.5 hour three times to evaluate the presence of cracks in the coating.

The evaluation standard was as follows.

Absence of crack (excellent)

Presence of cracks  $\times$  (bad).

3. Gasoline resistance

The test sheet was immersed in gasoline for 1 hour to the coating. The evaluation standard was (no change; excellent),  $\Delta$  (slightly change; acceptable) and  $\times$  (considerably change; bad).

# 4. Polishing property

The test sheet was ground with an abrasive paper (#1500), rubbed with Unicon FMC-830H (trade name, made by Ishihara Sangyo Kaisha, Ltd.) as a repair abrasive, and further polished with Soft 99 Luster (trade name, made by Nitto Chemical Industry Co., Ltd.) as a 65 polishing wax to evaluate the appearance of the coating. The evaluation standard was as follows.

no reduction of gloss as compared with initial stage: (excellent)

slight reduction of gloss as compared with initial stage:  $\Delta$  (acceptable)

considerable reduction of gloss as compared with initial stage: ×(bad).

5. Impact resistance at low temperature (High-speed 5 impact test)

A value of impact energy when a point of impact shot through the test sheet was measured by means of a high-speed impact testing machine made by Rheometric Corporation under such conditions that a tip diameter of impact point was 1.6 cm ( $\frac{5}{8}$  inch), a holder was 5.1 cm (2 inch) and an impact speed was 11.1 m/sec., from which a yield energy value (joule) at  $-40^{\circ}$  C. was calculated.

The larger the numerical value, the better the impact resistance at low temperature.

TA	RI	F	20	(a)	1-1
17	JL	-	~	a	J- 1

				IUNE	_ L(a)-1									
Test items		Example												
Sheet material	ì	2	3	4	5	6	7	9	10	11	12			
Steel sheet					•		_	_	_					
chipping resistance CP-II chipping resistance CP-II heating-cooling cycle property gasoline resistance polishing property	0000	0000	0000	0000	0000	00000	0000	0000	0000	0000	0000			
chipping resistance CP-I heating-cooling cycle property gasoline resistance polishing property impact resistance at low temperature (joule)	0000 10~12	0000 10~12	0000	0000	0000	0000	0 0 0 0 10~12	0 0 0 0 10~12	0 0 0 10~12	0 0 0 0 10~12	0000			
chipping resistance CP-I heating-cooling cycle property gasoline resistance polishing property impact resistance at low temperature (joule)	0 40∼50	000 40∼50	0000 40∼50	00 40∼50	0 40~50	0 40∼50	00 40∼50	0000 <b>40∼5</b> 0	0000 <b>40</b> ∼ <b>5</b> 0	0000 <b>40</b> ∼ <b>5</b> 0	0000 <b>40</b> ∼ <b>5</b> 0			

**TABLE 2(a)-2** 

				_										
Test items	Example													
Sheet material	1	2	3	4	5	6	7	9	10	11	12			
SMC chipping resistance CP-I			0	0	0	$\circ$	0	0	0	Q	Q			
heating-cooling cycle property gasoline resistance	Ŏ	Ŏ	Ŏ	00	00	0	00	00	00	0	00			
polishing property impact resistance at low temperature (joule)	<b>4</b> 0∼50	<b>40∼50</b>	<b>40∼5</b> 0	<b>40∼50</b>	<b>40~50</b>	<b>4</b> 0~ <b>5</b> 0	<b>4</b> 0~50	<b>4</b> 0~50	<b>4</b> 0~50	40~50	40~50			
PU chipping resistance CP-I		$\bigcirc$	$\circ$	$\circ$	$\circ$	0	0	0	0	0	0			
heating-cooling cycle property gasoline resistance	Ŏ	Ŏ	Ŏ	Ŏ	Ŏ	Ŏ	Ŏ	Ö	00	0	00			
polishing property impact resistance at low temperature (joule)	○ 30~40	○ 30~40	○ 30~40	○ 30~40	○ 30~40	○ 30~40	30~40	30~40		30~40	30~ <b>4</b> 0			
PC chipping resistance CP-I heating-cooling cycle property	0	0	8	0	0	0	0	0	0	0	Q			
gasoline resistance polishing property impact resistance at low temperature (joule)	Ŏ 40∼50	Ŏ 40∼50	Ö 40∼50	0 40∼50	0 40∼50	<b>40∼50</b>	<b>40∼50</b>	<b>40∼5</b> 0	<b>40∼50</b>	<b>40∼50</b>	<b>40∼5</b> 0			

