

**PRIMER COMPOSITIONS FOR PRETREATMENT OF POLYOLEFIN AND  
RUBBER SUBSTRATES**

The present invention relates to a primer  
composition which has an excellent bonding ability to  
5 polyethylene, polypropylene and synthetic rubbers and  
is easily bonded to functional coatings so that a  
composite layer having a function of addition is formed  
on the surface of these materials by coating or the  
like, and to a thermal treatment process by far  
10 infrared rays therefor.

## Summary of the Invention

The present invention is a primer which can be designed so as not only to improve the appearance of polyolefins such as polyethylene or rubbers by the coloring of them, but also to improve extensively the durability by the ultraviolet-screening effect, prevent the oxidative deterioration of synthetic rubbers caused by oxygen or ozone, the contamination or the smelling of the synthetic rubbers, and improve their abrasion resistance as well. Furthermore, different from the black coloration of the conventional polyethylene and rubber intended to maintain their weatherabilities, colorful appearances can be afforded to the polyethylene and rubber without impairing their weatherabilities, and the heat resistance, resistance to gasoline and resistance to chemicals of the primer itself can be improved.

The Polyethylene includes those such as of low density (LDPE) and of high density (HDPE) and a super high density polyethylene. The rubber includes for example natural rubbers (NR), a butadiene rubber (BR), a styrene-butadiene rubber (SBR), an acrylnitrile rubber (NBR), an ethylene-propylene rubber (EPT), a chloroprene rubber (CR), a butyl rubber (IIR), an urethane rubber and a chlorosulfonated polyethylene rubber (CSM) (except a silicone rubber).

## Background of the Invention

Polyethylenes have hitherto been developed as inexpensive engineering plastics such as a high strength product, a super high molecular weight product or the like, although it was impossible to coat or print paints or inks directly on them because of their non-polarity and extreme inertness and thus it was difficult to expand their application field in spite of their high performance and their low cost.

The high density polyethylene has hitherto been used to a wide range of applications owing to its excellent physical properties and low cost. However, the high density polyethylene will be crystallized promptly by ultraviolet rays and deteriorated by crackings, so that it is not suitable for the use in the open.

Therefore, polyethylenes reinforced with carbon or an anti-aging agent is placed on the market, but the powers of carbon or an anti-aging agent are limited and such a product having a black appearance has a limited use. Accordingly, coating technique of polyethylene products has been researched for the purpose of obtaining an effective means for not only improving the appearance of articles by their decorative finishing but also extensively improving the field durability by the screening of ultraviolet rays.

However, polyethylene comprises absolutely a non-polar molecular structure and has no surface activity, so that it

cannot be coated without any special surface treatments.

As the surface treatment method which has hitherto been used most generally, there is mentioned a method in which the surface layer is oxidized with flame, arcing or a strong oxidizing agent and next coated with a topcoat.

However, such a treatment method is not suitable for practical use, since it is a method which is difficult to maintain a constant adhesion due to the uneven treatment state and which is dangerous due to the high toxicity. As for the liquid primers for adhering polyethylene, the effectiveness of the primers such as those of the types of aminosilane, organic titanium, organic aluminium and the like is well known, but these primers are sensitive to humidity (and reactive rapidly with humidity) and is required to coat thereon with a topcoat (or an organic adhesive of a cyanoacrylate type) (or to apply an adhesive) within a very short time of a few minutes, so that they cannot be applied at all to the use for a large area as in the case of paintings.

Furthermore, rubber requires additionally other properties depending on portions or time to be applied with the use of stretchability as an elastomer. As the synthetic rubbers, there are mentioned a variety of rubbers of a heat resistant type, an oil resistant type, a weatherable type, an energy saving type, a highly functionalized special type and the like which correspond to these requirements. In particular, basic

requirements to the tires of automobiles are safety and long-term durability, and molecules of a butadiene rubber, a styrene-butadiene rubber, an isoprene rubber and natural rubbers have been respectively designed according to the requirements for tires.

That is to say, one of natural rubbers or a variety of synthetic rubbers is selected and incorporated with additives such as a vulcanizing agent, a vulcanization accelerator, an anti-aging agent, a reinforcing agent, a filler and a softener in consideration of their combination. For example, in order to improve weatherability, a rubber having fewer unsatisfied bonds is selected, and to the one having inferior vulcanizability are added the third components. In order to improve weatherability, carbon black may be added as a reinforcing agent.

However, these properties may be contrary to each other and often must be controlled by a compromise of each other.

Most of the synthetic rubbers have intrinsically unsaturated bonds, and thus they have essentially problems of weatherability, ozone resistance or the like. Therefore, these problems cannot be completely solved by designing the mixture of materials. The solution by admixture will always bring about secondary defects. For instance, the color of a material is limited to black by the addition of carbon black, and such a limitation is not desirable in a colorful fashion as one of various life modes of the day.

Detailed Description of the Invention

The object of the present invention is to solve the problems in rubber which are contrary to each other and the difficulty of the pretreatment of polyethylene by providing a primer which has a good adhesion both to polyethylene, polypropylene and synthetic rubbers and to functional coatings in order to deal the functions such as weatherability, ozone resistance or the like which relate to only the surface layer with a coating having such functions, thus to realize a development of a novel article comprising composite materials of polyethylene, polypropylene and synthetic rubber and a resin.

