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(54) **Maleic anhydride modified polymers**

(57) The catalytic grafting of an ethylenically unsaturated monomer onto a copolymer in the presence of a catalyst wherein the monomer is selected from the group consisting of ethylenically unsaturated carbocylic acids, anhydrides esters and other derivatives thereof and the copolymer is selected from the group consisting of copolymers of ethylene with at least one monomer selected from the group consisting of vinyl alkylates, carbon monoxide, acrylic acid, methacrylic acid, acrylate esters and methacrylate esters, and mixtures thereof, and ionomers of such copolymers takes place in the presence of an organic peroxide and, as catalyst, (i) organic phosphite compounds of the formula $P(OR)_3$, where each R is independently selected from alkyl, aryl and alkaryl, (ii) organic phosphite compounds of the formula $(OR_1)_2P{-}O{-}R_2{-}O{-}P(OR_3)_2$, where each of R_1, R_2 and R_3 is independently selected from alkyl, aryl and alkaryl, or (iii) di-substituted pentaerythritol diphosphite in which the substituents are alkyl, aryl and alkyl groups. The grafted polymer has improved colour, and is useful in adhesive systems and as a compatibilizer for polymers and other materials.

PROCESS FOR THE PREPARATION OF GRAFTED POLYMERS OF IMPROVED COLOUR

The present invention relates to a catalyzed process for the grafting of ethylenically unsaturated monomers onto polymers and especially to the grafting of such monomers onto copolymers of ethylene with derivatives of certain carboxylic acids, such derivatives being ethylenically unsaturated. In particular, the invention relates to such a process in which the grafted polymer is obtained in higher yield and with improved colour.

Copolymers of ethylene with unsaturated carboxylic acid and ester monomers, are known and include ethylene/vinyl acetate copolymers, ethylene/(meth)acrylate copolymers and ethylene/(meth)acrylic acid copolymers. Such copolymers have a variety of end-uses and in embodiments are used in the manufacture of adhesives, as coatings and in the form of blends with other polymers e.g. polyolefins.

It is known that the properties of polyolefins may be modified by the grafting of ethylenically unsaturated carboxylic acids and anhydrides onto hydrocarbon alpha-olefins. Published European patent application No. 0 266 994 of P.C. Wong, published 1988 May 11, discloses a process for the melt grafting of an ethylenically unsaturated monomer onto a copolymer. In the process, an admixture of the copolymer, monomer and an organic peroxide is mixed in an extruder at a temperature above the melting point of the copolymer for a period of time that is at least four times the half-life of the organic peroxide. The resultant grafted copolymer is extruded into a shaped article. The preferred monomers are maleic acid and maleic anhydride. Japanese patent application No. 57 030 745 of Toyo Soda, published 1982 February 19, discloses blends of (a) phenol resin and (b) carboxyl-modified ethylene/vinyl acetate copolymer that preferably are prepared by reacting

100 parts by weight of ethylene/vinyl acetate copolymer with alpha, beta unsaturated carboxylic acid or anhydride under melt conditions in the presence of 0.001-1 parts by weight of a radical initiator e.g. di-tert.butyl peroxide or tert.butyl peracetate.

The use of copolymers, including graft copolymers, of ethylene and ethylenically unsaturated carboxylic acids and anhydrides in film laminates is known. For example, European patent application No. 160 984-A of Kuraray K.K., published 1985 November 13, describes such a use of ethylene/acrylate ester/ethylenically unsaturated carboxylic acid and anhydride copolymers. The use of copolymers of (meth)acrylate esters and ethylenically unsaturated acids or anhydrides is disclosed in Japanese patent application No. 59 152 852 of Kuraray K.K., published 1984 August 31, and the use of the related copolymers of ethylene/vinyl acetate is disclosed in Japanese patent applications No. 59 229 338 of Kuraray K.K. and No. 59 024 665 of Dainippon Printing K.K., published 1983 June 10 and 1984 February 08, respectively. Hot melt adhesives, formed from ethylene/vinyl acetate copolymers that have been peroxygenated with atmospheric oxygen and then grafted with methacrylic acid units, are disclosed in U.S. Patent 4 602 056 of H. Waniczek et al., which issued 1986 July 22. The production of laminates using ethylene/vinyl acetate copolymers graft-modified with unsaturated carboxylic acid or anhydrides is disclosed in Japanese patent application No. 59 055 743 of Mitsubishi Petrochemical Co. Limited, published 1984 March 30.

