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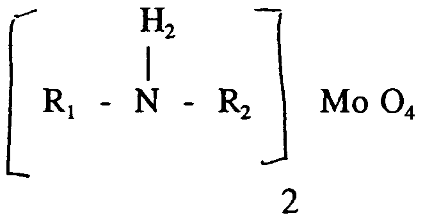
(54) Vapor phase corrosion inhibitor material.

(57) A method of inhibiting the corrosion of an item, using a vapor phase corrosion inhibitor formulation comprising finely divided anhydrous amine molybdate having the structural formula :



$$\left[R_1 - \overset{\overset{\displaystyle H_2}{|}}{N} - R_2 \right]_2 \mathrm{Mo\,O_4}$$

wherein either (i) R_1 is either a 2-ethylhexyl radical, or an aliphatic hydrocarbon having up to 7 carbon atoms, and wherein R_2 is either hydrogen or an aliphatic hydrocarbon having up to 7 carbon atoms, or (ii) R_1 and R_2 are 2-ethylhexyl radicals. The formulation has a vapor pressure which contributes to an ongoing availability of anti-corrosion protection. The formulation can be extruded with polyolefin films, and can be used in laminates.

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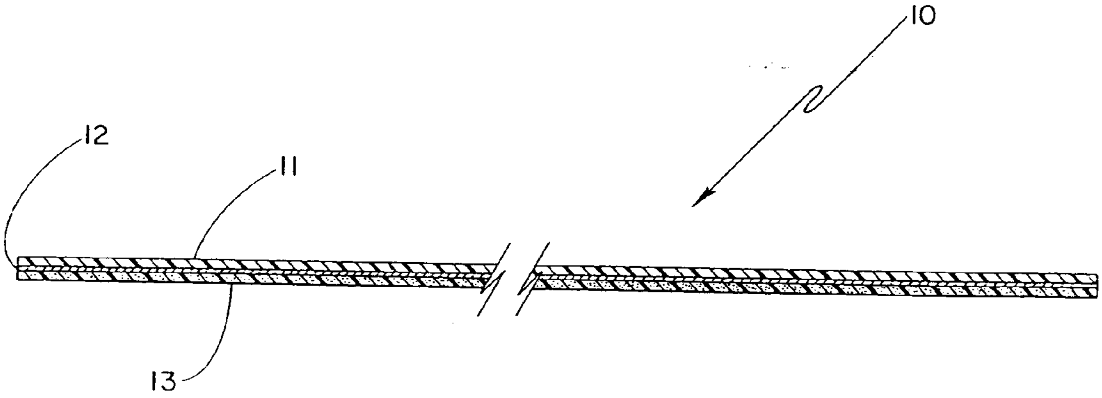
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The present invention relates to a method of inhibiting the corrosion of an item by using an anhydrous amine molybdate as a vapor phase corrosion inhibitor.

In commerce and industry today, the useful life of corrodible items may be extended and/or preserved by providing corrosion inhibitors which protect the corrodible item from the adverse effects of its ambient environment. Corrosion inhibitors, particularly vapor phase corrosion inhibitors, have been found useful in protecting certain corrodible items against reaction with elements or compounds which may be found within their environment, and thereby losing their effectiveness, reducing their useful life, or otherwise diminishing their value. Such protection is typically needed during times of packaging, handling, shipment, or during end use. Elements or compounds which are normally of primary concern are gases such as oxygen, water vapor, sulfides, carbon dioxide, and the like. The formulations of the present invention find particular application in the preparation of packaging material, particularly through in-situ extrusion of the material with such films, with the films thereafter forming an envelope or other enclosure about the article being protected. These films may also be employed as a member of a multi-layer laminate including a metallized film having good tear resistant properties such as stress-oriented polyethylene terephthalate containing a vapor deposited film or layer of metallic aluminum. Such films are commercially available and are commonly designated as "aluminized" films.