The first feature of the present invention is a primer composition which comprises:

(A) polymers (i) and (ii), or polymers (ii) and (iii), or polymers (i), (ii) and (iii), wherein polymers (i), (ii) and (iii) are:

(i) a graft polymer (referred to hereinafter as a "grafted EVA") of an unsaturated dicarboxylic acid and an ethylene-vinyl acetate copolymer (referred to hereinafter as "EVA"),

(ii) a chlorinated polypropylene wherein a graft polymer of an unsaturated dicarboxylic acid and polypropylene is submitted to chlorine substitution (referred to hereinafter as a "grafted chlorinated polypropylene") or a chlorinated polypropylene in which polypropylene is merely submitted to chlorine substitution, and

(iii) a graft polymer (referred to hereinafter as a "grafted EEA") of an unsaturated dicarboxylic acid and an ethylene-ethyl acrylate copolymer (referred

to hereinafter as "EEA") or a product obtained from chlorine substitution of the graft polymer; and

(B) a solvent.

5 A first embodiment of the first feature of the present invention consists in a primer composition which comprises:

- 10 (1) a grafted EVA in an amount of ca. 2 - 30 parts by weight (referred to hereinafter merely as "parts");
- (2) a grafted chlorinated polypropylene or a chlorinated polypropylene in which polypropylene is merely submitted to chlorine substitution in an amount of ca. 0.5 - 25
- 15 parts;
- (3) a pigment in an amount of ca. 0 - 30 parts; and
- (4) a solvent in an amount of ca. 40 - 97.5 parts;
- 20 the total being 100 parts.

Thus, the primer according to one aspect of the present invention comprises a graft polymer of an ethylene-vinyl acetate copolymer soluble in a solvent and having an excellent adhesion to polyethylene, 25 polypropylene and rubber and an unsaturated dicarboxylic acid such as maleic anhydride or the like, a graft chlorinated polypropylene and a solvent. A pigment or an organic titanium compound can be optionally added to the primer.

30 The term "unsaturated dicarboxylic acid" used herein means the anhydrides of such acids as well as the acids themselves.

Even if such a pigment or an organic titanium compound are not incorporated, satisfactory adhesion to 35 polyethylene can be obtained.

Using only the EVA, the hot melt adhesiveness to

polyethylene or the adhesion to a topcoat can be obtained to a certain extent by controlling the concentration or molecular weight of the vinyl acetate.

- 5 If the concentration of the polyethylene component is high in the EVA, the hot melt adhesiveness of the EVA to polyethylene is good while the

adhesion of the topcoat is lowered. In contrast with this, if the concentration of the vinyl acetate component in the EVA is high, the adhesion of the topcoat is good, while the hot melt adhesiveness to the polyethylene is lowered.

In other words, the balance of the polyethylene and vinyl acetate in the EVA gives to the hot melt adhesiveness and the adhesion of the topcoat to the polyethylene effects which are contrary to each other, and thus it cannot be expected to obtain results which correspond satisfactorily with the object by using only the EVA.

The graft polymer of an EVA and an unsaturated dicarboxylic acid such as maleic anhydride or the like according to the present invention represented by the general formula:



wherein R represents an EVA, and X represents an unsaturated dicarboxylic acid, is used, because the use of the graft polymer gives good adhesion of a topcoat even if an EVA having a comparatively low concentration of the vinyl acetate (and thus a high concentration of the polyethylene component) and good adhesiveness of a hot melt to the polyethylene is obtained as well because of a high concentration of the polyethylene component in the graft polymer.

If the graft polymer is constituted as described above,

the polarity affording effect by the unsaturated dicarboxylic acid can be expected. Even if an EVA having a relatively low concentration of the vinyl acetate is used, good adhesion of a topcoat is obtained and good adhesiveness of a hot melt to polyethylene can be secured. As for rubber, good adhesiveness can be secured as well by adjusting the solubility parameter (SP value) of the graft polymer close to that of the rubber.

10       The graft polymer used in the present invention has preferably a weight average molecular weight of  $1 - 2 \times 10^5$  and an vinyl acetate content of 15 - 35%.

15       When a trace amount of an organic titanium compound is used in a primer, the acetyl groups or the carbonyl groups in the graft polymer of the EVA and the unsaturated dicarboxylic acid are crosslinked by the organic titanium compound to give a film having a higher hardness. Moreover, the pigment and the surface of the polyethylene in the primer composition are also crosslinked only in a small proportion by the organic titanium compound to give an adhesiveness of the polyethylene stronger than that in the case using no such titanium compound.

25       The pigment for the primer is used for the purpose of coloring and of increasing a little the film strength, and a pigment having a coloring ability and an extender pigment having no coloring ability are used in combination, which will cause no problem unless specific limitation is given for the kind of pigments, hue, or the like.

30       The solvent for the primer is preferably toluene or xylene. Benzene, tetrahydrofuran or trichloroethylene can also be used as a solvent, but they are not preferable for the primer because of their strong toxicity and irritation.

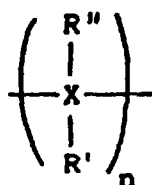
35       The use of the graft chlorinated polypropylene

aims at an improvement of the physical properties of the film and of its adhesion to a topcoat.

The graft chlorinated polypropylene preferably has a weight average molecular weight of  $6 - 10 \times 10^4$  and a chlorine content in the range from 20 to 30%.

This constitution is represented as a resin component of the general formula:

10



(II)

wherein R' represents a chlorinated polypropylene, and X represents an unsaturated dicarboxylic acid.

The grafted chlorinated polypropylene or the chlorinated polypropylene represented by the general formula:



20 wherein y denotes 0.3 - 0.8 is incorporated so as to improve the film strength and the topcoat adhesion and to make possible of bonding to polypropylene. The amount of the grafted EVA is in the range from 2 to 30 parts. The reason is that if the amount of the grafted  
25 EVA is less than 2 parts, bonding to polyethylene cannot be expected in the case of increasing the amount of the grafted chlorinated polypropylene or the merely chlorinated polypropylene to be incorporated, and if it exceeds 30 parts, the composition is not given as a  
30 liquid.