It is important in the grafting of monomers onto polymers that a uniform product be obtained. Furthermore, it is important that the grafted polymer be of a commercially-acceptable colour, especially if the grafted product is to be used in association with clear or lightly coloured materials e.g. as an adhesive in the bonding or laminating of clear thermoplastic films. However, the grafting of monomers onto copolymers of ethylene and ethylenically unsaturated carboxylic acids or esters tends to result in significant increases in the colour of the product.

A process has now been found for the grafting, in the presence of a catalyst, of ethylenically unsaturated carboxylic acids and anhydrides onto copolymers of ethylene with derivatives of certain carboxylic acids, such derivatives being ethylenically unsaturated, in a manner that produces grafted copolymers in higher yields and with improved colour.

Accordingly, the present invention provides a process for the grafting of an ethylenically unsaturated monomer onto a copolymer in the presence of a catalyst, said monomer being selected from the group consisting of ethylenically unsaturated carboxylic acids, anhydrides, esters and other derivatives thereof, said copolymer being selected from the group consisting of copolymers of ethylene with at least one monomer selected from the group consisting of vinyl alkylates, carbon monoxide, acrylic acid, methacrylic acid, acrylate esters and methacrylate esters, and mixtures thereof, and ionomers of such copolymers, and said catalyst being selected from the group consisting of (i) organic phosphite compounds of the formula $P(OR)_3$, where each R is independently selected from alkyl, aryl and alkaryl, (ii) organic phosphite compounds of the formula $(OR_1)_2P-O-R_2-O-P(OR_3)_2$, where each of R_1, R_2 and R_3 is independently selected from alkyl, aryl and alkaryl, and (iii) di-substituted pentaerythritol diphosphites in which the substituents are alkyl, aryl and alkyl groups,
said process comprising:

(i) admixing copolymer, monomer, at least 100 ppm of catalyst and 25-2500 ppm of an organic peroxide having a half-life of from about 1 minute to about 120 minutes at 150°C, and admixing at a temperature above the melting point of said copolymer for a period of time that is at least 4 times the half-life of the organic peroxide so as to obtain a uniform distribution of monomer, catalyst and peroxide in the copolymer;

(ii) extruding the resultant grafted copolymer into a shaped article.

In preferred embodiments of the process of the present invention, the ethylenically unsaturated acid and anhydride are maleic acid and maleic anhydride, respectively.

In a further embodiment, the catalyst is in the form of a concentrate in a polymer, said polymer being compatible with the copolymer.

In addition, the present invention provides a grafted copolymer composition having 0.5 to 5% by weight of a monomer grafted thereon, said copolymer being selected from the group consisting of copolymers of ethylene with at least one monomer selected from the group consisting of vinyl alkylates, carbon monoxide, acrylic acid, methacrylic acid, acrylate esters and methacrylate esters, and mixtures thereof, and ionomers of such copolymers, and said monomer being selected from the group consisting of ethylenically unsaturated carboxylic acids, anhydrides, esters and other derivatives thereof, said grafted polymer having a melt index that is 20-99% of the melt index of the copolymer prior to grafting, said grafted copolymer having been formed by grafting the monomer onto molten copolymer in the presence of 25-2500 ppm of an organic peroxide having a half-life of from about 1 minute to about 120 minutes at 150'C and at least 100 ppm of a catalyst selected from the group consisting of (i) organic phosphite compounds of the formula $P(OR)_3$, where each R is independently selected from alkyl, aryl and alkaryl, (ii) organic phosphite compounds of the formula $(OR_1)_2P-O-R_2-O-P(OR_3)_2$, where each of R_1, R_2 and R_3 is independently selected from alkyl, aryl and alkaryl, and (iii) di-substituted pentaerythritol diphosphites in which the substituents are alkyl, aryl and alkyl groups.