Among the common indications of corrosion manifested in useful metallic articles are oxidation, pitting, tarnishing, mottling, or discoloration of the surfaces of these items. These manifestations occur in the articles, particularly when exposed to oxygen and in either gaseous or liquid phase. Additionally, sulfides may present corrosion or tarnishing problems as well. Inasmuch as both oxygen and water, including water vapor, occur normally and are available in nature, it is normally necessary to take precautions against corrosion when packaging metallic items for shipment, or when subjecting such items to normal use. Metals which are frequently found to be susceptible to corrosion under normal atmospheric and ambient conditions are iron, steel, copper, brass, aluminum, silver, and alloys of these metals. Care must frequently be taken to protect articles fabricated from both ferrous and non-ferrous metals, eg. aluminium, copper and brass, even when their surfaces have been treated so as to be provided with sacrificial or aesthetic coatings of zinc or cadmium on their surfaces. Such sacrificial or aesthetic coatings are, or course, in wide use, but restrictions of use of these materials may appear from time to time due to their potential contribution to pollution or the like. Accordingly, means must be provided to find alternate techniques for the protection and/or preservation of metallic articles.

In the past, it has been known to provide a package or other enclosure which includes one or more inhibiting compounds along with the corrodible item or items to be protected. Additionally, articles have been protected by means of utilization of protective coatings in the form of solids, liquids, greases, or pastes, however such coatings tend to be temporary in nature and further present certain disadvantages to normal handling and packaging. Furthermore, removal of such protective coatings may present problems either due to incomplete removal, or the costs of such removal.

Solid phase and liquid phase compounds have been used in the past to provide a source of vapor phase corrosion inhibitors. These materials typically undergo either evaporation or sublimation so as to provide the substantially constant availability of the inhibitors. In other words, vapor phase corrosion inhibitors typically emit vapors which protect corrodible surfaces through the deposition or condensation of a protective film or coating upon the surface. In order to be assured that a constant supply of inhibitor be present, adequate quantities of the solid phase or liquid phase corrosion inhibiting compounds must be provided, with the corrosion inhibiting compounds being released at or adjacent the location where needed.

Typical corrosion inhibiting articles and materials used in the past are disclosed in Miksic et al U.S. Patent No. 4,051,066 and Miksic et al U.S. Patent No. 4,275,835.

US-A-4,298,657 discloses a corrosion inhibitor that is deposited, painted or sprayed on an item which is to be protected from corrosion. The inhibitor includes sodium molybdate.

EP-A-0,015,496 discloses the use of an amine molybdate as a smoke retardant.

JP-A-60071799 discloses a rust-proofing paper including a volatile rustproofing agent in the form of ammonium molybdate.

None of the above documents relates to the use of an amine molybdate as a vapor phase corrosion inhibitor.

The present invention relates to a method of inhibiting corrosion of an item, as set out in claim 1. The precharacterising part of claim 1 is based on JP-A-60071799, and the distinguishing features of the present invention are set out in the characterising part of claim 1.

The present invention also relates to the use of an amine molybdate in the manufacture of an inhibitor for the purpose of vapor phase corrosion inhibition.

In one embodiment, the inhibitor may be extruded with a film material such as an olefinic film, polyethylene, or the like, and placed within the confines of an enclosure housing the item being protected. Alternatively, the inhibitor may be placed within packages containing items which are to be protected from corrosion. Anhydrous mixtures of an amine molybdate along with sodium nitrite and benzotriazole are preferred for these applications, with this mixture further being preferably extruded into polyethylene film at a rate of from between about 2 percent and 3 percent by weight.

Film materials extruded with the inhibitor may in one embodiment, in turn, by laminated to a second metallized film, such as, for example, metallized polyethylene terephthalate. The combined laminate provides a means to reduce and/or eliminate static build-up in or along the film, and accordingly improves the properties of the film when employed as an enclosure.

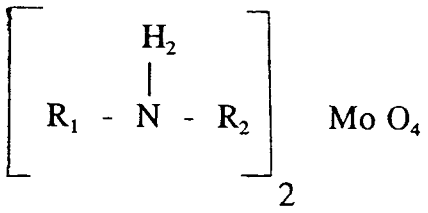
When a laminate is formed in which one layer comprises a heat sealable film such as polyethylene with the inhibitor extruded in-situ, and with a second layer being a material such as metallized stress-oriented polyethylene terephthalate, a desirable combination of properties are achieved. Specifically, the polyethylene film layer retains its conventional heat sealing properties, while the stress-oriented polyethylene terephthalate provides a tear-resistant property. The metallized layer is utilized to reduce and/or eliminate static build-up thereby further enhancing the properties and qualities of the laminate. Stress-oriented polyethylene terephthalate is normally biaxially oriented, and is, of course, commercially available.

