(12) UK Patent Application (19) GB (11) 2 220 944 (13) A

(43) Date of A publication 24.01.1990

(21) Application No 8912739.3

(22) Date of filing 02.06.1989

(30) Priority data
(31) 07423 (32) 03.06.1988 (33) FR

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(51) INT CL4
C08K 5/00 3/06, C08L 1/00 3/00 // C08J 5/18, C08L

(52) UK CL (Edition J)
C3K KQA K102 K111 K124 K125 K126 K201 K244 K262
C3M MXC M119 M138 M139 M140 M141 M143 M144 M154 M158 M160 M163 M170
C3W W207 W208 W217 W218 W219
U1S S1015 S1574 S3002 S3007 S3055 S3072

(56) Documents cited
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(58) Field of search
UK CL (Edition J) C3K, C3M, C3V
Online:Derwent WPI

(54) Polyolefin compositions for photo-biodegradable films

(57) A film-forming composition comprises, per 100 parts by weight of at least one polyolefin:
(a) 0.001 to 0.02 parts by weight of iron in the form of at least one ionic iron salt,
(b) 0.001 to 0.1 parts by weight of sulphur in the form of sulphur and/or at least one dialkyl polysulphide, and
(c) 5 to 40 parts by weight of at least one polysaccharide.
It may also contain:
- 0.5 to 5 parts by weight of at least one iron oxide and
- 1 to 10 parts by weight of at leat one silicate.

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"POLYOLEFIN COMPOSITIONS FOR PHOTO-BIODEGRADABLE FILMS". 2220944

This invention relates to polyolefinic compositions containing additives which make them simultaneously photodegradable and biodegradable. Films produced from these compositions show, particularly when they are used for covering the ground around plants, an increased rate of degradation as a result of the joint action of ultraviolet irradiation and microorganisms present in the soil.

French patent 2 199 757 describes compositions comprising an olefinic polymer and 10 to 200 mg of iron in the form of at least one ionic iron salt per kg of polymer and 10 to 1000 mg of sulphur, in the form of a stabilizer chosen from sulphur and dialkyl polysulphides, per kg of polymer. These compositions can be made into films which possess good biodegradability by sunlight.

French patent 2 252 385 describes biodegradable compositions comprising a synthetic resin containing carbon-carbon bonds which is made of small biodegradable particles, of uniform size, which are stable to heat and have a limited solubility in water, and a substance which in a natural environment undergoes autoxidation to form a peroxide and/or a hydroperoxide. More specifically, these compositions contain 5 to 30% by weight of biodegradable particles which may be a natural starch. Because of the simultaneous presence of biodegradable particles and a substance which undergoes autoxidation (such as an ester of an unsaturated fatty acid), the compositions in accordance with the above-mentioned patent may be considered to be biodegradable and autoxidizable.

The compositions of French patent 2 199 757, after they have been used as protective films, are destroyed by the action of sunlight after a variable exposure time which depends on the content of photodegradation additives. This content is chosen so that the film is destroyed when protection is no longer required for the plants which they protect. However, this destruction forms shreds of quite large dimensions which, as a result of bad weather become covered with earth and humus and consequently are no longer exposed to the effect of sunlight. Their destruction then stops and the large sized shreds which persist in the

soil are a nuisance during subsequent ground clearance (spraying of weed killers, for example) and soil preparation (ploughing, rolling, etc.) after harvest.

The compositions of French patent 2 252 385 can be made into films which possess good biodegradability. Their biodegradation, which transforms the films into small pieces then into a powder which is not a nuisance during subsequent operations, is only assured as a result of close contact with the culture medium containing the microorganisms which cause this biodegradation. If the films are not in close contact with the soil they degrade only gradually and slowly, as a result of the action of particles of soil transported by bad weather. After harvest the films can be buried in the ground so that they degrade. This additional operation is lengthy and costly and cannot be performed conveniently by ploughing.

Consequently, and this is the problem which the invention aims to overcome, there is a continual search for materials which, when used in the form of films for covering soils, degrade after the time required for growth of the plants, as a result of the dual action of sunlight and microorganisms present in the soil.

To resolve this problem, the present invention proposes polyolefinic compositions which are easily made into films by usual techniques, which films are both photodegradable when they are not in the soil and biodegradable when they are subsequently buried. It has been observed that the presence of substances which cause autoxidation of the macromolecular chains of the polyolefin is not essential and that the films degrade in a period compatible with the delays between harvest and subsequent preparation of the ground. If the degradation must be accelerated, the presence of substances causing autoxidation can be envisaged.

Accordingly, the present invention provides a polyolefinic composition comprising, per 100 parts by weight of at least one

polyolefin :

(a) 0.001 to 0.02 parts by weight of iron in the form of at least one ionic iron salt,

(b) 0.001 to 0.1 parts by weight of sulphur in the form of sulphur and/or at least one dialkyl polysulphide, and

(c) 5 to 40 parts by weight of at least one polysaccharide.

By polyolefin is meant a compound chosen from :

- olefinic homopolymers such as high and low density polyethylenes, polypropylene, and poly-1-butene,

- copolymers of olefins such as copolymers of ethylene and at least one α-olefin such as propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, and 1-octene, obtained by coordination catalysis, or copolymers, obtained in the presence of free radical initiators for example, with other copolymerizable monomers such as vinyl acetate, vinyl chloride, methyl and ethyl vinyl ether, acrylonitrile, esters of acrylic and methacrylic acid with alcohols containing 1 to 8 carbon atoms, carbon dioxide and sulphur dioxide,

- copolymers of propylene and ethylene having a high content of structures derived from propylene,

- and their mixtures.

