(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 346 956 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **89201168.5**

(51) Int. Cl.4: **C11D 3/37 , C11D 1/22**

(22) Date of filing: **13.03.89**

(30) Priority: **12.03.88 JP 58688/88**

(43) Date of publication of application:
20.12.89 Bulletin 89/51

(84) Designated Contracting States:
BE DE FR GB IT NL

(71) Applicant: **CHISSO CORPORATION**
6-32, Nakanoshima 3-chome Kitaku
Osaka(JP)

(72) Inventor: **Takasu, Hiroshi**
15-10, Wakamiya 5-chome
Ichiharashi Chibaken(JP)
Inventor: **Obama, Kenjiro**
17-8, Sakuradai 3-chome
Ichiharashi Chibaken(JP)
Inventor: **Fujii, Hiroyuki**
167-4, Ichihara
Ichiharashi Chibaken(JP)

(74) Representative: **Hansen, Bernd, Dr.rer.nat. et al**
Hoffmann, Eitle & Partner Patentanwälte
Arabellastrasse 4 Postfach 81 04 20
D-8000 München 81(DE)

(54) A cleaning resin composition.

(57) A cleaning resin composition by the use of which it is possible to effect color exchange inside various molding machines by exchanging the composition for the preceding colored resin or to clean the inside of the machines or to effect resin exchange for the preceding resin inside the machines, in a small quantity of the composition, in a simple operation and in a short time is provided,
which composition comprises a polyolefin resin such as polyethylene, polypropylene, etc. and a neutral salt of an alkylbenzenesulfonic acid, an inorganic filler and a water-repellent compound blended with the polyolefin resin.

EP 0 346 956 A2

A cleaning resin composition

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a cleaning resin composition used for cleaning the inside of various molding machines. More particularly it relates to a cleaning resin composition obtained by blending a neutral salt of an alkylbenzenesulfonic acid, an inorganic filler and a water-repellent compound with a polyolefin resin.

2. Description of the Related Art

Recent molding of thermoplastic resins has been more and more diversified and production of more grades in smaller quantities has been intended. Further, due to appearance of engineering plastics, etc., color exchange or resin exchange inside molding machines has been carried out within a broad temperature region, and the frequency of the color exchange or resin exchange has also been increasing.

Heretofore, at the time of such color exchange or resin exchange, in order to remove contaminants caused by the preceding resin inside the molding machine i.e. in order to clean the inside of the molding machine, the following processes have been employed:

a process of drawing out the contaminated screw inside the molding machine, followed by scraping off the contaminants on the screw or the inner wall of the cylinder by means of a brush or the like i.e. the so-called hand sweeping, or a process of flowing a colorless resin (hereinafter abbreviated to cleaning resin) through the inside of the cylinder to clean the screw together with the cylinder (hereinafter referred to as co-cleaning) without drawing out the screw.

However, such processes require a long time for completely cleaning the screw and the inside of the cylinder, and in the case of the co-cleaning, a large quantity of cleaning resins is used to cause a large loss in the economical aspect.

Thus, in order to solve such problems, a cleaning agent composed mainly of a hard resin such as acrylic resins, a cleaning agent obtained by blending a nonionic surfactant with a thermoplastic resin, a cleaning agent obtained by blending a lubricant such as stearic acid with a thermoplastic resin, etc. have been developed.

However, in the former case, since the acrylic resins have high melt viscosity, a high load is applied at the time of cleaning the inside of the molding machine and also it is necessary to raise the temperature of the molding machine up to a considerably high temperature, there is a drawback that the resins are susceptible to thermal decomposition.

Further, there are drawbacks that operations are troublesome and require a considerably long time, for example, before the cleaning agent is used, the die screen pack, etc. of the molding machine should be removed, and further if the cleaning agent remains inside the molding machine after completion of the cleaning, the remaining cleaning agent mixes in the molded product of the succeeding resin so that the agent in the form of a foreign matter deteriorates the appearance or the physical properties of the molded product.

