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ETHYLENE/VINYL PHOSPHINE OXIDE COPOLYMERS AND BLENDS OF SAME WITH POLYPROPYLENE

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4 Claims. (Cl. 260—88.1)

This application is a continuation-in-part of Ser. Nos. 189,313, filed Apr. 23, 1962 and now abandoned; 189,267, filed Apr. 23, 1962 and now abandoned; and 319,993, Oct. 30, 1963.

This invention relates to polypropylene compositions having improved dye-receptability, and to novel copolymers employed in such compositions.

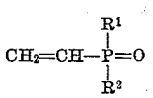
Polypropylene has found widespread use in the production of films and fibers. However, one serious drawback to the use of polypropylene in these and other applications is its inability to receive common dyes. This serious disadvantage has severely restricted the use of polypropylene and prevented its full commercial exploitation.

Various attempts have been made to solve this problem, but these usually have proven unsuccessful for one reason or another. Now, however, in accordance with the instant invention, it has been discovered that polypropylene compositions having excellent dyeability and printability can be prepared by blending polypropylene with a copolymer of a vinylphosphine oxide with ethylene or with an alkoxyethyl acrylate. The compositions produced by such procedure are characterized by improved dyeability and printability than the polypropylene from which they are produced, while the other physical properties of the polypropylene, such as, for example, stiffness, tensile strength, elongation and dielectric strength, heat and light stability, etc., do not appear to undergo any significant deterioration.

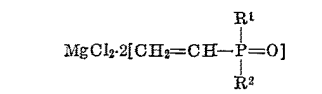
The compositions of the instant invention are produced by mixing a copolymer of the type herein described with polypropylene to produce a homogeneous blend of the two polymers. Blending can be effected by any conventional means, such as by means of a two-roll mill or a Banbury mixer, or by the use of a common solvent for the two polymers. When a two-roll mill or a Banbury mixer is employed, blending can be easily effected at temperatures above the melting point of the polymers, for example, from about 160° C. to about 225° C., preferably from about 165° C. to about 175° C. The polypropylene employed is solid and preferably has a melt index of from about 0.1 decigram/minute to about 100 decigrams/minute at 230° C., and a density greater than about 0.89 gram/cc. If desired, fillers, antioxidants, heat stabilizers, light stabilizers, and other additives can be added to the blend.

The modifying copolymers employed in the instant invention are obtained by copolymerizing a vinylphosphine oxide with ethylene or an alkoxyethyl acrylate.

The vinylphosphine oxides which can be employed in producing the modifying copolymers employed in the instant invention can be represented by the formula



wherein R^1 and R^2 are monovalent hydrocarbon radicals free of aliphatic unsaturation, such as alkyl and aryl, containing from 1 to 14 carbon atoms, preferably from 1 to 6 carbon atoms. If desired a magnesium chloride complex of the vinylphosphine oxide can be employed in lieu of the vinylphosphine oxide itself. These complexes can be represented by the formula



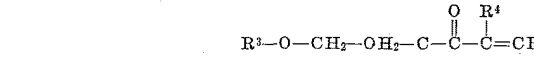
wherein R^1 and R^2 are as above defined. These complexes can be readily prepared by reacting magnesium chloride with a suitable vinylphosphine oxide in accordance with the technique disclosed in application Ser. No. 319,992, entitled "Coordination Complexes Of Vinylphosphine Oxides And Metal Salts, And Polymers Thereof," filed Oct. 30, 1963, by Frank J. Welch and Herbert J. Paxton, Jr., which disclosure is incorporated herein by reference.