The amount of the grafted chlorinated polypropylene or the merely chlorinated polypropylene to be incorporated is in the range from about 0.5 to 25 parts. The reason is that when the amount is in the  
35 range less than 0.5 part the improvement of the film strength and the adhesion of the topcoat cannot be

expected, and when it exceeds 25 parts the composition cannot be given as a liquid owing to the increase of the loading of the grafted chlorinated polypropylene or the merely chlorinated polypropylene and the grafted  
5 EVA in order to prevent the loss of adhesion to polyethylene or rubber by increasing the amount of the grafted EVA to be incorporated.

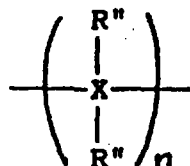
A second embodiment of the first feature of the present invention comprises:

- 10 (1) a grafted EEA or a product obtained by the substitution of the graft polymer with chlorine in an amount of ca. 2 - 40 parts;
- (2) a grafted chlorinated polypropylene or a  
15 chlorinated polypropylene in which polypropylene is merely submitted to chlorine substitution in an amount of ca. 0.5 - 15 parts;
- (3) a pigment in an amount of ca. 0 - 30 parts;  
and
- (4) a solvent in an amount of ca. 40 - 97.5 parts;  
20 the total being 100 parts.

The grafted EEA preferably has a weight average molecular weight of  $5 - 15 \times 10^4$  and an ethyl acrylate content in the range of 15% or less.

The product obtained by the substitution of the  
25 graft polymer with chlorine has preferably the chlorine content from 10 to 25%.

This constitution is represented as a resin component of the general formula:



(III)

wherein R'' represents an EEA or a chlorinated EEA, and X represents an unsaturated dicarboxylic acid. The reason why the chlorine substitution product of the graft polymer is used is that the good adhesion of the topcoat is given by employing this graft polymer even in the case of an EEA having a relatively low concentration of ethyl acrylate (and a high concentration of a polyethylene component) and the good adhesiveness of a hot melt to polyethylene is given owing to the high concentration of the polyethylene component in the graft polymer.

By constituting the grafted EEA as described above, the polarity affording effect by the unsaturated dicarboxylic acid can be expected. Furthermore, the good adhesiveness of the hot melt to polyethylene is obtained even in the case of an EEA having a relatively low concentration of ethyl acrylate and the good adhesiveness of the hot melt to polyethylene can be maintained as well. Also the good adhesiveness to rubber can be maintained, as the solubility parameter (SP value) of the graft polymer or the chlorine substitution product of the graft polymer is close to that of the rubber.

The grafted EEA produces a film softer than that obtained from the grafted EVA and thus functions more efficiently as a primer for rubber.

This constitution is characterized in that the grafted chlorinated polypropylene or the chlorinated polypropylene is incorporated to improve the film strength and the adhesion of a topcoat and to make possible of bonding to polypropylene.

The amount of the grafted chlorinated polypropylene or the chlorinated polypropylene to be incorporated is in the range of 0.5 - 15 parts. The reason is that if the amount thereof is less than 0.5 parts, the improvement of the film strength and the adhesion of the topcoat cannot be expected. If the amount exceeds 15 parts, adhesiveness to rubber is lost unless the amount of the grafted EEA or its chlorine substitution product is increased, and if the amount is increased, the amount or the resins in the composition becomes too much to give the composition as a liquid.

If the blending rate of the grafted EEA or its chlorine substitution product is less than 2 parts, the amount of the grafted chlorinated polypropylene or the chlorinated polypropylene to be incorporated is increased to lose the adhesiveness to rubber. If the rate exceeds 40 parts, the composition is not given as a liquid .

A third embodiment in the first feature of the present invention consists in a primer composition which comprises:

- (1) a grafted EVA in an amount of ca. 1 - 30 parts;
- (2) a grafted EEA or a chlorine substitution product of the graft polymer in an amount of ca. 1-29.5 parts;
- (3) a grafted chlorinated polypropylene or a chlorinated polypropylene wherein polypropylene is merely substituted with chlorine in an amount of ca. 0.5 - 15 parts;

- 15 -

(4) a pigment in an amount of ca. 0 - 30 parts;  
and

(5) a solvent in an amount of ca. 40 - 97.5 parts;  
the total being 100 parts.

- 5      This constitution is characterized in that the grafted chlorinated polypropylene or the chlorinated polypropylene is incorporated to improve the film strength and the adhesiveness

to the topcoat and to make possible of bonding to polypropylene, the grafted EEA or the chlorine substitution product of the graft polymer is incorporated to improve the follow-up ability to rubber, and the grafted EVA is incorporated to make possible of better bonding to polyethylene.

The amount of the grafted EVA is in the range from 1 to 30 parts. The reason is that if it is less than 1 part, adhesiveness to polyethylene cannot be expected, and if it exceeds 30 parts, the composition is not given in a liquid state.

If the amount of the grafted EEA or its chlorinated product to be incorporated is less than 1 part, the follow-up ability to rubber is not expected, and if it exceeds 29.5 parts, the amount of the grafted chlorinated polypropylene or the chlorinated polypropylene to be incorporated (the blending balance of the grafted EVA and the grafted EEA or its chlorinated product and grafted chlorinated polypropylene or the chlorinated polypropylene) cannot be maintained in an appropriate level.