The copolymer that is subjected to the process of the present invention may be a copolymer of ethylene and a vinyl alkanoate, especially ethylene/vinyl acetate copolymers. Alternatively, the copolymer may be a copolymer of ethylene and an acrylate ester, examples of which are ethylene/ethyl acrylate copolymers, ethylene/methyl acrylate copolymers and ethylene/butyl acrylate copolymers. Similarly, the copolymer may also be a copolymer of ethylene and a methacrylate ester e.g. ethylene/methyl methacrylate. Other copolymers include copolymers of ethylene with acrylic acid or methacrylic acid, and analogous ionomers viz. copolymers having the acid groups thereof partially neutralized by metals especially with sodium, zinc or aluminum. Additionally, the copolymer may be a copolymer of ethylene with carbon monoxide, optionally also with one of the aforementioned monomers, examples of which are ethylene/carbon monoxide, ethylene/butyl acrylate/carbon monoxide, and ethylene/vinyl acetate/carbon monoxide copolymers. Such copolymers are known in the art and many examples thereof are available commercially.

The copolymers may have a relatively high ethylene content, and tend to be non-tacky copolymers, or lower ethylene contents, and tend to be relatively tacky copolymers. The latter include copolymers that in pellet form tend to agglomerate. In addition, the copolymers are available in a variety of molecular weights, which is usually expressed in terms of melt index. Melt index is measured by the procedure of ASTM D-1238 (condition E). The nature of the copolymer, especially with respect to ethylene content and molecular weight, that is subjected to the process of the present invention will depend in particular on the intended end-use of the grafted copolymer that is obtained from the process. Copolymers having a wide variety of properties may be subjected to the process described herein.

The organic peroxide, which as used herein includes hydroperoxides, may for example be a peroxy ester, bis(tert. alkyl peroxy alkyl) benzene, dicumyl peroxide or acetylenic diperoxy compound. Other organic peroxides are known to those skilled in the art, including t-butyl hydroperoxide and di-t-butyl peroxide. The organic peroxides used in the process of the present invention have a half-life at 150°C of from about one minute to about 120 minutes. Preferred organic peroxides are 2,5-dimethyl-2,5-di(t-butyl peroxy) hexane and 2,5-dimethyl-2,5-di(t-butyl peroxy) hexyne-3 which are available under the trade marks Lupersol 101 and Lupersol 130, respectively, from Lucidol Division of Pennwalt Corporation.

The grafting monomer is selected from the group consisting of ethylenically unsaturated carboxylic acids and ethylenically unsaturated carboxylic acid anhydrides, including derivatives of such acids. Examples of the acids and anhydrides, which may be mono-, di- or polycarboxylic acids, are acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, crotonic acid, itaconic anhydride, maleic anhydride and substituted maleic anhydride e.g. dimethyl maleic anhydride, nadic anhydride, nadic methyl anhydride and tetrahydro phthalic anhydride. Examples of derivatives of the unsaturated acids are salts, amides, imides and esters e.g. mono- and disodium maleate, acrylamide, maleimide, glycidyl methacrylate and diethyl fumarate.

The amount of organic peroxide will depend in particular on the characteristics of the copolymer but will be in the range of 25-2500 ppm, especially 100-2000 ppm, based on the weight of the copolymer in the admixture fed to the extruder, and particularly in the range of 500-1500 ppm. It is an important characteristic of the present invention that low levels of organic peroxide may be used, while still effecting high levels of grafting. Such low levels result in relatively small changes in the properties of the copolymer, especially relatively small changes in the melt index thereof on extruding the polymer mixture.

The amount of monomer will depend in particular on the reactivity of the monomer and the level of grafting that is to be achieved. For example, if the monomer is maleic anhydride, the amount of monomer may be as high as about 5%, especially 0.1-3%, by weight of the copolymer, and particularly in the range of 0.2-2% by weight. With other monomers, different amounts of monomer may be preferred.

The compositions fed to the extruder contain at least 100 ppm, especially at least 500 ppm and in particular at least 800 ppm of a catalyst. High levels of the catalyst may be used, e.g. up to 5000 ppm or higher, but in preferred embodiments the amount of catalyst is in the range of 800 to 2500 ppm. The catalyst is selected from the group consisting of (i) organic phosphite compounds of the formula $P(OR)_3$, where each R is independently selected from alkyl, aryl and alkaryl, (ii) organic phosphite compounds of the formula $(OR_1)_2P\text{-}O\text{-}R_2\text{-}O\text{-}P(OR_3)_2$, where each of R_1, R_2 and R_3 is independently selected from alkyl, aryl and alkaryl, and (iii) di-substituted pentaerythritol diphosphites in which the substituents are alkyl, aryl and alkyl groups. In other embodiments, the substituents, especially R_2, may contain oxygen atoms e g. oxygen atoms in the form of ether linkages.