Among the vinylphosphine oxides which be employed as comonomers are

vinyldimethylphosphine oxide,
vinyldiethylphosphine oxide,
vinylmethylethylphosphine oxide,
vinyldipropylphosphine oxide,
vinyldiisopropylphosphine oxide,
vinyldibutylphosphine oxide,
vinyldiisobutylphosphine oxide,
vinyl-di-tertiary-butylphosphine oxide,
vinyldipentylphosphine oxide,
vinyldiisopentylphosphine oxide,
vinyl-di-tertiary-pentylphosphine oxide,
vinyldihexylphosphine oxide,
vinyldicyclohexylphosphine oxide,
vinyldi-(2-methylpentyl)-phosphine oxide,
vinyldiheptylphosphine oxide,
vinyldioctylphosphine oxide,
vinyldi-(2-ethylhexyl)phosphine oxide,
vinyldinonylphosphine oxide,
vinyldidecylphosphine oxide,
vinyldihendecylphosphine oxide,
vinyldidodecylphosphine oxide,
vinylditridecylphosphine oxide,
vinylditetradecylphosphine oxide,
vinyldibenzylphosphine oxide,
vinyldiphenethylphosphine oxide,
vinyldi-(p-methylbenzyl)phosphine oxide,
vinyldiphenylphosphine oxide,
vinyldi-(p-methylphenyl)phosphine oxide,
vinyldi-(2,3-dimethylphenyl)phosphine oxide,
vinyldinaphthylphosphine oxide,
vinyldi-(p-ethylphenyl)phosphine oxide,
vinyldi-(3-methylnaphthyl)phosphine oxide,
vinyldi-(2,3-dimethylnaphthyl)-phosphine oxide,
magnesium chloride-vinyldimethylphosphine oxide complex,
magnesium chloride-vinyldiethylphosphine oxide complex,
magnesium chloride-vinylmethylethylphosphine oxide complex,
magnesium chloride-vinyldipropylphosphine oxide complex,
magnesium chloride-vinyldiisopropylphosphine oxide complex,
magnesium chloride-vinyldibutylphosphine oxide complex,
magnesium chloride-vinyldiisobutylphosphine oxide complex,
magnesium chloride-vinyl-di-tertiary-butylphosphine oxide complex,
magnesium chloride-vinyldipentylphosphine oxide complex,
magnesium chloride-vinyldiisopentylphosphine oxide complex,
magnesium chloride-vinyl-di-tertiary-pentylphosphine oxide complex,
magnesium chloride-vinyldihexylphosphine oxide complex,

magnesium chloride-vinyldicyclohexylphosphine oxide complex,
magnesium chloride-vinyldi-(2-methylpentyl)phosphine oxide complex,
magnesium chloride-vinyldiheptylphosphine oxide complex,
magnesium chloride-vinyldioctylphosphine oxide complex,
magnesium chloride-vinyldi-(2-ethylhexyl)phosphine oxide complex,
magnesium chloride-vinyldinonylphosphine oxide complex,
magnesium chloride-vinyldidecylphosphine oxide complex,
magnesium chloride-vinyldihendecylphosphine oxide complex,
magnesium chloride-vinyldidodecylphosphine oxide complex,
magnesium chloride-vinylditridecylphosphine oxide complex,
magnesium chloride-vinyl-ditetradecylphosphine oxide complex,
magnesium chloride-vinyldibenzylphosphine oxide complex,
magnesium chloride-vinyldiphenethylphosphine oxide complex,
magnesium chloride-vinyldi-(p-methylbenzyl)phosphine oxide complex,
magnesium chloride-vinyldiphenylphosphine oxide complex,
magnesium chloride-vinyldi-(p-methylphenyl)phosphine oxide complex,
magnesium chloride-vinyldi-(2,3-dimethylphenyl) phosphine oxide complex,
magnesium chloride-vinyldinaphthylphosphine oxide complex,
magnesium chloride-vinyldi-(p-ethylphenyl)phosphine oxide complex,
magnesium chloride-vinyldi-(3-methylnaphthyl) phosphine oxide complex,
magnesium chloride-vinyldi-(2,3-dimethylnaphthyl) phosphine oxide complex, and the like.

The alkoxyethyl acrylates which can be employed in producing the modifying copolymers employed in the instant invention can be represented by the formula



wherein R^3 is an alkyl radical containing from 1 to about 30 carbon atoms, preferably from about 1 to about 12 carbon atoms, and R^4 is a hydrogen or methyl radical. Illustrative of the alkoxyethyl acrylates which can be employed are such compounds as 2-methoxyethyl acrylate, 2-methoxyethyl methacrylate, 2-ethoxyethyl acrylate, 2-ethoxyethyl methacrylate, 2-n-propoxyethyl acrylate, 2-n-propoxyethyl methacrylate, 2-isopropoxyethyl acrylate, 2-isopropoxyethyl methacrylate, 2-n-butoxyethyl acrylate, 2-n-butoxyethyl methacrylate, 2-isobutyoxyethyl acrylate, 2-isobutoxyethyl methacrylate, 2-n-pentoxyethyl acrylate, 2-n-pentoxyethyl methacrylate, 2-n-hexoxyethyl acrylate, 2-n-hexoxyethyl methacrylate, 2-cyclohexoxethyl acrylate, 2-cyclohexoxyethyl methacrylate, 2-n-heptoxyethyl acrylate, 2-n-heptoxyethyl methacrylate, 2-(2-ethylhexoxy) ethyl acrylate, 2-(2-ethylhexoxy)ethyl methacrylate, 2-n-decoxyethyl acrylate, 2-n-decoxyethyl methacrylate, 2-(2,2-dimethyldecoxy)ethyl acrylate, 2-(2,2 - dimethyldecoxy)ethyl methacrylate, 2-n-eicosoxyethyl acrylate, 2-n-eicosoxyethyl methacrylate, 2-n-tetracosoxyethyl acrylate, 2-n-tetracosoxyethyl methacrylate, 2-n - heptacosoxyethyl acrylate, 2-n-heptacosoxyethyl methacrylate, 2-n-triacontoxyethyl acrylate, 2-n-triacontoxyethyl methacrylate, and the like.