On the other hand, in the latter case, the cleaning agent obtained by blending stearic acid or the like with a thermoplastic resin is insufficient in the cleaning effect inside the molding machine, and in the case of the cleaning agent obtained by blending a nonionic surfactant with a thermoplastic resin, if the service temperature of the cleaning agent exceeds 250 °C, vigorous evolution of decomposition gas occurs and also a characteristic odor occurs to have a bad influence upon the operational environment, and further the cleaning effect is insufficient with such a cleaning agent.

The present inventors have made extensive research in order to obtain a cleaning resin composition by the use of which it is possible to effect color exchange inside various molding machines by exchanging the composition for the preceding colored resin or to clean the inside of the machines or to effect resin exchange for the preceding resin inside the machines, in a small quantity of the composition, in a simple operation and in a short time.

As a result we have found that a composition obtained by blending a neutral salt of an alkylbenzenesulfonic acid, an inorganic filler and a water-repellent compound with a polyolefin resin is a cleaning resin composition capable of solving the above-mentioned problems and have achieved the present invention

based on this finding.

SUMMARY OF THE INVENTION

The present invention resides in the following constitutions:

(1) a cleaning resin composition comprising a polyolefin resin and a neutral salt of an alkylbenzenesulfonic acid, an inorganic filler and a water-repellent compound blended with said polyolefin resin;

(2) a cleaning resin composition according to item (1) wherein the proportions of said neutral salt of an alkylbenzenesulfonic acid, said inorganic filler and said water-repellent compound are 1 to 20%, 1 to 30% and 0.5 to 10% each by weight, based on the weight of said composition, respectively;

(3) a cleaning resin composition according to item (1) or item (2) wherein said polyolefin resin is polyethylene or polypropylene; and

(4) a cleaning resin composition according to item (1) or item (2), which is in the form of pellets obtained by melt-kneading.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Examples of the polyolefin resin used in the present invention are polyethylene resins such as high density polyethylene, linear low density polyethylene, low density polyethylene, etc., polypropylene resins such as crystalline propylene homopolymer, crystalline propylene-ethylene copolymer, crystalline propylene-ethylene-butene-1 terpolymer or crystalline propylene-butene-1 copolymer each containing 70% by weight or more of propylene component, polybutene-1, non-crystalline ethylene-propylene copolymer (EPR), non-crystalline ethylene-propylene-diene terpolymer (EPDM) and mixtures of the foregoing. Among these, preferred resins are high density polyethylene, linear low density polyethylene, crystalline propylene homopolymer, crystalline propylene-ethylene copolymer, crystalline propylene-ethylene-butene-1 terpolymer and mixtures of the foregoing.

As the neutral salt of an alkylbenzenesulfonic acid used in the present invention, sodium salt of an alkylbenzenesulfonic acid is preferably used. This sodium salt of an alkylbenzenesulfonic acid is one kind of anionic surfactants and its decomposition-initiation temperature is as high as 300 °C. Examples of suitable alkyl groups for the neutral salt of an alkyl benzenesulfonic acid include linear or branched alkyl groups of C_6 to C_{20}.

Thus, the surfactant displays a powerful effect upon cleaning of the inside molding machines even within a high temperature region; thus a superior cleaning effect is exhibited over from a low temperature region to a high temperature region.

The quantity of the neutral salt of an alkylbenzenesulfonic acid blended is preferably 1 to 20% by weight, more preferably 5 to 15% by weight based on the weight of the composition. If the quantity thereof blended is less than 1% by weight, the cleaning effect is small when the inside of molding machines is cleaned with the resulting composition, while if it exceeds 20% by weight, notable foaming occurs when the resulting composition is granulated.

Examples of the inorganic filler used in the present invention are those usually blended with polyolefin resins such as calcium carbonate, talc, calcium sulfate, magnesium silicate, silica, alumina, etc.