By ionic iron salt is meant preferably a compound chosen from the ferric salts of organic acids. Examples of those which can be used are ferric naphthenate, ferric stearates such as ferric tristearate and ferric monostearate, or ferric salts of saturated or unsaturated fatty acids, linear or branched, aliphatic, cyclanic or aromatic, which have 2 to 22 carbon atoms (ferric formate, acetate or salicylate).

The sulphur is in the form either of sulphur itself, in the powdered state as in flowers of sulphur, or in the form of a dialkyl polysulphide having the general formula $R-S_n-R'$, wherein R and R', which may be identical or different, are chosen from the hydrocarbon radicals which have 1 to 20 carbon atoms, for example, and n is an integer between 4 and 10.

By polysaccharide is meant, advantageously, according to the present invention, polyholosides such as cellulose, starch and glycogen. Starch is used preferably because it is more easily destroyed than cellulose and cheaper than glycogen. The starch may be obtained from various sources : for example it may be corn starch or rice starch. Preferably the water content of the starch is reduced by any known method to a value below 10% by weight and advantageously below 1% by weight. Preferably, moreover, the starch grains have an average size compatible with the thickness of the film to be prepared from the polyolefinic composition, in other words slightly less than the thickness of the film. This average size is advantageously between 5 and 150 µm when the film thickness is between 7 and 250 µm, respectively. During the manufacture of films by extrusion of the polyolefinic compositions, it is not necessary that the starch grains should be concentrated on at least one face of the film since, the film also being photodegradable, the microorganisms in the soil will reach the grains situated in the interior of the film during a phase succeeding the photodegradation.

The compositions according to the invention may also contain additives which make the film transparent to infra-red radiations of short wave-length and opaque to visible light. These films then contribute to heating the ground. Advantageously such compositions also contain, per 100 parts by weight of polyolefin :

- 0.5 to 5 parts by weight of at least one iron oxide and
- 1 to 10 parts by weight of at least one silicate.

The iron oxide present in the composition according to the invention may be an oxide having the formula Fe_3O_4 or, preferably, the formula Fe_2O_3. The latter contains about 70% by weight of iron and almost no water of crystallization which would be a nuisance during extrusion. Preferably it is in the substantially γ crystallographic form.

By silicate is meant a compound chosen from the silicates and alumino-silicates of alkali and alkaline earth metals. Silicates which are advantageously used are a magnesium silicate such as talc, a calcium

silicate such as wollastonite, an alumium silicate such as kaolinite, an alumium and magnesium silicate such as pyrope, an alumium and calcium silicate such as prehnite, a magnesium and calcium silicate such as diopside, or a silico-aluminate of sodium polysulphide such as bleu d'outremer. The average particle size of the silicates used is preferably between 1 and 5 um.

The compositions according to the invention may also contain 0.02 to 0.2 parts by weight, per 100 parts by weight of polyolefin, of at least one compound which, whilst retaining the opacity of the film to visible light and the transparency to infra-red of short wavelength, contributes a specific colour to the film. This may be, for example, a compound of the family of copper phthalocyanines.

The compositions according to the invention may also contain usual additives well known to a person skilled in the art, such as antioxidants, anti-UV compounds, lubricating agents and pigments which are not opaque to infra-red radiations of short wavelength.

The compositions according to the invention may be produced by any means allowing dispersal of an ionic iron salt, sulphur and a polysaccharide in the molten polyolefin. Thus it is possible to proceed by mixing in an internal mixer, or in an extruder or on a calender. The mixing temperature is preferably below 200°C.

The invention also provides films produced from the above-mentioned compositions, by blow extrusion moulding of sheets or by extrusion through a flat extruder die. The thickness of the fims is advantageously between 7 and 250 um. Very thin films may, in particular, be obtained with the copolymers described in patents EP-A-16707 and 70220.

CLAIMS

1. An olefinic composition comprising, per 100 parts by weight of at least one polyolefin :

(a) 0.001 to 0.02 parts by weight of iron in the form of at least one ionic iron salt,

(b) 0.001 to 0.1 parts by weight of sulphur in the form of sulphur and/or at least one dialkyl polysulphide, and

(c) 5 to 40 parts by weight of at least one polysaccharide.

2. A composition according to Claim 1 wherein the polyolefin is chosen from the homopolymers of olefins such as ethylene, propylene and 1-butene, copolymers of the said olefins, copolymers of at least one of the said olefins with copolymerizable monomers such as vinylic monomers, acrylic monomers, carbon dioxide and sulphur dioxide.

3. A composition according to one of Claims 1 and 2, wherein the ionic iron salt is chosen from ferric naphthenate, ferric stearates, ferric salts of fatty acids which have 2 to 22 carbon atoms, and ferric salicylate.

4. A composition according to one of Claims 1 to 3, wherein the dialkyl polysulphide is a compound having the general formula $R-S_n-R'$, wherein R and R', which may be identical or different, are chosen from the hydrocarbon radicals which have 1 to 20 carbon atoms and n is an integer between 4 and 10.

5. A composition according to one of Claims 1 to 4, wherein the polysaccharide is starch.

6. A composition according to one of Claims 1 to 5, which also contains :

- 0.5 to 5 parts by weight of at least one iron oxide and
- 1 to 10 parts by weight of at least one silicate.

7. A composition according to one of Claims 1 to 6, wherein the silicate is chosen from talc, kaolinite, wollastonite or bleu d'outremer.

8. A composition according to one of Claims 1 to 7, wherein the average particle size of the silicate is between 1 and 5 um.

9. A composition according to one of Claims 1 to 8, which further contains 0.2 to 2 parts by weight, per 100 parts by weight of polyolefin, of at least one compound of the family of copper phthalocyanines.

10. An olefinic composition as claimed in claim 1, substantially as hereinbefore described.

11. A film produced from at least one composition according to one of Claims 1 to 10.

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