**TABLE 2(b)-1** 

				2 2 2 2 2 2 2	12 2(0)	<u> </u>						
Test items			Example			Comparative Example						
Sheet material	13	14	15	16	17	1	2	3	4	5	6	7
Steel sheet  chipping resistance CP-I  chipping resistance CP-II  heating-cooling cycle property  gasoline resistance  polishing property  PA	0000	00000	00000	00000	00000	<b>X</b> 000	00 <b>x</b> 00	<b>x</b>	<b>4 0 0 0</b>	<b>4 0 0 0</b>	4000	000 <b>x</b>
chipping resistance CP-I heating-cooling cycle property gasoline resistance polishing property impact resistance at low temperature (joule)	0000 10~12	0000 10~12	0000	0 0 0 0 10~12	0 0 0 0 10~12	<b>∆</b> ○○○ <b>½</b> 9	O X O 10~12	<b>∆</b> ⊖⊖⊖ <b>¥</b> 9	<b>∆</b> ○○○ <b>§</b> 9	<b>∆</b> ○○○ <b>≦</b> 9	X X X O 10~12	○ X X 10~12

TABLE 2(b)-1-continued

Test items	Example						Comparative Example						
Sheet material	13	14	15	16	17	1	2	3	4	5	6	7	
PBT						· · · · ·		<del></del>				<u> </u>	
chipping resistance CP-I heating-cooling cycle property gasoline resistance polishing property impact resistance at low temperature (joule)	00 40∼50	0000 <b>40∼50</b>	0000 <b>40</b> ∼50	0000 <b>40∼5</b> 0	00 40∼50	<b>∆</b> ○○○≦9	O X O 40∼50	<b>∆</b> ○○○ ≦9	∆ ○ ≦9	<b>∆</b> ○○○ <b>≦</b> 9	X X X 0 40~50	○ X X 40~50	

**TABLE 2(b)-2** 

				* * * * * * * * * * * * * * * * * * * *		-						
Test items			Example			Comparative Example						
Sheet material	13	14	15	16	17	1	2	3	4	5	6	7
SMC												
chipping resistance CP-I	0	0	0	0	0	X	0	X	Δ	Δ	X	0
heating-cooling cycle property	$\circ$	$\circ$	$\circ$	Ò	Q	Q	X	Ŏ	Q	Ŏ	X	Ô
gasoline resistance polishing property	X	$\mathcal{C}$	$\simeq$	X	$\simeq$	$\simeq$	$\stackrel{\mathbf{x}}{\cap}$	X	$\simeq$	$\simeq$	$\stackrel{\mathbf{X}}{\circ}$	X
impact resistance at low	40~50	40~50	40~50	40~50	<b>4</b> 0∼50	10~20	40~50	10~20	10~20	10~20	40~50	40~50
temperature (joule) PU												
chipping resistance CP-I	Q	Q	Q	Q	Q	Δ	Q	Δ	Δ	Δ	X	Ō
heating-cooling cycle property gasoline resistance	$\sim$	$\otimes$	$\sim$	$\sim$	$\otimes$	$\otimes$	$\overset{\mathbf{X}}{\sim}$	$\sim$	$\otimes$	$\otimes$	X X	$\overset{\bigcirc}{\mathbf{x}}$
polishing property	$\mathcal{S}$	$\tilde{a}$	$\mathcal{C}$	$\sim$	$\mathcal{C}$	$\sim$	$\sim$	$\sim$	$\sim$	$\mathcal{S}$	Ô	x
impact resistance at low	$30 \sim 40$	$30 \sim 40$	30~40	30~40	30~40	<b>≦</b> 9	30~40	<b>≦</b> 9	<b>≦</b> 9	<b>≨</b> 9	30~40	$30 \sim 40$
temperature (joule) PC												
chipping resistance CP-I	0	O	0	0	0	Δ	$\circ$	Δ	Δ	Δ	X	0
heating-cooling cycle property	$\bigcirc$	$\circ$	$\circ$	0	$\circ$	Q	X	$\circ$	$\bigcirc$	Q	X	Ô
gasoline resistance polishing property	$\simeq$	$\sim$	$\simeq$	$\approx$	$\approx$	$\simeq$	$\simeq$	$\simeq$	$\simeq$	$\geq$	×	X
impact resistance at low	40~50	40~50	40~50	40~50	40~50	<u>≤</u> 9	40~50	<u>≤</u> 9	⊖ <b>≦</b> 9	<u>≤</u> 9	40~50	40~50
temperature (joule)												