The modifying copolymers employed in the instant invention contain from about 0.5 percent by weight to about 60 percent by weight, preferably from about 2.5 percent by weight to about 40 percent by weight, of polymerized vinylphosphine oxide, and from about 40 percent by weight to about 99.5 percent by weight, preferably from about 60 percent by weight to about 97.5 percent by weight, of polymerized ethylene or alkoxyethyl acrylate. Most preferably such copolymers contain from about 10 percent by weight to about 30 percent by weight of polymerized vinylphosphine oxide and from about 70 percent by weight to about 90 percent by weight of polymerized ethylene or alkoxyethyl acrylate.

The modifying copolymers employed in the instant invention can be prepared by copolymerizing a mixture of a vinylphosphine oxide with ethylene or an alkoxyethyl acrylate, by means of a catalyst capable of producing free radicals under the polymerization conditions employed. The monomer mixture can contain from about 0.1 percent by weight to about 70 percent by weight, or more, of the vinylphosphine oxide, and from about 30 percent by weight to about 99.9 percent by weight of the ethylene or alkoxyethyl acrylate. Preferably the mixture contains from about 1 percent by weight to about 50 percent by weight of the vinylphosphine oxide and from about 50 percent by weight to about 99 percent by weight of the ethylene or alkoxyethyl acrylate. The most preferred concentrations are from about 5 percent by weight to about 40 percent by weight of the vinylphosphine oxide and from about 60 percent by weight to about 90 percent by weight of the ethylene or alkoxyethyl acrylate.

When copolymerizing a vinylphosphine oxide with an alkoxyethyl acrylate, temperatures of from about —80° C. to about 150° C., preferably from about 35° C. to about 100° C., are suitable, while temperatures of from about 40° C. to about 350° C., preferably from about 60° C. to about 200° C., are suitable when polymerizing the vinylphosphine oxide with ethylene. Atmospheric pressure is usually employed when copolymerizing the alkoxyethyl acrylate, although subatmospheric pressure or superatmospheric pressure can also be employed. When copolymerizing ethylene, pressures of from about 500 atmospheres to about 10,000 atmospheres, preferably from about 800 atmospheres to about 3000 atmospheres, are suitable.

The catalysts employed in effecting copolymerization are those capable of producing free radicals under the polymerization conditions employed. Among the compounds which can be employed as catalysts are oxygen, either alone or together with a trialkylboron, such as trimethylboron, triethylboron and tripropylboron; peroxides such as hydrogen peroxide, diethyl peroxide, dipropionyl peroxide, dilauroyl peroxide, dibutyryl peroxide, dibenzoyl peroxide, distearyl peroxide, di-tertiary-butyl peroxide, tertiary-butyl hydroperoxide, diacetyl peroxide, distearoyl peroxide, acetyl benzoyl peroxide, perbenzoic acid, perlauric acid, and peracetic acid; azo compounds such as α,α'-azo-bis-isobutyronitrile, 2,2'-dicyanoazobenzene and 2,2'-azo-bis(2-methylpropionitrile); percarbonates such as diisopropyl percarbonate and di-tertiary-butyl percarbonate; peresters such as tertiary-butyl perbenzoate and acetaldehyde monoperacetate; persulfates such as sodium persulfate, potassium persulfate and ammonium persulfate; perborates such as sodium perborate, potassium perborate and ammonium perborate; and compounds which together form redox type catalyst systems, such as a combination of ammonium persulfate and sodium bisulfite, or other combinations of oxidizing agents and reducing agents. These catalysts are employed in amounts which are conventionally employed in the art, either individually or in various mixtures thereof. Thus such catalysts can be employed in an amount of from about 0.001 percent by weight to about 5 percent by weight, preferably from about 0.01 percent by weight to about 2 percent by weight, of the total amount of comonomers present.

Copolymerization of a vinylphosphine oxide with ethylene or an alkoxyethyl acrylate can be carried out in a continuous manner or in a batchwise manner. The copolymerization can be carried on in bulk, in which

extraneous diluents are absent; in solution, in which diluents which maintain the reactants and/or products in solution are present; or in emulsion or suspension, in which diluents and additives to maintain the reaction in said conditions are present. In the last instances water, organic diluents, or combinations of water with organic diluents such as benzene, toluene, heptane, etc., are used, together with the emulsifying or suspending agents when desired.