The blending rate of the grafted chlorinated polypropylene or the chlorinated polypropylene is in the range from 0.5 - 15 parts. The reason is that if the rate is less than 0.5 part, the film strength and the adhesion to the topcoat will not be improved, and if exceeding 15 parts, the amount of the grafted EVA and the grafted EEA or its chlorinated product to be

incorporated cannot be kept in an appropriate level and thus the adhesiveness to rubber is lost.

The aforementioned primers become liquid paints at ordinary temperature by mixing and dispersing  
5 respective primer constituting components, and thus can be coated by spraying, brushing or roller coating.

When the primer is coated on polyethylene, it is coated to ensure that the dry film has a thickness of ca. 15 $\mu$ m. After the solvent has been evaporated, the  
10 film is irradiated with far infrared rays to form a strong bonding to polyethylene. Irradiation time of far infrared rays varies depending on the capacities of heaters or kinds of polyethylenes. In the case of HDPE, irradiation is carried out with a 4 KW far  
15 infrared heater for ca. 2.5 - 5 minutes per 0.1 m<sup>2</sup> of a material to be irradiated to afford a good adhesiveness.

Also, in the case of coating of rubber, the film may have the same thickness as in the case of  
20 polyethylene and is bonded strongly to rubber by the heat treatment by means of far infrared rays or a hot-air oven.

A second feature of the present invention consists in a pellet or powder primer composition in a solid  
25 state at ordinary temperature wherein a solvent has been removed from the constituting primer according to the aforementioned first primer.

In other words, the second feature of the present invention consists in that the primer composition  
30 contains polymers (i) and (ii), or polymers (ii) and (iii), or polymers (i), (ii) and (iii), wherein polymers (i), (ii) and (iii) are:

(i) the grafted EVA,

(ii) the grafted chlorinated polypropylene or a  
35 chlorinated polypropylene in which polypropylene is merely substituted with chlorine, and

(iii) the grafted EEA or a chlorine substitution product of the graft polymer.

The grafted EVA has preferably a weight average molecular weight of  $1 - 2 \times 10^5$  and a vinyl acetate content of 15 - 35%.

The grafted chlorinated polypropylene has preferably a weight average molecular weight of  $6 - 10 \times 10^4$  and a chlorine content of 20 - 30%. Also, the aforementioned chlorinated polypropylene in which polypropylene is substituted with chlorine has preferably a weight average molecular weight of  $1 - 3 \times 10^5$  and a chlorine content of 20 - 40%.

The aforementioned grafted EEA has preferably a weight average molecular weight of  $5 - 15 \times 10^4$  and an ethyl acrylate content of 15% or less. Also, the chlorine substitution product of the last graft polymer has preferably a chlorine content of 10 - 25%.

A first embodiment in the second feature of the present invention consists in that the primer composition comprises:

- (1) a grafted EVA in an amount of ca. 20 - 95 parts;
- (2) a grafted chlorinated polypropylene or a chlorinated polypropylene in which polypropylene is merely substituted with chlorine in an amount of ca. 5 - 60 parts; and
- (3) pigment in an amount of ca. 0 - 50 parts; the total being 100 parts.

If the amount of the grafted EVA is less than 20 parts, the grafted chlorinated polypropylene or the chlorinated product of polypropylene must be incorporated in an amount of at least 30 parts or more and dechlorination reaction occurs too vigorously to prepare the primer composition under such a condition by a dry method.

The amount of the grafted EVA exceeds 95 parts, the proper amount of the grafted chlorinated polypropylene or the merely chlorinated polypropylene

to be incorporated cannot be kept.

If the amount of the grafted chlorinated polypropylene or the merely chlorinated polypropylene is less than 5 parts, the improvement of the topcoating ability and the adhesiveness to polyethylene cannot be expected.

If the amount exceeds 60 parts, the proper amount of the grafted EVA to be incorporated in the preparation cannot be secured, and dechlorination reaction occurs too vigorously to prepare the primer composition under such a condition by a dry method.

A second embodiment of the second feature of the present invention consists in that the primer composition comprises:

- (1) a grafted EEA or a chlorinated product thereof in an amount of ca. 20 - 95 parts;
- (2) a grafted chlorinated polypropylene or a chlorinated polypropylene in which polypropylene is merely substituted with chlorine in an amount of ca. 5 - 60 parts; and
- (3) a pigment in an amount of ca. 0 - 50 parts; the total being 100 parts.

If the amount of the grafted EEA is less than 20 parts, the grafted chlorinated polypropylene must be incorporated in an amount of at least 30 parts or more, and dechlorination reaction occurs too vigorously to prepare the primer composition under such a condition by a dry method.

The amount of the grafted EEA exceeds 95 parts, the proper amount of the grafted chlorinated polypropylene or the merely chlorinated polypropylene to be incorporated cannot be secured.

If the amount of the grafted chlorinated polypropylene or the merely chlorinated polypropylene is less than 5 parts, the improvement of the topcoating ability and the adhesiveness to polyethylene cannot be

expected.

If the amount of the grafted chlorinated polypropylene or the merely chlorinated polypropylene exceeds 60 parts, the proper amount of the grafted EEA to be incorporated in the preparation cannot be secured, and dechlorination reaction occurs too vigorously to prepare the primer composition under such a condition by a dry method.

A third embodiment of the second feature of the present invention consists in that the primer composition comprises:

- (1) a grafted EVA in an amount of ca. 10 - 85 parts;
- (2) a grafted EEA or a chlorinated product thereof in an amount of ca. 10 - 85 parts;
- (3) a grafted chlorinated polypropylene or a chlorinated polypropylene in which polypropylene is merely substituted with chlorine in an amount of ca. 5 - 60 parts; and
- (4) a pigment in an amount of ca. 0 - 50 parts; the total being 100 parts.

