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(54) **Packaging**

(57) An improved packaging material for metal protection, employing multiple protection components which together provide optimum corrosion protection. One of the protection components is a "mixed inhibitor" VCI, having a combination of chemical compounds in which the electron density distribution causes the molecules to be attracted to both the anodic and cathodic sites. The metal-protecting components include a desiccant, and an

oxygen scavenger. The metal-protecting components further comprise a cathodic protector. Polyethylene is the bulk component, and the metal-protecting components are dispersed in said bulk component. The volatile corrosion inhibitor preferably includes phosphate esters, acids, and amines. The acids preferably include caprylic acid and isononanoic acid. The amines preferably include amino-2methyl-1-propanol. The desiccant is preferably a silica gel.

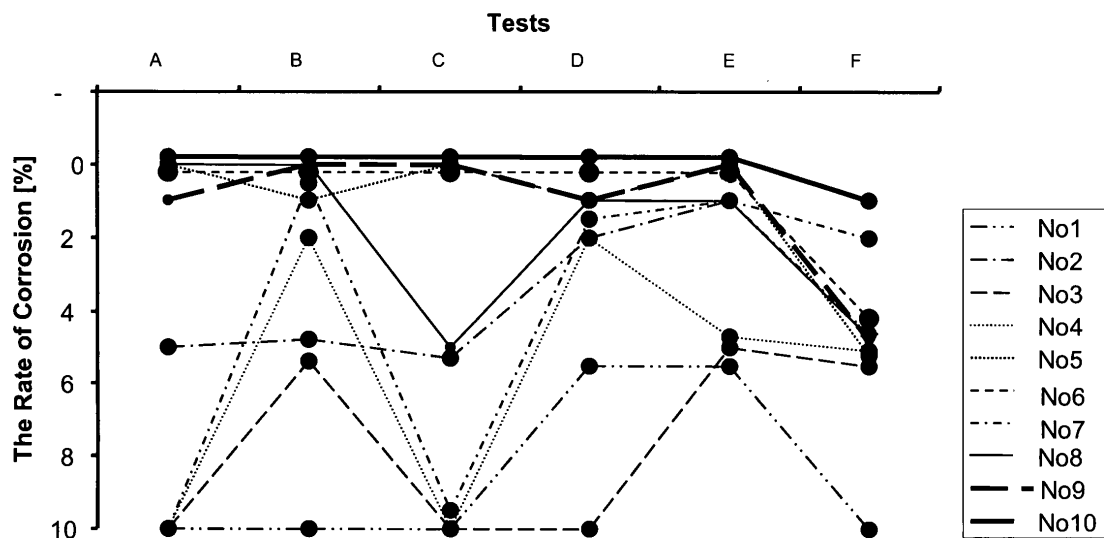


Fig. 1

**Description**Introduction

- 5 **[0001]** The invention relates to packaging, and particularly to protection of packaged metal items.
- [0002]** Packaging is a very important part of the supply chain of metal parts due to the effects of humidity, for example during transportation and storage.
- [0003]** Volatile Corrosion Inhibitor (VCI) technology has been developed for controlling corrosion in closed systems. VCI components in packaging decrease atmospheric corrosion due to the reaction of the metal with the environment, even in recessed areas where the packaging is not in direct contact with the metal surface. VCIs are organic type inhibitors, being chemical compounds that have significant vapour pressure that allow vaporization of the molecules and subsequent adsorption onto metallic surfaces. Adsorbed onto the metal surface, the VCI creates a uniform thin monomolecular corrosion-protecting layer. The monomolecular layer serves as a buffer, which maintains pH level at its optimum range for corrosion resistance. Fig. A presents the mechanism of VCI protection.
- 10 **[0004]** Once the VCI protective ions are adsorbed onto the surface, the electrochemical process of corrosion is interrupted as the ions create a protective barrier to contaminants such as oxygen, water and other corrosion accelerators. With the protective barrier in place the corrosion cell cannot form and corrosion is halted.
- [0005]** The invention is directed towards providing an improved packaging material for metal protection.