The inhibitor is particularly useful in providing protection to both ferrous and non-ferrous metals, including such non-ferrous metals as aluminum, copper and brass.

Additionally, the vapor phase corrosion inhibitor produces little, if any, visible residue. The lack of residue enhances the utility of the inhibitor inasmuch as little, if any, mechanical or electrical problems result from the continuous use of this inhibitor.

The inhibitor is particularly well adapted to be employed as an extrudate with films fabricated from aliphatic hydrocarbon such as polyethylene and polypropylene. In one embodiment, the inhibitor is utilized for retention and/or packaging within modestly porous envelopes or other enclosures formed of plastic film or plastic foam. Typically, those certain enclosures disclosed and claimed in the Miksic et al U.S. Patents 4,051,066 and 4,275,835, as identified hereinabove, are well adapted for use with the inhibitor.

In accordance with a preferred embodiment, the vapor phase corrosion inhibitor comprises an anhydrous amine-molybdate having the general structural formula:



$$\left[R_1 - \overset{H_2}{\overset{|}{N}} - R_2 \right]_2 \mathrm{Mo}\,O_4$$

wherein either, (i) R_1 is either a 2-ethylhexyl radical or an aliphatic hydrocarbon having up to 7 carbon atoms, and wherein R_2 is either hydrogen or an aliphatic hydrocarbon having up to 7 carbon atoms, or (ii) R_1 and R_2 and 2-ethylhexyl radicals. The preferred amine molybdates are derived from the group consisting of dicyclohexylamine, 2-ethylhexylamine, and cyclohexylamine. Such molybdates are readily synthesized and can be prepared in anhydrous form without requiring unusual processing or handling problems.

Other objects of the present invention will become apparent to those skilled in the art upon a study of the following specification, appended claims, and accompanying drawings.

IN THE DRAWING

The figure is a cross-sectional view of a typical laminate prepared in accordance with the present invention, with the center or metallized layer being shown in somewhat exaggerated form due to limitations of draftsmanship.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In accordance with the preferred embodiment, a particularly useful vapor phase corrosion inhibitor for extruded polyethylene film includes a mixture of anhydrous amine molybdates, together with sodium nitrite and benzotriazole.

While there are various techniques that may be employed for providing the appropriate extrudate including, for example, polyethylene and a vapor phase corrosion inhibitor of the type described herein, one particular technique has been found to be particularly useful. Specifically, the formation is formed and rendered as uniform as possible, and passed through the barrel of a conventional extruder to form a master batch. The resultant master batch is then chopped and rendered into pellet form. These pellets are, in turn, extruded as the film containing a vapor phase corrosion inhibitor of the type described.

In order to describe alternate materials useful in connection with the present invention, the synthesis of three amine-molybdate compounds will be described hereinbelow, it being understood that each resultant compound possesses appropriate physical and chemical properties in its anhydrous form so as to be highly useful in connection with the various aspects of the present invention.

The aliphatic amines employed are from the group consisting of dicyclohexylamine, 2-ethylhexylamine, and cyclohexylamine, it being understood that other aliphatic amines within this general category may be found useful as well.

AMINE-MOLYBDATE "A"

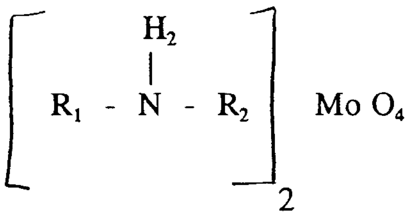
Pursuant to this embodiment, dicyclohexylamine having a molecular weight of 181.36 and the empirical formula $C_{12}H_{23}N$ is employed. The method and procedure set forth in Example I hereinbelow is followed.

EXAMPLE I

A formulation is prepared with the following components:

Component	Percent by Weight
Dicyclohexylamine	10%
Phosphoric acid	4%
Water	36%
Aqueous solution of ammonium molybdate (20%)	50%

The 20% ammonium molybdate solution is prepared by adding pure molybdenum trioxide to a 5% aqueous solution of ammonium hydroxide. The pH of the resulting solution is normally in the range of 7.5 to 8.5. The dicyclohexylamine, phosphoric acid and water are mixed together to form a neutral to slightly alkaline solution, the pH being in the range of 7.5 to 8.5. The 20% aqueous solution of ammonium molybdate is then added. The reaction that occurs is a simple displacement reaction in which a white powdery precipitate is formed upon addition of the ammonium molybdate solution. Following the completion of the reaction, the mixture is cooled to approximately 60°F., after which the precipitate is filtered, washed, and dried until the anhydrous form is obtained. The anhydrous finished product is a fine white powder having the following structural formula:



$$\left[R_1 - \overset{\overset{\large H_2}{|}}{N} - R_2 \right]_2 \mathrm{Mo}\,O_4$$

wherein R_1 and R_2 are cyclohexyl radicals.