The blending rate of the grafted EVA is the range from 10 to 85 parts. If the amount of the grafted EVA is less than 10 parts, the effect of blending the grafted EVA cannot be expected, and if exceeding 85 parts, the blending rate of the grafted EEA and the grafted chlorinated polypropylene or the merely chlorinated product of polypropylene is lowered and the effect of these two components cannot be expected.

The amount of the grafted EEA to be incorporated is in the range from 10 to 85 parts. If the amount is less than 10 parts, the effect of blending the grafted EEA cannot be expected. If the amount exceeds 85 parts, the blending rate of the grafted EVA and the grafted chlorinated polypropylene or the merely chlorinated product of polypropylene is lowered and the

effect of these two components cannot be expected.

The amount of the grafted chlorinated polypropylene or the merely chlorinated product of polypropylene is in the range from 5 to 60 parts. if  
5 the amount of the grafted chlorinated polypropylene or the merely chlorinated polypropylene is less than 5 parts, the adhesiveness to polypropylene cannot be expected, and if exceeding 60 parts, the proper amount of the grafted EVA or the grafted EEA to be  
10 incorporated in the preparation cannot be secured, and dechlorination reaction occurs too vigorously to prepare the primer composition under such a condition by a dry method.

The effective method of mixing and dispersing the  
15 components is a hot melt blending (dry method) with a double-screw extruder.

Pulverization can be easily performed by freeze-pulverizing a blended solid product obtained by the use of the double-screw extruder.

20 The powder type primer is coated on polyethylene, rubber or the like by a fluidized dipping method. The primer must not necessarily be melted and levelled during its coating by fluidized dipping as it is subjected to thermal treatment by the irradiation of  
25 far infrared rays after the coating step, and thus a material to be coated must only be heated preliminarily at about 100°C.

The primer coated by the fluidized dipping method forms a particulate layer on the surface of the  
30 material to be coated such as polyethylene (e.g. HDPE), rubber or the like, which layer is melted and levelled by irradiating with far infrared rays and forms strong bond to the material to be coated. Treatment time of the primer by far infrared rays varies

depending on primers, film thicknesses and materials to be coated. When the primer of the second feature of the present invention and a polyethylene (HDPE) as a material to be coated are used and the film has a  
5 thickness of 50  $\mu\text{m}$ , the thermal treatment time is 3 minutes with a 4 KW heater per  $0.1\text{m}^2$  of the material to be coated. Under the same conditions of the primer, film thickness and the heater except that the material to be coated is rubber, the thermal treatment time is  
10 about 40 seconds.

Intimate mixing of a material to be coated (polyethylene, polypropylene or rubber) and a primer (a grafted EVA, EEA or the like) is enhanced in the interface of these molecules by heating, and better  
15 adhesiveness can be obtained.

The absorption wave length of infrared rays for heating the primer is in the range of 5 - 50  $\mu\text{m}$  and the primer must only have a function of forming a chemical bond to only the surface of a material to be coated  
20 such as polyethylene or rubber. Therefore, the heater used in the present invention is a far infrared heater, and the wave length of the infrared rays irradiated is in the range of 3 - 50  $\mu\text{m}$ . It may be said in this connection that the wave lengths of infrared rays  
25 irradiated by other heaters are in the range of 0.7 - ca. 2  $\mu\text{m}$  for a nichrome wire, 0.7 - ca. 3  $\mu\text{m}$  for an infrared lamp and 0.7 - ca 7  $\mu\text{m}$  for a quartz-sheathed element heater.

According to the present invention, the far  
30 infrared heater efficiently generates far infrared rays in a wide range of 3 - 50  $\mu\text{m}$  and bonding reaction on the superficial layer finishes in a short time, so that a product bonded to polyethylene or rubber is obtained with little decomposition by heating.

35 As described above the material of the present invention has a SP value close to those of

polyethylene, polypropylene and synthetic rubbers, so that they are easily blended and wetted with each other. Also, a graft polymer of an unsaturated dicarboxylic acid and EVA or EEA has a SP value close  
5 to those of polyethylene and rubber and exhibits a very good topcoating ability by a intramolecular polarization by a vinyl acetate group, an ethyl acrylate group, in particular a carbonyl group in the case of maleinization.

10 Furthermore, the grafted EVA and EEA (in particular, EEA) have good flexibility.

A Cl group bonded to a polymer inhibits crystallization caused by the arrangement of the polymer and affords the polymer flexibility.

15 Thus, polyethylene, polypropylene or rubber can be subjected to coating or thermocontact bonding to coat or print a paint or an ink. For instance, if a polyethylene pipe used outdoors such as a petroleum pipe line is treated by the present invention to coat a  
20 fluorine resin paint, the appearance of the pipe is improved by coloration and the durability of the pipe is extensively improved by the ultraviolet screening effect of the paint as well. If the primer of the present invention is coated on the internal surface of  
25 a mold on the injection molding of a polyethylene article, a polyethylene injection-molded article which can be optionally coated or printed after mold release and has an excellent weatherability can be

obtained. Also, a solid primer composition prepared by the heat fusion kneading without solvent can be molded together with polyethylene by a two layer extrusion method to form a pipe, a plate or other articles which can be coated or printed.