The polypropylene and modifying copolymer can be blended together in amounts varying over rather wide ranges, with the minimum amount of copolymer depending upon the dyeability improvement desired, and the maximum amount limited solely by the compatibility and ease of compounding of the copolymer with the polypropylene. In general, amounts of copolymer of from about 1 percent by weight to about 80 percent by weight, based on the total weight of the mixture, give satisfactory results. Preferably, amounts of copolymer of from about 2 percent by weight to about 40 percent by weight, most preferably from about 5 percent by weight to about 30 percent by weight, based on the total weight of the mixture, are employed.

The dyeable compositions of the instant invention are especially useful in spinning fibers. Any conventional spinning technique, such as melt spinning or solution spinning, can be employed to produce such fibers. The fibers produced by such procedures can then be stretched by conventional means to orient the fiber molecules and produce fibers having desirable tensile properties.

The fibers produced from the compositions of this invention can be readily dyed by conventional dyeing techniques to produce much deeper shades of color than have heretofore been obtainable from unmodified polypropylene fibers. Among the dyes that can be employed for this purpose are the well known acid dyes, basic dyes, disperse dyes, soluble vat dyes, azoic dyes, premetallized dyes, and the like. In a typical dyeing procedure employing acid dyes and premetallized dyes, a 50 to 1 dye bath ratio (ratio of the total weight of liquid in the dye bath to the weight of fiber present) can be employed, with the bath containing 1 per cent by weight of a methyl polyethanol quaternary amine, 2 percent by weight of sulfuric acid, and 3 percent by weight of the dye, all based on the weight of the fiber. The fiber is heated in the dye bath for about ninety minutes at the boil, and then rinsed scoured, and dried. When a disperse dye is employed, dyeing can be effected in one hour at the boil in a bath having a dye bath ratio of about 40 to 1, and containing 1 percent of N-methyl-N-oleoyl taurate and 2 to 3 percent of the disperse dye. For basic dyes, dyeing can be effected in ninety minutes at the boil in a bath having a dye bath ratio of about 40 to 1, and containing 1 percent of an alkyl phenyl polyethylene glycol and 2 percent of the basic dye. If desired, known dye carriers can be employed in the bath to assist dyeing.

The amount of dye absorbed by the fiber, or its depth of color, is approximately proportional to, and can be measured by, the K/S value of the fiber, which is a measure of the light reflected by the dyed sample. The larger the K/S value, the deeper the shade, with a K/S value of 20 indicating a shade approximately twice as deep as the shade represented by a K/S value of 10. The K/S value of a sample is determined in accordance with the procedure set forth in an article by D. B. Judd, "Color in Business," Science and Industry, 1952, pages 314–342.

Among the dyes that can be employed in dyeing the compositions of the instant invention are the following:

Acid:
- Yellow 1—C.I. 10316
- Yellow 3—C.I. 47005
- Yellow 7—C.I. 56205
- Yellow 11—C.I. 18820

Acid:—Continued
- Yellow 23—C.I. 19140
- Yellow 29—C.I. 18900
- Yellow 36—C.I. 13065
- Yellow 42—C.I. 22910
- Yellow 54—C.I. 19010
- Yellow 99—C.I. 13900
- Orange 1—C.I. 13090/1
- Orange 7—C.I. 15510
- Orange 10—C.I. 16230
- Orange 24—C.I. 20170
- Orange 49—C.I. 23260
- Orange 72—C.I. 18740
- Orange 74—C.I. 18745
- Red 1—C.I. 18050
- Red 12—C.I. 14835
- Red 14—C.I. 14720
- Red 26—C.I. 16150
- Red 34—C.I. 17030
- Red 37—C.I. 17045
- Red 73—C.I. 27290
- Red 85—C.I. 22245
- Red 89—C.I. 23910
- Red 115—C.I. 27200
- Red 116—C.I. 26660
- Red 134—C.I. 24810
- Red 179—C.I. 19351
- Red 225—
- Violet 1—C.I. 17025
- Violet 7—C.I. 18055
- Violet 17—C.I. 42650
- Violet 43—C.I. 60730
- Blue 1—C.I. 42045
- Blue 9—C.I. 42090
- Blue 22—C.I. 42755
- Blue 25—C.I. 62055
- Blue 59—C.I. 50315
- Blue 83—C.I. 42660
- Blue 102—C.I. 50320
- Green 1—C.I. 10020
- Green 3—C.I. 42085
- Green 16—C.I. 44025
- Green 20—C.I. 20495
- Green 50—C.I. 44090
- Brown 14—C.I. 20195
- Brown 42—C.I. 14251
- Black 1—C.I. 20470
- Black 24—C.I. 26370
- Black 48—C.I. 65005
- Black 52—C.I. 15711