It will be understood by those skilled in the art that some additives may have detrimental effects on the grafting process and for that reason it may be preferable not to use certain combinations of additives.

The compositions may be fed to the extruder in a number of ways. For example, the copolymer may be fed to the extruder and heated to a molten condition. The organic peroxide, grafting monomer and catalyst may then be fed directly into the molten copolymer, at the same or at separate addition ports of the extruder. Alternatively, one or more of the organic peroxide, grafting monomer and catalyst may be fed to the extruder simultaneously with the copolymer, especially the organic peroxide; feeding to the extruder in this manner permits dispersion of, in particular, the peroxide in the copolymer prior to contact of the organic peroxide and grafting monomer, thereby facilitating production of grafted copolymer of more uniform properties. For example, one or more of the organic peroxide, grafting monomer and catalyst may be fed to the extruder in the form of concentrates in a suitable carrier polymer. In a further alternative embodiment, one or more of the organic peroxide, grafting monomer and catalyst are fed to the extruder with the copolymer by spraying or otherwise admixing such materials with the copolymer. In a preferred embodiment of the process of the present invention, the organic peroxide and catalyst are in the form of concentrates in a carrier polymer and are fed to the extruder with the copolymer.

The process of the present invention may be used to produce compositions of monomer grafted onto the copolymers that have improved colour. The shaped articles produced by the process of the present invention will usually be pellets or other comminuted shapes, but are not restricted thereto. The grafted polymers may be used as such or as blends with other polymers, especially in the form of adhesive compositions for use with polymers and/or metals, in co-extrusion of multiple layer structures, in coating compositions, as compatibilizers in filled compositions and to improve the dyeability and paintability of polymers.

The present invention is illustrated by the following examples.

Example I

An admixture was formed of an ethylene/vinyl acetate copolymer having a vinyl acetate content of 9% by weight and a melt index of 2.0 dg/min, an organic peroxide and maleic anhydride. The organic peroxide was Lupersol 101 and was added in the form of a concentrate in the above ethylene/vinyl acetate copolymer such that the admixture contained 1000 ppm of the organic peroxide. The maleic anhydride was added directly into the first zone of the extruder, in an amount of 1.5% by weight of the copolymer. A variety of catalysts or, in comparative runs, other materials, were added in the form of pellet concentrates in the above ethylene/vinyl acetate copolymer.

The resultant admixture was blended in an extruder and then extruded into water in the form of a strand and then pelletized. The colour of the pellets was measured using a Hunter* L,a,b colorimeter, the measurement being made on the pellets. The melt index and yellowness index of the grafted copolymer were measured using the procedure of ASTM D-1238 (Condition E) and ASTM D-1925-70, respectively. The graft monomer content of the grafted copolymer and the residual, unreacted, graft monomer content were also measured.

The results obtained are given in Table I.

TABLE I

Run No.	Graft Amount (%)	Graft Yield (%)	Melt Index dg/min	Catalyst	Catalyst Amount (ppm)	Yellowness Index
1*	0.81	54	1.46	-	-	36.5
2	1.06	71	0.66	A	1000	4.9
3*	0.85	57	1.38	-	-	34.3
4	1.22	81	0.79	B	1100	7.7
5*	1.05	70	1.35	-	-	44.7
6	1.24	83	1.10	C	1000	11.3
7*	1.00	67	1.27	-	-	38.9
8	1.26	84	0.66	A	1000	11.3

* comparative runs, without addition of catalyst

In Table I, the catalysts or other compounds added were as follows:

A	distearyl pentaerythritol diphosphite
B	bis (2,4 di-tert. butyl phenyl) pentaerythritol diphosphite
C	trioctadecyl phosphite

The results show that distearyl pentaerythritol diphosphite, bis (2,4 di-tert. butyl phenyl) pentaerythritol diphosphite and trioctadecyl phosphite gave improvements in both yield and colour of the grafted copolymer.

Example II

The procedure of Example I was repeated using an ethylene/vinyl acetate copolymer having a vinyl acetate content of 28% and a melt index of 6 dg/min, except that the amount of maleic anhydride was 1.6% by weight and the catalyst was bis (2,4 di-tert. butyl phenyl) pentaerythritol diphosphite.