Furthermore, the present invention has an excellent follow-up ability to rubber. Therefore, the present invention not only can work for the prevention of oxidative deterioration of synthetic rubbers by oxygen or ozone, the prevention of contamination by dust or the like, the prevention of smelling of synthetic rubbers and the improvement of abrasion but also can make the appearance of polyethylene, polypropylene and rubber colorful without deterioration of them as compared with the black coloration of polyethylene and rubber as a measure of conventional weatherability. Also, the present invention improves extensively heat resistance, resistance to gasoline and resistance to chemicals of the primer itself.

As the result, the primer composition of the present invention and the polyethylene which is subjected to the far infrared rays treatment as a heating means after coating with the primer can keep their forms very easily. Also, for synthetic rubbers, products coated with the primer can be obtained without little deterioration of the properties, and the thermal treatment can be completed easily and effectively in a very short time. Therefore, it is apparent that the present invention plays a great effect on the enlargement of the application or

demand of the polyethylene, polypropylene and rubber articles.

The following Table shows the properties of examples of the primers according to the present

5 invention.

TABLE

| Example No.                               | 1   | 2   | 3   |
|-------------------------------------------|-----|-----|-----|
| Component incorporated                    |     |     |     |
| Maleinized EVA *1                         | 7   | -   | 5   |
| 10 Maleinized EEA *2                      | -   | 7   | 5   |
| Chlorinated polypropylene *3              | 7   | 7   | 5   |
| Titanium oxide (rutile type)              | 5   | 5   | 5   |
| Toluene                                   | 80  | 81  | 80  |
| Total Amount                              | 100 | 100 | 100 |
| 15 Film property of primer composition *4 |     |     |     |
| Breaking strength (kg/cm <sup>2</sup> )   | 65  | 40  | 55  |
| Elongation (%)                            | 240 | 150 | 205 |

-26-

Example No.

1

2

3

Adhesion of primer to matrix \*5

|    |      |         |         |         |
|----|------|---------|---------|---------|
| 5  | LDPE | 100/100 | 80/100  | 100/100 |
|    | HDPE | 100/100 | 80/100  | 100/100 |
|    | PP   | 100/100 | 100/100 | 100/100 |
|    | NR   | 100/100 | 90/100  | 100/100 |
|    | SBR  | 100/100 | 90/100  | 100/100 |
|    | NBR  | 100/100 | 100/100 | 100/100 |
|    | CR   | 100/100 | 100/100 | 100/100 |
| 10 | EPT  | 100/100 | 90/100  | 100/100 |

Topcoat adhesion \*6

|                     |         |         |         |
|---------------------|---------|---------|---------|
| Urethane type paint | 100/100 | 100/100 | 100/100 |
|---------------------|---------|---------|---------|

|                     |         |         |         |
|---------------------|---------|---------|---------|
| Fluorine type paint | 100/100 | 100/100 | 100/100 |
|---------------------|---------|---------|---------|

Heat resistance \*7

Δ

Δ

-

Table (continued)

| Example No.                               | 4   | 5   | 6   |
|-------------------------------------------|-----|-----|-----|
| Component incorporated                    |     |     |     |
| Maleinized EVA *1                         | 40  | -   | 20  |
| 5 Maleinized EEA *2                       | -   | 40  | 20  |
| Chlorinated polypropylene *3              | 20  | 20  | 20  |
| Titanium oxide (rutile type)              | 40  | 40  | 40  |
| Toluene                                   | -   | -   | -   |
| Total Amount                              | 100 | 100 | 100 |
| 10 Film property of primer composition *4 |     |     |     |
| Breaking strength (kg/cm <sup>2</sup> )   | 85  | 55  | 70  |
| Elongation (%)                            | 250 | 190 | 210 |

| Example No.                                 |                     | 4       | 5       | 6       |
|---------------------------------------------|---------------------|---------|---------|---------|
| Adhesion of primer to matrix * <sup>5</sup> |                     |         |         |         |
| 5                                           | LDPE                | 100/100 | 80/100  | 100/100 |
|                                             | HDPE                | 100/100 | 80/100  | 100/100 |
|                                             | PP                  | 100/100 | 100/100 | 100/100 |
|                                             | NR                  | 100/100 | 90/100  | 100/100 |
|                                             | SBR                 | 100/100 | 90/100  | 100/100 |
|                                             | NBR                 | 100/100 | 100/100 | 100/100 |
|                                             | CR                  | 100/100 | 100/100 | 100/100 |
| 10                                          | EPT                 | 100/100 | 90/100  | 100/100 |
| Topcoat adhesion * <sub>6</sub>             |                     |         |         |         |
|                                             | Urethane type paint | 100/100 | 100/100 | 100/100 |
|                                             | Fluorine type paint | 100/100 | 100/100 | 100/100 |

Notes:

- 15      \*1      Graft polymer of an ethylene-vinyl acetate copolymer and maleic anhydride having a weight average molecular weight of ca.  $1.7 \times 10^5$  and a vinyl acetate content of 25%.
- 20      \*2      Chlorinated graft polymer of an ethylene-ethyl acrylate copolymer and maleic anhydride having a weight average molecular weight of ca.  $10^5$ , an ethyl acrylate content of ca. 10% and a chlorine content of ca. 20%.
- 25      \*3      Chlorinated graft polymer of polypropylene and maleic anhydride having a weight average molecular weight of ca.  $8 \times 10^4$  and a chlorine content of ca. 25%.
- 30      \*4      According to the tensile test of the "vulcanized rubber, physical tests" (1) of JIS-K-6301, using a test piece of dumbbell #1.
- 35      \*5      According to the grid test of the "general test methods of paints" 6.15 of JIS-K-5400; each primer composition having a film thickness of 15 $\mu$ m (except 50  $\mu$ m for a powder type). LDPE: low density polyethylene; HDPE:

high density polyethylene; PP: polypropylene;  
NR: natural rubber; SBR: styrene-butadiene  
rubber; NBR: acrylonitrile rubber; CR:  
chloroprene rubber; EPT: ethylene-propylene  
rubber.