Basic:
- Yellow 1—C.I. 49005
- Yellow 9—C.I. 46040
- Orange 2—C.I. 11270
- Orange 12—C.I. 46045
- Red 1—C.I. 45160
- Red 9—C.I. 42500
- Violet 1—C.I. 42535
- Violet 3—C.I. 42555
- Violet 14—C.I. 42510
- Blue 4—C.I. 51004
- Blue 5—C.I. 42140
- Blue 7—C.I. 42595
- Blue 26—C.I. 44045
- Green 4—C.I. 42000
- Brown 2—C.I. 21030

Disperse:
- Yellow 1—C.I. 10345
- Yellow 3—C.I. 11855
- Yellow 31—C.I. 48000
- Orange 1—C.I. 11080
- Orange 3—C.I. 11005
- Orange 7—C.I. 11240
- Red 1—C.I. 11110
- Red 4—C.I. 60755

Disperse:—Continued
Red 11—C.I. 62015
Red 13—C.I. 11115
Red 15—C.I. 60710
Red 17—C.I. 11210
Violet 1—C.I. 61100
Violet 4—C.I. 61105
Violet 8—C.I. 62030
Violet 13—C.I. 11195
Blue 1—C.I. 64500
Blue 3—C.I. 61505
Blue 7—C.I. 62500
Black 1—C.I. 11365
Black 7—C.I. 11035
Azoic diazo components:
Diazo 1—C.I. 37135
Diazo 2—C.I. 37005
Diazo 3—C.I. 37010
Diazo 4—C.I. 37210
Diazo 5—C.I. 37125
Diazo 6—C.I. 37025
Diazo 8—C.I. 37110
Diazo 10—C.I. 37120
Diazo 13—C.I. 37130
Diazo 20—C.I. 37175
Diazo 28—C.I. 37151
Diazo 32—C.I. 37090
Diazo 34—C.I. 37100
Diazo 35—C.I. 37255
Diazo 38—C.I. 37190
Diazo 41—C.I. 37165
Diazo 44—C.I. 37000
Diazo 48—C.I. 37235
Azoic coupling components:
Coupling 2—C.I. 37505
Coupling 3—C.I. 37575
Coupling 5—C.I. 37610
Coupling 7—C.I. 37565
Coupling 10—C.I. 37510
Coupling 12—C.I. 37550
Coupling 13—C.I. 37595
Coupling 14—C.I. 37558
Coupling 17—C.I. 37515
Coupling 20—C.I. 37530
Coupling 29—C.I. 37527
Coupling 34—C.I. 37531
Coupling 36—C.I. 37585
Soluble vat:
Yellow 2—C.I. 67301
Yellow 4—C.I. 59101
Yellow 5—C.I. 56006
Orange 1—C.I. 59106
Orange 2—C.I. 59706
Orange 5—C.I. 73336
Red 1—C.I. 73361
Red 10—C.I. 67001
Violet 1—C.I. 60011
Violet 2—C.I. 73386
Violet 3—C.I. 73396
Blue 1—C.I. 73002
Blue 5—C.I. 73066
Blue 6—C.I. 69826
Blue 7—C.I. 70306
Green 1—C.I. 59826
Green 2—C.I. 59831
Green 3—C.I. 69501
Brown 1—C.I. 70801
Brown 3—C.I. 69016
Brown 5—C.I. 73411
Black 1—C.I. 73671

and the like. The Colour Index (C.I.) numbers are those listed in the latest Colour Index.

The polypropylene compositions of this invention are readily extruded by conventional procedures to produce fibers, rods, films, and protective coatings. The films so obtained are amenable to printing by conventional procedures without any further surface treatment of the film being necessary.

The modifying copolymers added to the propylene polymers to produce the polypropylene compositions of this invention are readily compatible with the propylene polymers and relatively clear, tough compositions are obtained. These blends show little sweat-out on heating, good product uniformity, improved printability, reduced fibrillation, and many other desirable properties.

The copolymers themselves can be used to produce filaments, films, and molded and extruded shaped articles. The copolymers can be liquid, wax-like, or solid, depending on the molecular weight as measured by specific viscosity. The solid copolymers have densities above about 0.91 gram/cc. and can be as high as 0.98 gram/cc. or more.

The following examples are set forth for purposes of illustration so that those skilled in the art may better understand this invention, and it should be understood that they are not to be construed as limiting this invention in any manner. The following test procedures were employed in evaluating the products obtained:

Density.—A.S.T.M. D–1505–57T.

Melt index.—Determined in accordance with A.S.T.M. D–1238–52T but at 230° C.

Melt flow.—Determined in a manner similar to melt index but at 1.15 p.s.i. and 230° C.

Tenacity, elongation and stiffness.—Measured on an Instron Tensile Tester using a modified version of A.S.T.M. D–1380–55T test procedure in which a ten-inch yarn specimen is elongated at a rate of 60 percent per minute. The stiffness modulus is calculated at 100 times the stress at 1 percent elongation.