20 Statements of Invention

- [0006]** The invention provides a packaging material comprising metal-protecting components including a volatile corrosion inhibitor, a desiccant, and an oxygen scavenger.
- [0007]** The metal-protecting components may further comprise a cathodic protector.
- 25 **[0008]** The packaging material may comprise polyethylene as a bulk component, and the metal-protecting components may be dispersed in said bulk component.
- [0009]** The volatile corrosion inhibitor may be in the form of a mixed inhibitor.
- [0010]** The volatile corrosion inhibitor may include phosphate esters, acids, and amines. The phosphate esters may be ammoniated phosphate esters. The acids may be carboxylic acids. For example, the acids may include caprylic acid and isononanoic acid. The amines may be primary amines. For example, the amines may include amino-2methyl-1-propanol.
- 30 **[0011]** The desiccant may comprise a silica gel.
- [0012]** The oxygen scavenger may comprise a triazole. For example, the triazole may be benzotriazole.
- [0013]** The cathodic protector may include a sacrificial anode. The sacrificial anode may comprise zinc oxide. Alternatively, the sacrificial anode may comprise a mixture of zinc oxide, titanium dioxide and silicon oxide.
- 35 **[0014]** The packaging material may further comprise an organic salt.
- [0015]** The packaging material may further comprise sodium benzoate.
- [0016]** The packaging material may further comprise ammonia anhydrous.
- [0017]** The packaging material may further comprise calcium carbonate.
- 40 **[0018]** The packaging material may further comprise calcium stearate.
- [0019]** The packaging material may be in the form of a film. The film may have a thickness of between 100µm and 140µm.
- [0020]** In a further aspect, the invention provides a method of manufacturing a packaging material as described herein comprising the step of mixing metal protection components with a bulk material. The bulk material may be a plastics material and the protection components and the plastics material may be mixed, heated, and extruded. The plastics material may be polyethylene.
- 45

Detailed Description of the Invention

- 50 **[0021]** The invention will be more clearly understood from the following description of some embodiments thereof, given by way of example only with reference to the accompanying drawings in which:-

Fig. 1 is a set of plots of test results;

- 55 Figs. 2 to 7 are images of samples which have undergone tests; and

Fig. 8 is a pair of diagrams illustrating the metal protection mechanisms, the left hand diagram showing operation of a conventional VCI-based film and the right-hand diagram showing a operation of a film of the invention.

**[0022]** The invention provides an improved packaging material for metal protection, employing multiple protection components which together provide optimum corrosion protection. In one aspect, the packaging material may provide protection against corrosion caused by oxygen and corrosion caused by moisture. One of the protection components is a "mixed inhibitor" VCI, having a combination of chemical compounds in which the electron density distribution causes the molecules to be attracted to both the anodic and cathodic sites. This forms a monomolecular film which acts as a buffer, maintaining pH at optimum range for corrosion resistance and provides a universal effect on corrosion process.

**[0023]** By "mixed inhibitor" we mean an inhibitor that functions as both an anodic and a cathodic inhibitor. Anodic corrosion is characterised by the oxidation of a metal surface causing the release of metal ions and electrons which results in a reduction in the pH level at the site of corrosion. Anodic corrosion inhibitors act by migrating to the anodic site to enhance chemisorption of dissolved oxygen thereby inhibiting the corrosion process. Cathodic corrosion is characterised by the reduction of a metal surface which results in an increase in the pH level at the site of corrosion. Cathodic corrosion inhibitors form deposits on the site of cathodic corrosion thereby preventing the reduction of oxygen to hydroxyl ions and inhibiting the cathodic corrosion process.

**[0024]** Packaging material of the invention can be used to protect both ferrous containing and non-ferrous containing metals from corrosion.

**[0025]** Ten packaging films were prepared as set out in Table 1 below, in which the films are labelled 1 through 10 across the first row.