In the cleaning composition, the inorganic filler exerts a function of rubbing off dirties in the molding machine and the preceding resin adhered thereonto through a mechanical force. The quantity thereof blended is preferably 1 to 30% by weight, more preferably 5 to 20% by weight based on the weight of the composition. If the blended quantity is less than 1% by weight, the cleaning effect is insufficient, while if exceeds 30% by weight, the melt-fluidity of the resulting cleaning resin composition is reduced and too a large load is applied onto the molding machine at the time of cleaning.

Examples of the water-repellent compound used in the present invention are synthetic waxes such as polyethylene wax, silicones, natural waxes, metal salts of higher fatty acids and mixtures of the foregoing. The quantity of the water-repellent compound blended is preferably 0.5 to 10% by weight, preferably 2 to 10% by weight. In the cleaning resin composition of the present invention, the water-repellent compound exerts a lubricating function. If the quantity of the water-repellent compound blended is less than 0.5% by weight, the lubricating effect is small, while if it exceeds 10% by weight, the lubricating properties are so strong that the mechanical force of the coexistant inorganic filler inside the molding machine is reduced.

Phenolic antioxidants, thioic antioxidants, phosphorus antioxidants, etc. usually blend with polyolefin

resins may be blended.

The composition of the present invention may be obtained by introducing a polyolefin and definite quantities of a neutral salt of an alkylbenzenesulfonic acid, an inorganic filler and a water-repellent compound and further at least one member of the above-mentioned antioxidants into an agitating and mixing device such as Henschel mixer (tradename), super mixer, etc. and agitating and mixing these materials for one to 5 minutes. Further, the resulting mixture may be subjected to melt-kneading and extruding at a melt-kneading temperature of 180° to 220°C, preferably 190° to 210°C by means of a single screw extruder or a twin-screw extruder into pellet form.

The present invention will be described in more detail by way of Examples and Comparative examples, but it should not be construed to be limited thereto. In addition, the proportions therein refer to % by weight.

Examples 1 - 5 and Comparative examples 1 - 4

The respective blending components described in Table 1 mentioned later were introduced into a Henschel mixer (tradename), followed by agitating and mixing them for 3 minutes, melt-extruding the resulting mixture at a melt-kneading temperature of 210°C by means of an extruder having a bore diameter of 35 mm and provided with a vent and extruding the resulting material into pellet form to obtain a cleaning resin composition of the present invention. Further, in Comparative examples 1 - 4, the respective blending components described in Table 1 mentioned later were agitated and mixed and melt-kneaded in the same manner as in Examples 1 - 5 to obtain pellets. With the cleaning resin compositions obtained in these Examples and Comparative examples, 1) cleaning of an injection molding machine and 2) cleaning of a blow molding machine were carried out in a manner of the gist described below, respectively.

Table 1

	Example 1	Example 2	Example 3	Example 4	Example 5	Comp. ex. 1	Comp. ex. 2	Comp. ex. 3	Comp. ex. 4
High density polyethylene	-	60.0%	68.5%	75.0%	-	35.0%	-	76.0%	-
Linear low density polyethylene	-	-	-	-	69.0%	-	41.0%	-	-
Polypropylene	75.0%	-	-	-	-	-	-	-	88.0%
Na alkylbenzenesulfonate	-	1.5	-	7.5	-	-	4.0	16.0	9.0
K alkylbenzenesulfonate	7.5	-	14.5	-	19.5	-	-	-	-
Polyoxyethylene cetyl ether	-	-	-	-	-	5.0	-	-	-
Ca carbonate	-	28.5	-	15.0	-	50.0	51.0	-	-
Talc	15.0	-	8.5	-	1.5	-	-	-	-
Polyethylene wax	2.0	9.5	2.5	2.5	-	-	-	6.0	-
Zn stearate	-	0.5	3.0	-	8.0	10.0	2.0	-	-
Na stearate	0.5	-	3.0	-	2.0	-	2.0	-	-
Silicon dioxide	-	-	-	-	-	-	-	2.0	1.0
Ca stearate	-	-	-	-	-	-	-	-	2.0