AMINE-MOLYBDATE "B"

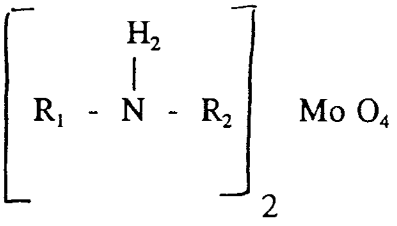
Pursuant to this embodiment, 2-ethylhexylamine having a molecular weight of 129.2 and the empirical formula $C_8N_{19}N$ is employed. The method and procedure set forth in Example II hereinbelow is followed.

EXAMPLE II

A formulation is prepared with the following components:

Component	Percent by Weight
2-ethylhexylamine	5%
Phosphoric acid	2.5%
Water	67.5%
Aqueous solution of ammonium molybdate (20%)	25%

The 20% ammonium molybdate solution is prepared as set forth in Example I hereinabove. The 2-ethylhexylamine, phosphoric acid and water are mixed together to form a neutral to slightly alkaline solution, the pH being in the range of 7.5 to 8.5. The 20% aqueous solution of ammonium molybdate is then added. The reaction that occurs is a simple displacement reaction in which a white powdery precipitate is formed upon addition of the ammonium molybdate solution. Following the completion of the reaction, the mixture is cooled to approximately 60°F., after which the precipitate is filtered, washed, and dried until the anhydrous form is obtained. The anhydrous finished product is a find white powder having the following structural formula:



$$\left[R_1 - \overset{H_2}{\overset{|}{N}} - R_2 \right]_2 Mo\ O_4$$

wherein R_1 is a 2-ethylhexyl radical and R_2 is hydrogen.

AMINE-MOLYBDATE "C"

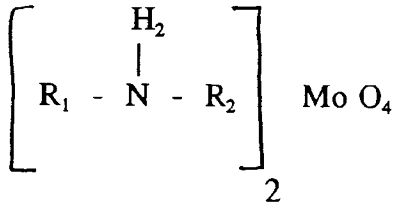
Pursuant to this embodiment, cyclohexylamine is employed in the preparation of cyclohexylamine-molybdate. Cyclohexylamine having a molecular weight of 99.17 and the empirical formula $C_6H_{11}NH_2$ is employed. The method and procedure set forth in Example III hereinbelow is followed.

EXAMPLE III

A formulation is prepared with the following components:

Component	Percent by Weight
Cyclohexylamine	20%
Molybdenum trioxide (pure)	13%
Water	67%

The water, molybdenum trioxide and cyclohexylamine are mixed together all at once. While mixing, the solution is heated to approximately 175°F. When the solution becomes clear, the mixture is cooled to 60°-70°CF., whereupon a grey-white precipitate forms. The precipitate is filtered, washed and dried until the anhydrous form is obtained. The anhydrous finished product is a white crystalline powder with the following structural formula:



$$\left[R_1 - \overset{\overset{H_2}{|}}{N} - R_2 \right]_2 Mo\,O_4$$

wherein R_1 is a cyclohexyl radical and wherein R_2 is hydrogen.

GENERAL COMMENTARY

The amine-molybdates as set forth above are, of course, employed in the anhydrous form. It has been found that such molybdates, when employed in the anhydrous form, will be readily incorporated into olefinic films such as polyethylene and polypropylene. Effective mixtures of the amine-molybdates are normally formulated utilizing 70% by weight anhydrous amine-molybdate of the type shown in Examples A, B and C above, 25% sodium nitrate and 5% benzotriazole.

In accordance with the examples, the aliphatic amine may be present in an amount ranging from between about 5% and 20%. In the interests of completeness of the reaction involved, it has been found that approximately 10% by weight of the aliphatic amine produces a desirable end product. The reactions involved occur quite rapidly and have been found to go substantially to completion at room temperature.