The results obtained are given in Table III.

TABLE II

Run No.	Graft Amount (%)	Graft Yield (%)	Melt Index dg/min	Catalyst	Catalyst Amount (ppm)	Yellowness Index
9*	1.07	67	4.0	no	-	36.1
10*	1.03	64	4.2	no	-	38.7
11	1.17	73	1.7	yes	1000	24.5
12	1.34	84	1.5	yes	1000	22.1

* comparative runs, without addition of catalyst

The results show an improvement in both graft yield and colour of the resultant grafted polymer.

Example III

An admixture was formed of an ethylene/vinyl acetate copolymer having a vinyl acetate content of 9% by weight and a melt index of 2.0 dg/min, an organic peroxide and maleic anhydride. The organic peroxide was Lupersol 101 and was added in the form of a concentrate in the above ethylene/vinyl acetate copolymer such that the admixture contained 1500 ppm of the organic peroxide. The maleic anhydride was added directly into the first zone of the extruder, in an amount of 1.7% by weight of the copolymer. The admixture also contained tris nonyl phenyl phosphite, which was added to the admixture at different levels and by different means, as discussed below.

The admixture was blended in an extruder and then extruded and pelletized under water.

The tris nonyl phenyl phosphite was added by one of the following techniques:

(a) The phosphite was injected in liquid form, in the form of a solution in mineral oil (1:1), directly into the extruder subsequent to the addition of maleic anhydride;

(b) The phosphite was sprayed onto pellets of the copolymer in the throat of the extruder, using the solution of (a);

(c) The phosphite was in the form of a pellet concentrate, at a level of 5% by weight, in the above ethylene/vinyl acetate copolymer.

The results obtained are given in Table III.

TABLE IV

Run No.	Graft Amount (%)	Graft Yield (%)	Melt Index dg/min	Catalyst Addition	Catalyst Amount (ppm)	Yellowness Index (YI)
13*	0.97	57	1.42	-	-	48.9
14	1.61	95	1.01	c	1100	7.9
15	1.37	81	0.99	c	1100	6.3
16*	1.05	62	1.40	-	-	40.1
18	1.03	61	1.41	a	500	37.9
19	1.01	59	1.43	a	1000	33.5
20	1.08	64	1.38	a	2000	18.1
21	1.07	63	1.34	a	2500	11.7
22	1.06	62	1.47	a	1000	30.8
23*	0.88	52	1.44	-	-	40.5
24	1.06	62	1.55	b	1000	29.9
25	1.03	61	1.32	b	2000	12.7

* comparative runs, without addition of tris nonyl phenyl phosphite

The results show that improvements in polymer colour were obtained, compared to the control runs in which tris nonyl phenyl phosphite was not added. It was also found that addition of the tris nonyl phenyl phosphite in the form of a concentrate in a polymer improved colour and grafting yield.

EXAMPLE IV

The procedure of Example III was repeated using an ethylene/vinyl acetate copolymer having a vinyl acetate content of 28% by weight and a melt index of 6.0 dg/min.

The results obtained are given in Table V.

TABLE IV

Run No.	Graft Amount (%)	Graft Yield (%)	Melt Index dg/min	Catalyst Addition	Catalyst Amount (ppm)	Yellowness Index (YI)
26*	1.29	76	2.9	-	-	67.1
27	1.52	89	1.5	a+c	3200	35.8

* comparative run, without addition of tris nonyl phosphite; data is an average of three runs.

The results show that addition of the tris nonyl phenyl phosphite gave a higher yield and grafted polymer of improved colour.

Example V

The procedure of Example III was repeated using an ethylene/vinyl acetate copolymer having a vinyl acetate of 18% by weight and a melt index of 8.0 dg/min and bis (2,4 di-tert. butyl phenyl) pentaerythritol diphosphite as catalyst. The amount of organic peroxide used was 1700 ppm and the amount of maleic anhydride used was 1.5% by weight.

The results obtained are given in Table V.