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\*6 Adhesion of urethane type and fluorine type  
paints to respective primer compositions of  
examples are measured according to the grid  
test of the "general test methods of paints"  
6.15 of JIS-K-5400; the urethane type paint  
used is "UNIMARIN" (trade name), and the  
fluorine type paint used is "FLOWREX" (trade  
name), the film thickness being 50  $\mu$ m, in  
each case.

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\*7 According to the measuring method of the  
softening temperature of the "test method of  
adhesives for automobile" 13 of JIS-K-6829;  
the test pieces were the samples subjected to  
a shear test, each of which is SBR coated  
with a primer composition of the example,  
subjected to thermal treatment and laminated  
with a cyanoacrylate type adhesive. The  
evaluation measure  $\Delta$  means 40 - 50°C.

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**CLAIMS**

1. A primer composition comprising:

(1) a graft polymer of an unsaturated dicarboxylic acid and an ethylene-vinyl acetate copolymer;

(2) a chlorinated polypropylene wherein a graft polymer of an unsaturated dicarboxylic acid and polypropylene is submitted to chlorine substitution or a chlorinated polypropylene in which polypropylene is merely submitted to chlorine substitution; and

(3) a solvent.

2. A primer composition comprising:

(1) a chlorinated polypropylene wherein a graft polymer of an unsaturated dicarboxylic acid and polypropylene is submitted to chlorine substitution or a chlorinated polypropylene in which polypropylene is merely submitted to chlorine substitution;

(2) a graft polymer of an unsaturated dicarboxylic acid and an ethylene-ethyl acrylate copolymer or a chlorinated product of the graft polymer; and

(3) a solvent.

3. A primer composition comprising:

(1) a graft polymer of an unsaturated dicarboxylic acid and an ethylene-vinyl acetate copolymer;

(2) a chlorinated polypropylene wherein a graft polymer of an unsaturated dicarboxylic acid and polypropylene is submitted to chlorine substitution or a chlorinated polypropylene in which polypropylene is merely submitted to chlorine substitution;

(3) a graft polymer of an unsaturated dicarboxylic acid and an ethylene-ethyl acrylate



copolymer or a chlorinated product of the graft polymer; and

(4) a solvent.

4. A primer composition according to claim 1 or 3, wherein said graft polymer of an unsaturated dicarboxylic acid and an ethylene-vinyl acetate copolymer has a weight average molecular weight of  $1 - 2 \times 10^5$  and a vinyl acetate content of 15 - 35%.

5. A primer composition according to claim 1, 2 or 3, wherein said chlorinated polypropylene wherein a graft polymer of an unsaturated dicarboxylic acid and polypropylene is submitted to chlorine substitution has a weight average molecular weight of  $6 - 10 \times 10^4$  and a chlorine content of 20 - 30%.

6. A primer composition according to claim 1, 2 or 3, wherein said chlorinated polypropylene in which polypropylene is submitted to chlorine substitution has a weight average molecular weight of  $1 - 3 \times 10^5$  and a chlorine content of 20 - 40%.

7. A primer composition according to claim 2 or 3, wherein said graft polymer of an unsaturated dicarboxylic acid and an ethylene-ethyl acrylate copolymer has a weight average molecular weight of  $5 - 15 \times 10^4$  and an ethyl acrylate content of 15% or less.

8. A primer composition according to claim 2 or 3, wherein said chlorinated product of the graft polymer of an unsaturated dicarboxylic acid and an ethylene-ethyl acrylate copolymer has a chlorine content of 10 - 25%.

9. A primer composition according to claim 1, comprising:

(1) said graft polymer of an unsaturated dicarboxylic acid and an ethylene-vinyl acetate copolymer in an amount of ca. 2 - 30 parts by weight;

(2) said chlorinated polypropylene wherein the



graft polymer of an unsaturated dicarboxylic acid and polypropylene is submitted to chlorine substitution or the chlorinated polypropylene in which polypropylene is merely submitted to chlorine substitution in an amount of ca. 0.5 - 25 parts by weight;

(3) a pigment in an amount of ca. 0 - 30 parts by weight; and

(4) said solvent in an amount of ca. 40 - 97.5 parts by weight;

the total being 100 parts by weight.

10. A primer composition according to claim 2, comprising:

(1) said chlorinated polypropylene wherein the graft polymer of an unsaturated dicarboxylic acid and polypropylene is submitted to chlorine substitution or the chlorinated polypropylene in which polypropylene is merely submitted to chlorine substitution in an amount of ca. 0.5 - 15 parts by weight;

(2) said graft polymer of an unsaturated dicarboxylic acid and an ethylene-ethyl acrylate copolymer or the chlorinated product of the graft polymer in an amount of ca. 2 - 40 parts by weight;

(3) a pigment in an amount of ca. 0. - 30 parts by weight; and

(4) said solvent in an amount of ca. 40 - 97.5 parts by weight;

the total being 100 parts by weight.

11. A primer composition according to claim 3, comprising:

(1) said graft polymer of an unsaturated dicarboxylic acid and an ethylene-vinyl acetate copolymer in an amount of ca. 1 - 30 parts by weight;



(2) said graft polymer of an unsaturated dicarboxylic acid and an ethylene-ethyl acrylate copolymer or the chlorinated product of the graft polymer in an amount of ca. 1 - 29.5 parts by weight;

(3) said chlorinated polypropylene wherein the graft polymer of an unsaturated dicarboxylic acid and polypropylene is submitted to chlorine substitution or the chlorinated polypropylene in which polypropylene is merely submitted to chlorine substitution in an amount of ca. 0.5 - 15 parts by weight;

(4) a pigment in an amount of ca. 0 - 30 parts by weight; and

(5) said solvent in an amount of ca. 40 - 97.5 parts by weight; the total being 100 parts by weight.