Table 1

| PROTECTION COMPONENT       |                         |                                                | DOSE<br>[w/w%] | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|----------------------------|-------------------------|------------------------------------------------|----------------|---|---|---|---|---|---|---|---|---|----|
| <b>VCI</b>                 | <u>Phosphate Esters</u> | Poly(oxy-1,2-ethanediol-hydro-hydroxy mono C12 | 0.85-1.25      |   |   |   |   | X | X | X | X | X | X  |
|                            | <u>Acids</u>            | 3,5,5 Trimethylhexanoic acid                   | 0.05-0.3       |   |   |   |   | X | X | X | X | X | X  |
|                            |                         | Caprylic Acid                                  | 0.15-0.35      |   |   |   |   | X | X | X | X | X | X  |
|                            | <u>Amines</u>           | 2, Amino-2methyl-1-propanol                    | 0.15-0.35      |   |   |   |   | X | X | X | X | X | X  |
| <u>OXYGEN SCAVENGER</u>    |                         | Triazole                                       | 0.10-0.20      |   | X |   |   |   | X | X | X | X | X  |
| <b>DESICCANT</b>           |                         | Silica Gel                                     | 1.00-1.30      | X |   |   |   | X | X | X | X | X | X  |
| <b>CATHODIC PROTECTION</b> |                         | Sacrificial anode                              | 0.35-1.00      |   |   | X |   |   |   |   |   | X | X  |
|                            |                         | Zinc Oxide                                     | 0.35-1.00      |   |   |   | X |   |   | X | X |   |    |
| <b>OTHERS</b>              | Sodium Benzoate         |                                                | 0.02-0.10      |   |   |   |   | X | X | X | X | X | X  |
|                            | Ammonia Anhydrous       |                                                | 0.05-0.15      |   |   |   |   | X | X | X | X | X | X  |
|                            | Processing Aids         |                                                | 1.0-3.0        | X | X | X | X | X | X | X | X | X | X  |
|                            | Calcium Carbonate       |                                                | 0.5-1.0        | X | X | X | X | X | X | X | X | X | X  |
|                            | Calcium Stearate        |                                                | 0.5-1.0        | X | X | X | X | X | X | X | X | X | X  |
|                            | Polyethylene            |                                                | 90-95          | X | X | X | X | X | X | X | X | X | X  |

**[0026]** The films 1 through 5 are for reference only, the films 6 through 10 being of the invention. In the above table the four main protection components are VCI, oxygen scavenger, desiccant, and cathodic protection. The VCI component includes phosphate esters and amines as molecules attracted to the cathodic metal sites, whereas the acids provide molecules attracted to the anodic metal sites. These acids are all carboxylic acids. Thus, in all of the films the VCI is a mixed inhibitor. The cathodic protection may be provided by either zinc oxide or a zinc oxide compound that includes zinc oxide, titanium dioxide, and silicon oxide. The cathodic protection element may be considered as a sacrificial anode.

**[0027]** Films of the invention may further comprise additional anodic and/or cathodic inhibitors. For example, sodium benzoate may be considered as an anodic inhibitor and calcium carbonate may be considered as a cathodic inhibitor.

**[0028]** The oxygen scavenger may be selected from the triazole class of compounds, for example the oxygen scavenger may be benzotriazole.

## Manufacture of Films

**[0029]** Acronyms used in the following examples:

MF22, Polyethylene in the form of powder,

MF08, Polyethylene in the form of granules,

PAE, Phosphate ester, and

AMP95, 2, Amino-2methyl-1-propanol.

### Film 1

**[0030]** In this example, the protection component is desiccant only, consisting of the product silica gel such as that available under the Trade Name Vulkasil.

**[0031]** 200g of Vulkasil and 100g of calcium stearate were blended for 5 mins using a high speed mixer. 100g of wax, 100g of calcium carbonate, 335g of MF22 and 165g of MF08 were blended with the first two ingredients for 5 mins using to the high speed mixer.

**[0032]** The resulting powder was then put through a twin screw extruder, producing a single strand, which was then pelletized.

**[0033]** 18g of the resulting pellets were added to 282g of polyethylene to make a 6% concentration. The mixture was extruded using an extrusion machine at 180-190°C to produce a mono-layered film of thickness 100µm.

### Film 2

**[0034]** In this example, the protection component is oxygen scavenger only, consisting of triazole.

**[0035]** 50g of triazole and 100g of calcium stearate were blended for 5 mins using a high speed mixer. 150g of wax, 150g of calcium carbonate, 360g of MF22, and 190g of MF08 were blended with the first two ingredients for 5 mins using to the high speed mixer.