TABLE V

Run No.	Graft Amount (%)	Graft Yield (%)	Melt Index dg/min	Catalyst Addition	Catalyst Amount (ppm)	Yellowness Index
28*	0.96	64	4.3	-	-	48.8
29**	1.27	85	2.9	c	1000	33.7

* comparative runs, without addition of catalyst

** the catalyst was introduced as a concentrate in an ethylene/vinyl acetate copolymer having a vinyl acetate content of 9% by weight and a melt index of 2 dg/min

The results show an improvement in the yield obtained.

Example VI

The procedure of Example I was repeated to determine effects of use of phenolic antioxidants in place of or in addition to catalysts according to the invention. The polymer was an ethylene/vinyl acetate copolymer having a vinyl acetate content of 9% and a melt index of 2 dg/min. The amount of maleic anhydride used was 1.7% by weight and the organic peroxide was Lupersol 101 in an amount of 1150 ppm. The catalyst was tris nonyl phenyl phosphite which, if added, was added in an amount of 800 ppm.

Further details and the results obtained are given in Table VI.

TABLE VI

Run No.	Antioxidant Type*/ Amount(ppm)	Graft Amount (%)	Graft Yield (%)	Melt Index dg/min	Catalyst	Yellowness Index
30*	BHT/80	1.30	76	1.09	no	45.6
31	BHT/700	1.22	72	1.09	no	48.3
32	BHT/700	1.52	89	0.73	yes	11.3
33	BHT/80	1.60	94	0.78	yes	11.0
34	BHT/80	1.39	82	1.13	no	48.5
35	D/1000	1.24	73	1.10	no	57.7
36	D/1000	1.56	92	0.78	yes	14.9

* BHT is 2,6-di-tert. butyl 4-methyl phenol
D is tetrakis-methylene-3-(3′,5′-di-tert. butyl-4-hydroxy phenyl) propionate methane

The results showed that the amount of 2,6-di-tert. butyl 4-methyl phenol antioxidant had little effect on either the grafting yield or colour of the grafted polymer. However, addition of catalyst, according to the invention, to polymer containing either of the levels of

2,6-di-tert. butyl 4-methyl phenol resulted in substantial improvement in grafting yield and a major improvement in the colour of the grafted polymer. The same result was obtained when the antioxidant was tetrakis-methylene-3-(3',5'-di-tert. butyl-4-hydroxy phenyl) propionate methane. Thus, the results show that (i) phenolic antioxidants may be present during the grafting reaction, and (ii) the catalysts of the present invention provide significant improvements in the grafting process.

Example VII

The procedure of Example I was repeated using different levels of catalyst, the catalyst being tris nonyl phenyl phosphite. The polymer was an ethylene/vinyl acetate copolymer having a vinyl acetate content of 9% and a melt index of 2 dg/min. The amount of maleic anhydride used was 1.7% by weight and the organic peroxide was Lupersol 101 in an amount of 1150 ppm.

TABLE VII

Run No.	Graft Amount (%)	Graft Yield (%)	Melt Index dg/min	Catalyst*	Catalyst Amount (ppm)	Yellowness Index
37	1.23	72	1.12	-	-	43.1
38	1.53	90	0.93	E	150	21.7
39	1.59	94	0.73	E	250	11.7
40	1.60	94	0.80	E	500	9.1
41	1.47	86	0.84	E	1000	6.7
42	1.30	76	1.04	F	4000	11.1

* Catalyst E was tris nonyl phenyl phosphite and Catalyst F was tris (2,4 di-tert. butyl phenyl) phosphite

The results show that the addition of low levels of tris nonyl phenyl phosphite catalyst result in significant improvements in, in particular, the colour of the grafted polymer. When tris (2,4 di-tert. butyl phenyl) phosphite was used as catalyst, significant improvements were obtained but at higher levels of catalyst.

Example VIII

The procedure of Example VII was repeated using ethylene/methyl acrylate copolymer having a methyl acrylate content of 20% by weight and a melt index of 6 dg/min. The catalyst was trioctadecyl phosphite.

Further details and the results obtained are given in Table VIII.

TABLE VIII

Run No.	Graft Amount (%)	Graft Yield (%)	Melt Index dg/min	Catalyst Addition	Catalyst Amount (ppm)	Yellowness Index
43	0.94	55	5.0	-	-	28.3
44	1.02	60	5.4	yes	1250	14.2

The results show that trioctadecyl phosphite is effective as a catalyst in the grafting reaction. This example also illustrates the process of the present invention with ethylene/methyl acrylate copolymers.