While dicyclohexylamine, 2-ethylhexylamine, and cyclohexylamine have been indicated as the most desirable materials, it will, of course, be appreciated that certain conditions of end use along with certain other considerations and parameters may dictate that somewhat smaller aliphatic chain lengths be employed. For example, use of the material in somewhat cooler environments may render it desirable to utilize materials having a somewhat shorter chain length in order to achieve an appropriate degree of sublimation while exposed to ambience. Other considerations may indicate utilization of such shorter chain lengths, as well.

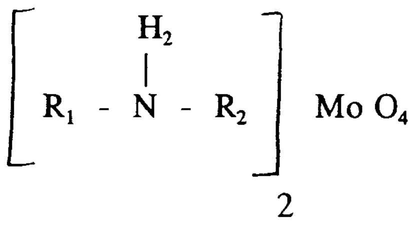
As has been indicated hereinabove, and with attention being directed to the figure of the drawing, the vapor phase corrosion inhibitors are well adapted for extrusion with resinous film material typically employed in the packaging industry. When employed as a member or layer of a laminate, and with continued attention being directed to the drawing, the film generally designated 10 includes a first layer of plastic film 11 having a metallic or metallizing layer 12 deposited thereon. Layer 13 of laminate 10 is impregnated with the inhibitor with the solid particles being introduced into the film through co-extrusion techniques. For example, the amine-molybdate of Example I is prepared, and introduced as a fine white powder into conventional polyethylene film. This impregnated film is, in turn, laminated to the metallized layer 12 of film 11 so as to form the composite. Laminating techniques for such films are, of course, well known in the art. Metallized films of biaxially oriented polyethylene terephthalate are readily bonded to and laminated with polyethylene films of the type shown at 13.

The vapor phase corrosion inhibitor compounds are also well adapted for retention and/or packaging within modestly porous envelopes or other enclosures. These envelopes may be formed of plastic film or plastic foam, or alternatively, may be fabricated from cellulosic products such as paper or the like. The addition to being retained and/or packaged within envelopes or enclosures, the material may be placed upon or within an appropriate substrate formed of either synthetic resin or cellulosic materials. Typical examples of useful material include polyethylene, polypropylene, paper, and the like. When paper is employed, it is preferred that the drying operation be undertaken so as to provide reasonably anhydrous amine-molybdate materials. As a still further alternative, the vapor phase corrosion inhibitors may be extruded or co-extruded with synthetic resin materials such as, for example, polyethylene, polypropylene, or the like. Conventional extrusion or co-extrusion techniques may be employed in this regard.

Claims

1. A method of inhibiting the corrosion of an item, comprising using a molybdate compound as a vapor phase corrosion inhibitor, characterised in that the molybdate compound is a substantially anhydrous amine molybdate.

2. The method of claim 1, wherein the amine molybdate is in powder form and has the structural formula:



$$\left[R_1 - \overset{H_2}{\overset{|}{N}} - R_2 \right]_2 \mathrm{Mo}\,O_4$$

wherein either (i) R_1 is either a 2-ethylhexyl radical, or an aliphatic hydrocarbon having up to 7 carbon atoms, and wherein R_2 is either hydrogen or an aliphatic hydrocarbon having up to 7 carbon atoms, or (ii) R_1 and R_2 are 2-ethylhexyl radicals.

3. The method as defined in claim 2 wherein R_2 is a cyclohexyl radical.

4. The method of claim 1, 2 or 3, including enclosing the item and vapor phase corrosion inhibitor in a porous modestly permeable envelope.

5. The method of claim 1, 2 or 3, including supporting the vapor phase corrosion inhibitor on a substrate comprising an aliphatic hydrocarbon film selected from the group consisting of polyethylene and polypropylene, by retaining said anhydrous amine molybdate within said substrate through extrusion of the said anhydrous amine molybdate with the film formation; and forming the film into an enclosure enclosing said item.

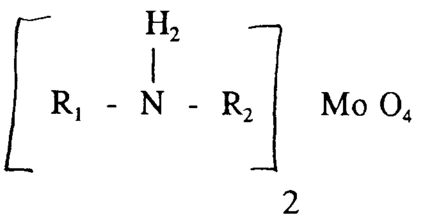
6. The method of claim 5, including extruding the amine molybdate into said film at a proportion of between 2% and 3% by weight.