**[0036]** The resulting powder was then put through a twin screw extruder, producing a single strand, which was then pelletized.

**[0037]** 18g of the resulting pellets were added to 282g of polyethylene to make a 6% concentration. The mixture was extruded using an extrusion machine at 180-190°C to produce a mono-layered film of thickness 100µm.

### Film 3

**[0038]** In this example, the protection component is cathodic protection only, consisting of zinc oxide compound as a hybrid of sacrificial anode.

**[0039]** 300g of zinc oxide, 200g of wax, 335g of MF22 and 165g of MF08 were blended for 5 minutes using a high speed mixer.

The resulting powder was then put through a twin screw extruder, producing a single strand, which was then pelletized.

18g of the resulting pellets were added to 282g of polyethylene to make a 6% concentration. The mixture was extruded using an extrusion machine at 180-190°C to produce a mono-layered film of thickness 100µm.

### Film 4

**[0040]** In this example, the protection component is cathodic protection only, consisting of zinc oxide.

**[0041]** 300g of zinc oxide, 200g of wax, 335g of MF22 AND 165g of MF08 were blended for 5 minutes using a high speed mixer.

**[0042]** The resulting powder was then put through a twin screw extruder, producing a single strand which was then pelletized.

**[0043]** 18g of the resulting pellets were added to 282g of polyethylene to make a 6% concentration. The mixture was

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extruded using an extrusion machine at 180-190°C to produce a mono-layered film of thickness 100µm.

### Film 5

**[0044]** In this example, the protection component is VCI and desiccant, consisting of ammoniated phosphate ester, caprylic acid, isononanoic acid, AMP 95, and Vulkasil).

**[0045]** 82g of PAE was placed in the mixing vessel. The PAE was ammoniated at 50 PSI for 1 hour. 12g of caprylic acid and 19g of isononanoic acid were added to the ammoniated PAE and heated to 100°C. 27g of AMP95 was then added to the mixture and heated to 100°C. 5g of sodium benzoate was then added to the mixture.

**[0046]** In a separate mixing vessel 117g of Vulkasil and 41g of calcium stearate were blended for 5 minutes using the high speed mixer. The amine salt mix was added to the blend and mixed for 2 minutes using the high speed mixer until a fine powder was attained. 100 g of wax, 100g of calcium carbonate, 320 of MF22 and 170g of MF08 was added to 310g of the fine powder. This was blended for 3 minutes using the high speed mixer.

**[0047]** The resulting powder was then put through a twin screw extruder, producing a single strand which was then pelletized.

**[0048]** 18g of the resulting pellets were added to 282g of polyethylene to make a 6% concentration. The mixture was extruded using an extrusion machine at 180-190°C to produce a mono-layered film of thickness 100µm.

### Film 6

**[0049]** In this example, the protection component is VCI, desiccant, and oxygen scavenger, consisting of ammoniated phosphate ester, caprylic acid, isononanoic acid, AMP 95, Vulkasil, and triazole.

**[0050]** 77g of PAE was placed in the mixing vessel. The PAE was ammoniated at 50 PSI for 1 hour. 18g of caprylic acid and 10g of isononanoic acid were added to the ammoniated PAE and heated to 100°C. 27g of AMP95 was then added to the mixture and heated to 100°C. 5g of sodium benzoate and 9g of triazole was then added to the mixture.

**[0051]** In a separate mixing vessel 114g of Vulkasil and 40g of calcium stearate were blended for 5 minutes using the high speed mixer. The amine salt mix was added to the blend and mixed for 2 minutes using the high speed mixer until a fine powder was attained. 100g of wax, 100g of calcium carbonate, 320g of MF22 and 170g of MF08 was added to 310g of the fine powder. This was blended for 3 minutes using the high speed mixer.

**[0052]** The resulting powder was then put through a twin screw extruder, producing a single strand which was then pelletized.

**[0053]** 18g of the resulting pellets were added to 282g of polyethylene to make a 6% concentration. The mixture was extruded using an extrusion machine at 180-190°C to produce a mono-layered film of thickness 100µm.