EXAMPLE IX

The procedure of Example V was repeated using a series of ethylene/vinyl acetate copolymers having vinyl acetate contents ranging from 18% to 33% and melt indices ranging from 8 to 800 dg/min, except that the amount of maleic anhydride was 1.1% and the catalyst was phosphorous acid. The catalyst was added as a 60% by weight solution in water onto the pellets in the throat of the extruder.

The results obtained are given in Table IX.

Table IX

	Copolymer		Catalyst	Graft	Graft	Melt Index	Yellowness
Run No.	VA (%)	Melt Index dg/min	Amount (ppm)	Amount (%)	Yield (%)	of Product dg/min	of Product Index
45	18	500	55	1.10	100	170	1.1
46	20	800	200	1.00	91	470	16.7
47	33	400	200	0.85	77	240	13.7
48	18	8.0	120	1.01	92	2.3	9.7
49	28	43	200	1.03	94	16	19.3
50	33	43	250	0.95	86	22	29.9

VA = vinyl acetate.

The results show that the addition of low levels of phosphorous acid produces grafted polymer having exceptional colour and graft yield.

CLAIMS:

1. A process for the grafting of an ethylenically unsaturated monomer onto a copolymer in the presence of a catalyst, said monomer being selected from the group consisting of ethylenically unsaturated carboxylic acids, anhydrides, esters and other derivatives thereof, said copolymer being selected from the group consisting of copolymers of ethylene with at least one monomer selected from the group consisting of vinyl alkylates, carbon monoxide, acrylic acid, methacrylic acid, acrylate esters and methacrylate esters, and mixtures thereof, and ionomers of such copolymers, and said catalyst being selected from the group consisting of (i) organic phosphite compounds of the formula $P(OR)_3$, where each R is independently selected from alkyl, aryl and alkaryl, (ii) organic phosphite compounds of the formula $(OR_1)_2P\text{-}O\text{-}R_2\text{-}O\text{-}P(OR_3)_2$, where each of R_1, R_2 and R_3 is independently selected from alkyl, aryl and alkaryl, and (iii) di-substituted pentaerythritol diphosphite in which the substituents are alkyl, aryl and alkyl groups,

said process comprising:

(i) admixing copolymer, monomer, at least 500 ppm of catalyst and 25-2500 ppm of an organic peroxide having a half-life of from about 1 minute to about 120 minutes at 150°C, and admixing at a temperature above the melting point of said copolymer for a period of time that is at least 4 times the half-life of the organic peroxide so as to obtain a uniform distribution of monomer, catalyst and peroxide in the copolymer;

(ii) extruding the resultant grafted copolymer into a shaped article.

2. The process of Claim 1 in which the ethylenically unsaturated acid and anhydride are maleic acid and maleic anhydride, respectively.

3. The process of Claim 1 in which the catalyst is in the form of a concentrate in a polymer, said polymer being compatible with the copolymer.

4. A grafted copolymer composition having 0.5 to 5% by weight of a monomer grafted thereon, said copolymer being selected from the group consisting of copolymers of ethylene with at least one monomer selected from the group consisting of vinyl alkylates, carbon monoxide, acrylic acid, methacrylic acid, acrylate esters and methacrylate esters, and mixtures thereof, and ionomers of such copolymers, and said monomer being selected from the group consisting of ethylenically unsaturated carboxylic acids, anhydrides, esters and other derivatives thereof, said grafted polymer having a melt index that is 20-99% of the melt index of the copolymer prior to grafting, said grafted copolymer having been formed by grafting the monomer onto molten copolymer in the presence of 25-2500 ppm of an organic peroxide having a half-life of from about 1 minute to about 120 minutes at 150'C and at least 500 ppm of a catalyst selected from the group consisting of (i) organic phosphite compounds of the formula $P(OR)_3$, where each R is independently selected from alkyl, aryl and alkaryl, (ii) organic phosphite compounds of the formula $(OR_1)_2P\text{-}O\text{-}R_2\text{-}O\text{-}P(OR_3)_2$, where each of R_1, R_2 and R_3 is independently selected from alkyl, aryl and alkaryl, and (iii) di-substituted pentaerythritol diphosphite in which the substituents are alkyl, aryl and alkyl groups.

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