7. The method of claim 5 or 6, including forming a laminate consisting of the first film (13) and a second film layer (11) bonded to a central metallic layer (12) to form a composite structure, wherein said second film (11) comprises a layer of biaxially stress-oriented polyethylene terephthalate; and forming the laminate into said enclosure.

8. The method of claim 7, including depositing said central metallic layer (12) upon the surface of said polyethylene terephthalate film, the metallic layer (12) being a film of aluminum.

9. Use of an amine molybdate in the manufacture of an inhibitor for the purpose of vapor phase corrosion inhibition.

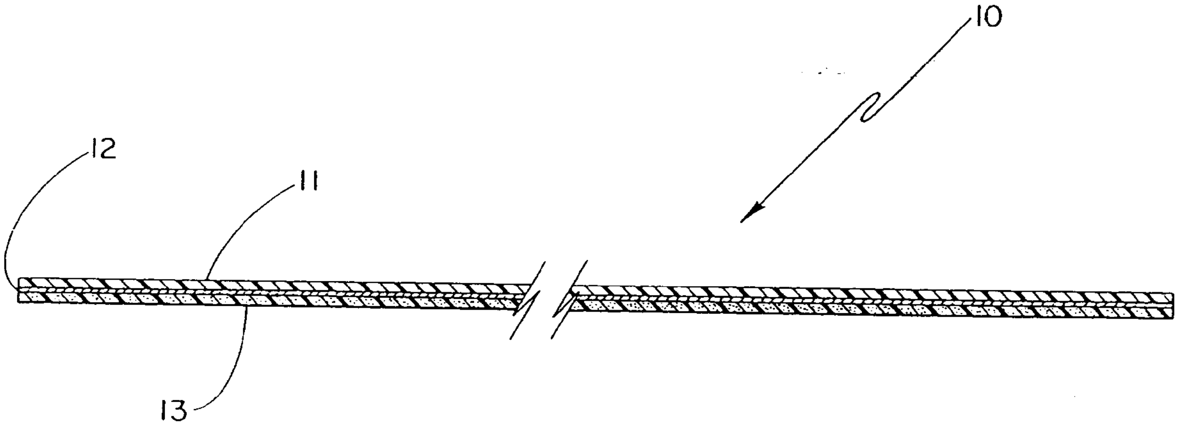
10. The use as in claim 9, wherein the amine molybdate is in powder form and has the structural formula:



$$\left[R_1 - \overset{H_2}{\overset{|}{N}} - R_2 \right]_2 \mathrm{Mo}\,O_4$$

wherein either (i) R_1 is either a 2-ethylhexyl radical, or an aliphatic hydrocarbon having up to 7 carbon atoms, and wherein R_2 is either hydrogen or an aliphatic hydrocarbon having up to 7 carbon atoms, or (ii) R_1 and R_2 are 2-ethylhexyl radicals.

11. The use as in claim 10, wherein R_2 is a cyclohexyl radical.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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 20 2936

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A,D	DATABASE WPI Section Ch, Week 8522, Derwent Publications Ltd., London, GB; Class E06, AN 85-132744 & JP-A-60 071 799 (KANZAKI PAPER MFG KK) 23 April 1985 * abstract * ---	1,9	C23F11/02 B65D81/26
A	PATENT ABSTRACTS OF JAPAN vol. 2, no. 131 (C-26) 31 October 1978 & JP-A-53 096 491 (KURITA KOGYO K. K.) 24 August 1978 * abstract * ---	1,9	
A	EP-A-0 205 165 (ASAHI DENKA KOGYO K. K.) * example 2; table 2 * ---	1,2,9,10	
A	US-A-4 973 448 (CORTEC CORPORATION) * claim 1 * ---	4	
A	GB-A-2 187 466 (INSTITUT MEKHANIKI METALLOPOLIMERSNYKH SISTEM AKADEMII NAUK BELORUSSKO) * page 2, line 37 - page 2, line 43; claim 1 * ---	5	TECHNICAL FIELDS SEARCHED (Int.Cl.5) C23F
A	FR-A-2 261 940 (THE ORCHARD CORPORATION OF AMERICA) * claims 1,13 * ---	7,8	
A,D	US-A-4 275 835 (B. A. MIKSIC) -----		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10 November 1994	Torfs, F

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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