Reduced viscosity (I_R).—Determined by the equation

$$I_R=\frac{\frac{\Delta N}{N_o}}{C}$$

wherein ΔN is the difference in seconds between the flow-time of a solution of polymer through a capillary viscometer and the flow-time of the solvent, N_o represents the flow-time of the solvent, and C is the concentration of polymer in said solution in grams per 100 milliliters of solvent. The value of $\Delta N/N_o$ is known as the specific viscosity.

Example 1

A stainless steel lined autoclave having a volume of 1480 cc. was charged with 900 grams of benzene, 5 grams of vinyldibutylphosphine oxide and 0.5 gram of dibenzoyl peroxide. The reaction vessel was purged three times with ethylene and pressured to 3,000 p.s.i. with oxygen-free ethylene while agitating. After heat was applied to bring the temperature of the reaction mixture to 70° C., the pressure was elevated to 15,000 p.s.i. During the reaction time of four hours in which the temperature ranged from 86° C. to 91° C., the pressure was maintained within the range of 14,000 p.s.i. to 15,000 p.s.i. by periodic injection of ethylene. There was produced and recovered 15 grams of a solid copolymer of ethylene and vinyldibutylphosphine oxide having an 8 percent by weight content of polymerized vinyldibutylphosphine oxide therein. The copolymer had a specific viscosity of 0.121 (as measured at 80° C. from a solution of 0.4 gram per 100 cc. of methylcyclohexane), a density of 0.9439 g./cc., and a room temperature stiffness of 43,947 p.s.i.

In similar manner the copolymers of ethylene with vinyldiethylphosphine oxide or vinyldi-(2-ethylhexyl)-phosphine oxide are produced by substitution of the respective comonomer in the initial feed to the autoclave.

Example 2

In a manner similar to that described in Example 1, a copolymer of ethylene and vinyldibutylphosphine oxide was produced. The autoclave charge was 1,000 grams of

distilled and deoxygenated water, 5 grams of vinyldibutylphosphine oxide and 1 gram of α,α'-azo-bis-isobutyronitrile. Ethylene was fed in to maintain a pressure of 14,000 p.s.i. to 15,000 p.s.i. at 65° C. to 76° C. for a reaction period of about three hours. There was produced 77 grams of the solid copolymer having a 2.9 percent by weight vinyldibutylphosphine oxide content, a specific viscosity of 0.280 (as measured at 80° C. from a solution of 0.4 gram per 100 cc. of methylcyclohexane), a density of 0.9286 g./cc., and a room temperature stiffness of 32,821 p.s.i.

Example 3

In a manner similar to that described in Example 1, a copolymer of ethylene and vinyldibutylphosphine oxide was produced. The autoclave charge was 750 grams of distilled and deoxygenated water, 18.5 grams of vinyldibutylphosphine oxide and 1 gram of α,α'-azo-bis-isobutyronitrile. Ethylene was fed in to maintain a pressure of 14,100 p.s.i. to 15,000 p.s.i. at 69° C. to 70° C. for a reaction period of five hours. There was produced 40 grams of the solid copolymer having an 18.2 percent by weight vinyldibutylphosphine oxide content, a specific viscosity of 0.155 (as measured at 80° C. from a solution of 0.4 gram per 100 cc. of methylcyclohexane), a density of 0.9298 g./cc., and a room temperature stiffness of 20,580 p.s.i.

A blend was prepared by roll milling 90 parts by weight of polypropylene having a melt index of 4 dg./min. and a density of 0.91 gram/cc. with 10 parts by weight of the above copolymer. The blending was carried out at 170° C., and it was readily accomplished without any sign of incompatibility between the two polymers being observed. The blended composition was melt spun at 270° C. through a spinnerette having 25 holes, each 0.030 inch in diameter. The orifice velocity was 3.1 feet per minute and the take-up velocity was 465 feet per minute. The multifilament yarn was then stretched 229 percent in a steam atmosphere (Yarn I).

A control yarn (Yarn II) was spun in the same manner for comparison purposes using the same polypropylene. The properties of the yarns are summarized below :

Yarn	I	II
Tenacity, g.p.d	3.5	4.4
Elongation, percent	35	30
Stiffness modulus, g.p.d	33	38
Shrinkage, percent in boiling water	7.2	8

Samples of the above yarns were dyed by the previously indicated procedures. Yarn I was dyed to deep shades, whereas Yarn II showed negligible dyeability. The results are tabulated below.