As seen from Tables 1 and 2, the use of the primer 35 composition according to the invention is excellent in chipping resistance, heating-cooling cycle property, gasoline resistance and polishing property for the steel sheet and excellent in chipping resistance, heating-cooling cycle property, gasoline resistance, polishing property and impact resistance at low temperature for all plastic sheets, so that it can ensure the good balance of total film performances required as a paint for automobiles.

On the contrary, Comparative Example 1 is poor in 45 the chipping resistance for the steel sheet and in the chipping resistance and impact resistance at low temperature for all plastic sheets because the ratio of component (A) to component (B) is 65/35.

Since Comparative Example 2 does not use the com- 50 ponent (B), the heating-cooling cycle property for the steel sheet and all plastic sheets is poor.

In Comparative Example 3, since the ratio of pigment to components (A)+(B) is 2.2, the chipping resistance for the steel sheet and the chipping resistance and im- 55 pact resistance at low temperature for all plastic sheets are poor.

In Comparative Examples 4 and 5, the chipping resistance for the steel sheet and the chipping resistance and impact resistance at low temperature for all plastic 60 tion furth sheets are poor because the component (A) of Comparative Example 4 has a glass transition temperature of higher than -20° C. and an elongation at break of less than 400% at 20° C., while the component (A) of Comparative Example 5 has an elongation at break of less 65 at 20° C. The higher than 400% at 20° C. The parative Example 5 has an elongation at break of less 65 at 20° C. The higher than 400% at 20° C. The parative Example 5 has an elongation at break of less 65 at 20° C.

In Comparative Example 6, the chipping resistance for the steel sheet and the chipping resistance, heating-

cooling cycle property and gasoline resistance for all plastic sheets are poor because the primer composition according to the invention is not used.

In Comparative Example 7, since the soft top coat is used instead of the hard top coat, the chipping resistance, heating-cooling cycle property and impact resistance at low temperature for the steel sheet and all plastic sheets are improved, but the polishing property for the steel sheet and the gasoline resistance and polishing property for all plastic sheets are poor, so that the good balance of total film performances cannot be ensured.

What is claimed is:

- 1. A primer composition consisting essentially of (A) at least one resin having a glass transition temperature of not higher than -20° C. and an enlogation at break of not less than 400% at 20° C. and (B) at least one crosslinking resin, the weight ratio as solid resin content of component (A) to component (B) being 70-99:30-1, said component (A) comprising polyurethane resin or a linear high molecular weight elastomer of a modified resin thereof, and said component (B) comprising polyisocyanate resin or a [linear high molecular weight elastomer of a] modified resin thereof, said composition further containing a pigment at a ratio of pigment to components (A) and (B) of not more than 2.
- 2. The primer composition of claim 1 wherein component (A) has a minimum glass transition temperature of -75° C. and a maximum elongation at break of 900% at 20° C.
- 3. The primer composition according to claim 1, wherein said component (B) contains a reactive functional group containing polyurethane resin.

- 4. The primer composition according to claim 1, wherein said pigment is selected from the group consisting of titanium dioxide, carbon black, conductive carbon black, talc, kaolin, calcium carbonate, magnesium carbonate, barium sulfate, iron oxide, cyanine blue and quinacridone red.
  - 5. The primer composition according to claim 1,

wherein said component (A) includes said linear high molecular weight elastomer of a modified resin.

[6. The primer composition according to claim 1, wherein said component (B) includes said linear high molecular weight elastomer of a modified resin.]

7. The primer composition of claim 1, wherein said component (B) includes a block isocyanate resin.

10

20

25

30

35

40

45

50

55

ፈን