% : by weight

1) Example of cleaning of injection molding machine:

Black resin pellets of any of ABS resin, PPS resin and modified PPO resin, difficult in color exchange, were injection-molded by means of a 35 tons injection molding machine in 50 shots, followed by cleaning the inside of the molding machine with cleaning resin compositions obtained in Examples 1-5 and Comparative examples 1-4, each in 100 g, by injection molding and repeating injection molding with a colorless polypropylene resin as a cleaning resin by the injection molding machine until the resulting molded products were not colored, to obtain the total quantity of the cleaning resin required therefor.

Further, the black ABS resin was injection-molded under the same conditions and repeating injection-molding with the colorless polypropylene resin as a cleaning resin without using the above-mentioned cleaning resin compositions until the resulting molded product was not colored, to obtain the total quantity of the cleaning resin required therefor. These results are collectively shown in Table 2.

Table 2

Colored resin	Cleaning resin composition		Quantity of cleaning resin used	
	Kind	Temperature at its use	Case of use of the composition	Case of non-use of the composition
Black modified PPO resin 1)	Composition of Ex. 4	320°C	600 (g)	3270 (g)
	that of Comp. ex. 1	"	2110	"
	that of Comp. ex. 3	"	2400	"
Black PPS resin 2)	that of Ex. 3	"	560	3120
	that of Comp. ex. 2	"	2050	"
	that of Comp. ex. 3	"	2250	"
Black ABS resin 3)	that of Ex. 4	300°C	100	910
	that of Comp. ex. 1	"	580	"
	that of Comp. ex. 3	"	600	"
	that of Ex. 1	"	120	"
	that of Comp. ex. 2	"	620	"
	that of Comp. ex. 4	"	590	"
Black ABS resin	that of Ex. 4	260°C	140	1230
	that of Ex. 3	"	180	"
	that of Ex. 2	"	190	"
	that of Comp. ex. 1	"	740	"
	that of Comp. ex. 2	"	760	"
	that of Comp. ex. 3	"	700	"

Table 2 (continued)

Colored resin	Cleaning resin composition		Quantity of cleaning resin used	
	Kind	Temperature at its use	Case of use of the composition	Case of non-use of the composition
Black ABS resin	composition of Ex. 4	230°C	260	1410
	that of Ex. 3	"	300	"
	that of Ex. 5	"	320	"
	that of Comp. ex. 1	"	860	"
	that of Comp. ex. 3	"	980	"
Black PP resin 4)	that of Ex. 3	230°C	240	1305
	that of Ex. 4	"	220	"
	that of Comp. ex. 1	"	840	"
	that of Comp. ex. 3	"	910	"
Black ABS resin	that of Ex. 4	200°C	360	1820
	that of Ex. 1	"	380	"
	that of Comp. ex. 2	"	1000	"
	that of Comp. ex. 3	"	1270	"

1) Polyphenylene oxide 2) Polyphenylene sulfide

3) Acrylonitrile-butadiene-styrene copolymer

4) Polypropylene

2) Exmaple of cleaning of blow molding machine:

Black resin pellets of either one of ABS resin or polyethylene reisn difficult in color exchange were extruded in 10 parisons (one parison: ca. 200g) by means of a blow molding machine having a die diameter of 21 mm and a core diameter of 19 mm, followed by cleaning the resulting blow molding machine with the cleaning resin compositions obtained in Examples 1-5 and Comparative example 1-4, each in 2,000 g, and then molding the parisons with a colorless polyethylene resin as a cleaning resin until the weld line of the resulting parisons where color exchange was most difficult was not colored to obtain the total quantity of the cleaning resin required therefor.