Yarn	K/S Values	
	I	II
Disperse Red 17	8.8	1.1
Acid Red 225	7.4	1.3

In a similar manner blends of polypropylene and copolymers of ethylene with vinyldimethylphosphine oxide or vinyldi-(2-ethylhexyl)phosphine oxide or vinyldiheptylphosphine oxide or vinyldiphenylphosphine oxide produce filaments which are readily dyeable to deeper shades than polypropylene per se.

Example 4

A blend was prepared as described in Example 3 by roll milling 70 parts by weight of polypropylene with 30 parts by weight of a 91.5/8.5 copolymer of ethylene/vinyldibutylphosphine oxide produced similarly to that in Example 3. The blended composition was converted to a 7 mils thick film by molding in a press at 140° C. at 400 p.s.i. pressure (Film I). A control film (Film II) was produced in the same manner for comparison purposes using the same polypropylene; and the two films were dyed by the previously indicated procedures. Film I was in all instances dyed to very deep shades with Disperse Red 17 and Acid Red 225. Upon cross-sectioning the film the dyeing was observed to be a uniform dyeing and not a surface phenomenon; Film II was not dyeable.

Films of blends of polypropylene and copolymers of ethylene with vinyldipropylphosphine oxide or vinyldi-(p-methylphenyl)phosphine oxide are also readily dyeable. In addition, the films are readily printable by conventional techniques used for printing on polyolefinic surfaces.

Example 5

In a manner similar to that described in Example 3 an 81.9/18.1 ethylene/vinyldiphenylphosphine oxide copolymer was produced. A blend was prepared containing 90 parts by weight of polypropylene (melt index 4 dg./min. and density 0.91 gram/cc.) and 10 parts by weight of the ethylene/vinyldiphenylphosphine oxide copolymer and converted to 7 mils thick film as described in Example 4. The film produced from this blend was dyed to deep shades by Disperse Red 17 and Acid 225, whereas a control polypropylene film was not dyeable.

Example 6

In a manner similar to that described in Example 3 an 81.5/18.5 ethylene/vinyldiphenylphosphine oxide copolymer was produced. A blend was prepared containing 90 parts by weight of polypropylene and 10 parts by weight of the ethylene/vinyldiphenylphosphine oxide copolymer and converted to 7 mils thick film as described in Example 4. The film produced from this blend was dyed to deep shades by Disperse Red 17 and Acid Red 225, whereas a control polypropylene film was not dyeable.

Example 7

In a manner similar to that described in Example 1, a coploymer of ethylene and vinyldiphenylphosphine oxide was produced. The autoclave charge was 750 grams of benzene, 12.5 grams of vinyldiphenylphosphine oxide, and 10 milliliters of a 1 percent solution of di-tertiary-butyl peroxide in benzene. Ethylene was fed in to maintain a pressure of 13,000 p.s.i. to 15,000 p.s.i. at 180° C. to 186° C. for a reaction period of about five and one third hours. There was produced 63 grams of the solid copolymer having a 12.2 percent by weight vinyldiphenylphosphine oxide content, a specific viscosity of 0.105 in methylcyclohexane at 80° C., a density of 0.9396 gram/cc., and a room temperature stiffness of 16,054 p.s.i.

In a similar manner the copolymer is produced by continuously feeding a mixture of ethylene, vinyldiphenylphosphine oxide and catalyst into a conventional tubular reactor, at reactor pressures of about 20,000 p.s.i. to 25,000 p.s.i.

A blend was prepared, as described in Example 3, containing 90 parts by weight of polypropylene and 10 parts by weight of the above autoclave-produced copolymer. The blended composition wast melt spun at 280° C. through a spinnerette having 25 holes, each 0.030 inch in diameter. The orifice velocity was 3.1 feet per minute and the take-up velocity was 620 feet per minute. The multifilament yarn was then stretched 240 percent in a steam atmosphere (Yarn III).

A second blend containing 15 parts by weight of the copolymer and 85 parts by weight of polypropylene was prepared and spun as described above with the sole exception that the multifilament yarn was steam stretched 225 percent (Yarn IV).

Samples of the above yarns were dyed as previously described and in both instances deep, bright shades were

obtained. The results are tabulated below together with a control.

Yarn	K/S Values		
	III	IV	II
Disperse Red 17	6.2	7.0	1.1
Acid Red 225	5.3	8.1	1.3

Example 8

In a manner similar to that described in Example 1, a copolymer of ethylene and vinyldiphenylphosphine oxide was produced. The autoclave charge was 750 grams of benzene, 6 grams of vinyldiphenylphosphine oxide and 3 grams of α,α'-azo-bis-isobutyronitrile. Ethylene was fed in to maintain a pressure of 14,500 p.s.i. to 15,000 p.s.i. at 87° C. to 92° C. for a reaction period of six hours. There was produced 34 grams of the solid copolymer having a 9.9 percent vinyldiphenylphosphine oxide content, a specific viscosity of 0.075 (as measured at 80° C. from a solution of 0.4 gram per 100 cc. of methylcyclohexane), a density of 0.9648 gram/cc., and a room temperature stiffness of 55,493 p.s.i.