12. A pellet type or powder type primer composition in a solid state at an ordinary temperature, comprising:

(1) a graft polymer of an unsaturated dicarboxylic acid and an ethylene-vinyl acetate copolymer; and

(2) a chlorinated polypropylene wherein a graft polymer of an unsaturated dicarboxylic acid and polypropylene is submitted to chlorine substitution or a chlorinated polypropylene in which polypropylene is merely submitted to chlorine substitution.

13. A pellet type or powder type primer composition in a solid state at an ordinary temperature, comprising:

(1) a chlorinated polypropylene wherein a graft polymer of an unsaturated dicarboxylic acid and polypropylene is submitted to chlorine substitution or a chlorinated polypropylene in



which polypropylene is merely submitted to chlorine substitution; and

(2) a graft polymer of an unsaturated dicarboxylic acid and an ethylene-ethyl acrylate copolymer or a chlorinated product of the graft polymer.

14. A pellet type or powder type primer composition in a solid state at an ordinary temperature, comprising:

(1) a graft polymer of an unsaturated dicarboxylic acid and an ethylene-vinyl acetate copolymer;

(2) a chlorinated polypropylene wherein a graft polymer of an unsaturated dicarboxylic acid and polypropylene is submitted to chlorine substitution or a chlorinated polypropylene in which polypropylene is merely submitted to chlorine substitution; and

(3) a graft polymer of an unsaturated dicarboxylic acid and an ethylene-ethyl acrylate copolymer or a chlorinated product of the graft polymer.

15. A primer composition according to claim 12 or 14, wherein said graft polymer of an unsaturated dicarboxylic acid and an ethylene-vinyl acetate copolymer has a weight average molecular weight of  $1 - 2 \times 10^5$  and a vinyl acetate content of 15 - 35%.

16. A primer composition according to claim 12, 13 or 14, wherein said chlorinated polypropylene in which a graft polymer of an unsaturated dicarboxylic acid and polypropylene is submitted to chlorine substitution has a weight average molecular weight of  $6 - 10 \times 10^4$  and a chlorine content of 20 - 30%.

17. A primer composition according to claim 12, 13 or 14, wherein said chlorinated polypropylene in which polypropylene is submitted to chlorine



substitution has a weight average molecular weight of 1 -  $3 \times 10^5$  and a chlorine content of 20 - 40%.

18. A primer composition according to claim 13 or 14, wherein said graft polymer of an unsaturated  
5 dicarboxylic acid and an ethylene-ethyl acrylate copolymer has a weight average molecular weight of 5 -  $15 \times 10^4$  and a ethyl acrylate content of 15% or less.

19. A primer composition according to claim 13 or 14, wherein said chlorinated product of the graft  
10 polymer of an unsaturated dicarboxylic acid and an ethylene-ethyl acrylate copolymer has a chlorine content of 10 - 25%.

20. A primer composition according to claim 12, comprising:

15 (1) said graft polymer of an unsaturated dicarboxylic acid and an ethylene-vinyl acetate copolymer in an amount of ca. 20 - 95 parts by weight;

(2) said chlorinated polypropylene wherein the graft polymer of an unsaturated dicarboxylic acid  
20 and polypropylene is submitted to chlorine substitution or the chlorinated polypropylene in which polypropylene is merely submitted to chlorine substitution in an amount of ca. 5 - 60 parts by weight; and

25 (3) a pigment in an amount of ca. 0 - 50 parts by weight;  
the total being 100 parts by weight.

21. A primer composition according to claim 13, comprising:

30 (1) said chlorinated polypropylene wherein the graft polymer of an unsaturated dicarboxylic acid and a polypropylene is submitted to chlorine substitution or the chlorinated polypropylene in which polypropylene is merely submitted to  
35 chlorine substitution in an amount ca. 5 - 60 parts by weight;



(2) said graft polymer of an unsaturated dicarboxylic acid and an ethylene-ethyl acrylate copolymer or the chlorinated product of the graft polymer is an amount of ca. 20 - 95 parts by weight; and

(3) a pigment in an amount of ca. 0 - 50 parts by weight;

the total being 100 parts by weight.

22. A primer composition according to claim 14, comprising:

(1) said graft polymer of an unsaturated dicarboxylic acid and an ethylene-vinyl acetate copolymer in an amount of ca. 10 - 85 parts by weight;

(2) said graft polymer of an unsaturated dicarboxylic acid and an ethylene-ethyl acrylate copolymer or the chlorinated product of the graft polymer in an amount of ca. 10 - 85 parts by weight;

(3) said chlorinated polypropylene wherein the graft polymer of an unsaturated dicarboxylic acid and polypropylene is submitted to chlorine substitution or the chlorinated polypropylene in which polypropylene is merely submitted to chlorine substitution in an amount of ca. 5 - 60 parts by weight; and

(4) a pigment in an amount of ca. 0 - 50 parts by weight;

the total being 100 parts by weight.

23. A process for treating a primer composition according to any of claims 1 to 22, wherein far infrared radiation is employed as a heating means for superficial treatment of the primer composition, after the primer composition has been coated on a substrate.

24. A primer composition according to claim 1, 2,



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3, 12, 13 or 14, substantially as described in any of the foregoing Examples.

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