Further, parisons were molded with the ABS resin under the same conditions, followed by molding the parisons with the colorless polyethylene resin as a cleaning resin without using the cleaning resin compositions until the weld line of the resulting parisons was not colored, to obtain the total quantity of the cleaning resin required therefor. These results are collectively shown in Table 3.

Table 3

Colored resin	Cleaning resin composition		Quantity of cleaning resin used	
	Kind	Temperature at its use	Case of use of the composition	Case of non-use of the composition
Black ABS resin	Composition of Ex. 3	260°C	3.3	30.5
	that of Ex. 4	"	2.9	"
	that of Comp. ex. 1	"	10.0	"
	that of Comp. ex. 3	"	11.8	"
Black ABS resin	that of Ex. 4	230°C	5.8	60.0
	that of Ex. 2	"	6.5	"
	that of Comp. ex. 1	"	17.4	"
	that of Comp. ex. 2	"	18.0	"
	that of Comp. ex. 3	"	23.0	"
Black HDPE resin 1)	that of Ex. 1	230°C	5.7	57.5
	that of Ex. 4	"	5.5	"
	that of Comp. ex. 2	"	17.7	"
	that of Comp. ex. 3	"	20.4	"
	that of Comp. ex. 4	"	22.8	"
Black ABS resin	that of Ex. 4	200°C	7.0	70.5
	that of Ex. 5	"	7.4	"
	that of Comp. ex. 1	"	18.0	"
	that of Comp. ex. 2	"	20.0	"
	that of Comp. ex. 3	"	26.0	"

1) High density polyethylene

According to the present invention, as seen from Tables 2 and 3, when the respective cleaning resin compositions shown in Examples 1-5 are used each in a small quantity, it is possible to far reduce the quantities of the cleaning resin used as compared with those shown in Comparative example 1-4. and display a notably excellent cleaning effect.

The cleaning resin composition of the present invention has a notably excellent cleaning effect at the time of color exchange of the preceding colored resin in various molding machines and also at the time of cleaning for exchange of the preceding resin.

Namely, by using the cleaning resin composition of the present invention in a small quantity or by using the composition in a small quantity together with a cleaning resin, it is possible to far reduce the quantity of cleaning resins consumed and also notably shorten the cleaning period of time, as compared with the case

where the inside of molding machines has so far been cleaned by exchange with cleaning resins each color exchange.

Such effect will be illustrated by cleaning of the inside of an injection molding machine. As seen from comparison of use of the cleaning resin composition of the present invention with use of cleaning resins alone, it is possible to reduce the quantity of the cleaning resins required down to about $^1/_5$ - $^1/_{10}$ and also to shorten the cleaning period of time down to about $^1/_5$ - $^1/_{10}$.

Further, the cleaning resin composition of the present invention displays a notably excellent effect at the time of color exchange and also at the time of resin exchange even in the case where engineering plastics such as modified PPO resin, polyphenylene sulfide resin, etc. as the preceding resin are molded at high temperatures.

Claims

1. A cleaning resin composition comprising a polyolefin resin and a neutral salt of an alkylbenzenesulfonic acid, an inorganic filler and a water-repellent compound blended with said polyolefin resin.

2. A cleaning resin composition according to claim 1 wherein the proportions of said neutral salt of an alkylbenzenesulfonic acid, said inorganic filler and said water-repellent compound are 1 to 20%, 1 to 30% and 0.5 to 10% each by weight, based on the weight of said composition, respectively.

3. A cleaning resin composition according to claim 1 wherein said polyolefin resin is polyethylene or polypropylene.

4. A cleaning resin composition according to claim 2 wherein said polyolefin is polyethylene or polypropylene.

5. A cleaning resin composition according to claim 1, which is in the form of pellets obtained by melt-kneading.

6. A cleaning resin composition according to claim 2, which is in the form of pellets obtained by melt-kneading.

7. Use of a cleaning resin composition according to any of the preceding claims for cleaning the inside of molding machines.