In a similar manner the copolymers of ethylene with vinyldi-(p-methylphenyl)phosphine oxide, or vinyldibenzylphosphine oxide, or vinyldinaphthylphosphine oxide are produced by substitution of the respective comonomer in the initial charge to the autoclave.

Example 9

To a nitrogen-purged 300-milliliter pressure bottle were charged 58 grams of 2-n-butoxyethyl acrylate, 24 grams of magnesium chloride - vinyldiphenylphosphine oxide complex, 50 milliliters of anhydrous methanol, and 0.82 gram of 2,2'-azo-bis(2-methylpropionitrile). The bottle was then capped and rotated for 20 hours in a constant temperature bath which was maintained at 50°/C. At the end of this time, the bottle was opened and the contents thereof was diluted with cold heptane in order to precipitate the desired copolymer. The copolymer was then washed three times with cold heptane, filtered, and dried under vacuum at a temperature of 40°/C. for about 50 hours. About 40.8 grams of copolymer were recovered in this manner. The copolymer contained 20 percent by weight of the combined magnesium chloride-vinyldiphenylphosphine oxide complex, and 80 percent by weight of combined 2-n-butoxyethyl acrylate. The copolymer had a reduced viscosity of 0.62 in benzene at 30° C. using a solution of 0.2 gram of polymer per 100 milliliters of solvent.

A blend of 10 parts by weight of the copolymer produced in accordance with the above procedure and 90 parts by weight of a polypropylene resin having a density of 0.91 gram/cc. and a melt flow of 4 decigrams/minute at 230° C. was produced by milling on an internally heated two-roll mill at 170° C. Various stabilizers were also incorporated during the milling so that the final blend contained 0.1 percent by weight of an amylphenol-formaldehyde resin antioxidant, 0.5 percent by weight of a diphenylpentaerythritol diphosphite antioxidant co-stabilizer, and 0.3 percent by weight of a commercially available benzotriazole type ultraviolet light absorber.

The blended composition was pressed into a film at a temperature of 150° C. to 160° C. Samples of the film were dyed with Disperse Red 17 (C.I. 11210) and Acid Red 225 in accordance with the procedures set forth above. The Disperse Red dye produced a deep red shade in the film and the Acid Red produced a light-medium shade.

When the dyeings were repeated employing in the dye bath a commercially available aqueous emulsion of butyl benzoate as a dye carrier, in an amount equal to 20 percent by weight of the film present, deep shades of red were obtained with both dyes.

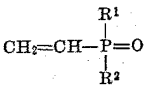
When vinyldiphenylphosphine oxide is employed instead of its magnesium chloride complex in the above procedure, similar results are obtained.

When the procedure was repeated with polypropylene film containing no modifying copolymer, only very slight staining of the film was obtained.

While the disclosure stresses polypropylene, it is to be noted that other polyolefins from mono-alpha-olefins having from 2 to about 10 carbon atoms can be substituted for polypropylene. For example, polyethylene, poly(butene-1), poly(4-methylbutene-1), poly(hexene-1), poly(decene-1), and the like, or mixtures thereof.

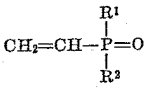
What is claimed is:

1. A copolymer of ethylene and a vinylphosphine oxide represented by the formula



wherein R^1 and R^2 are monovalent hydrocarbon radicals free of aliphatic unsaturation containing from 1 to 14 carbon atoms, said copolymer having a polymerized vinyl-phosphine oxide content of from 2.5 to 40 percent by weight and a density of from 0.91 gram/cc. to 0.98 gram/cc.

2. A copolymer of ethylene and a vinylphosphine oxide represented by the formula



wherein R^1 and R^2 are monovalent hydrocarbon radicals free of aliphatic unsaturation containing from 1 to 6 carbon atoms, said copolymer having a polymerized vinylphosphine oxide content of from 2.5 to 40 percent by weight and a density of from 0.91 gram/cc. to 0.98 gram/cc.

3. The copolymer of ethylene and vinyldibutylphosphine oxide as in claim **1.**

4. The copolymer of ethylene and vinyldiphenylphosphine oxide as in claim **1.**

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,355,440 Dated November 28, 1967

Inventor(s) Nathan L. Zutty et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 46, the formula should read as follows:

$$R^3\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}\overset{\overset{R^4}{|}}{C}=CH_2$$

Column 10, line 27, after "acid" insert --Red--; line 63, "wast" should read --was--.

Signed and Sealed this

ninth Day of September 1975

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks

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