### Film 7

**[0054]** In this example, the protection components are VCI, oxygen scavenger, desiccant, and cathodic protection, consisting of ammoniated phosphate ester, caprylic acid, isononanoic acid, Amp 95, Vulkasil, triazole, and zinc oxide.

**[0055]** 77g of PAE was placed in the mixing vessel. The PAE was ammoniated at 50 PSI for 1 hour. 18g of caprylic acid and 10g of isononanoic acid were added to the ammoniated PAE and heated to 100°C. 27g of AMP95 was then added to the mixture and heated to 100°C. 5g of sodium benzoate and 9g of triazole was then added to the mixture.

**[0056]** In a separate mixing vessel 114g of Vulkasil and 40g of calcium stearate were blended for 5 minutes using the high speed mixer. The amine salt mix was added to the blend and mixed for 2 minutes using the high speed mixer until a fine powder was attained. 100g of wax, 100g of calcium carbonate, 320g of MF22. and 170g of MF08 was added to 310g of the fine powder. This was blended for 3 minutes using the high speed mixer.

**[0057]** The resulting powder was then put through a twin screw extruder, producing a single strand, which was then pelletized.

**[0058]** 15g of the resulting pellets and 3g of zinc oxide pellets were added to 282g of polyethylene to make a 6% concentration. The mixture was extruded using an extrusion machine at 180-190°C to produce a mono-layered film of thickness 100µm.

### Film 8

**[0059]** In this example, the protection components are VCI, oxygen scavenger, desiccant, and cathodic protection, consisting of ammoniated phosphate ester, caprylic acid, isononanoic acid, AMP 95, triazole, Vulkasil, and zinc oxide.

**[0060]** 77g of PAE was placed in the mixing vessel. The PAE was ammoniated at 50 PSI for 1 hour. 18g of caprylic acid and 10g of isononanoic acid were added to the ammoniated PAE and heated to 100°C. 27g of AMP95 was then added to the mixture and heated to 100°C. 5g of sodium benzoate and 9g of triazole was then added to the mixture.

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[0061] In a separate mixing vessel 114g of Vulkasil and 40g of calcium stearate were blended for 5 minutes using the high speed mixer. The amine salt mix was added to the blend and mixed for 2 minutes using the high speed mixer until a fine powder was attained. 100 g of wax, 100g of calcium carbonate, 308g of MF22, 164g of MF08 and 36g of zinc oxide was added to 310g of the fine powder. This was blended for 3 minutes using the high speed mixer.

[0062] The resulting powder was then put through a twin screw extruder, producing a single strand which was then pelletized.

[0063] 18g of the resulting pellets were added to 282g of polyethylene to make a 6% concentration. The mixture was extruded using an extrusion machine at 180-190°C to produce a mono-layered film of thickness 100µm.

### Film 9

[0064] In this example, the protection components are VCI, oxygen scavenger, desiccant, and cathodic protection, consisting of ammoniated phosphate ester, caprylic acid, isononanoic acid, AMP 95, triazole, Vulkasil, and zinc oxide compound.

[0065] 77g of PAE was placed in the mixing vessel. The PAE was ammoniated at 50 PSI for 1 hour. 18g of caprylic acid and 10g of isononanoic acid were added to ammoniated the PAE and heated to 100°C. 27g of AMP95 was then added to the mixture and heated to 100°C. 5g of sodium benzoate and 9g of triazole was then added to the mixture.

[0066] In a separate mixing vessel 114g of Vulkasil and 40g of calcium stearate were blended for 5 minutes using the high speed mixer. The amine salt mix was added to the blend and mixed for 2 minutes using the high speed mixer until a fine powder was attained. 100 g of wax, 100g of calcium carbonate, 320g of MF22 and 170g of MF08 was added to 310g of the fine powder. This was blended for 3 minutes using the high speed mixer.

[0067] The resulting powder was then put through a twin screw extruder, producing a single strand which was then pelletized.

[0068] 15g of the resulting pellets and 3g of hybrid of sacrificial anode pellets (zinc oxide compound) were added to 282g of polyethylene to make a 6% concentration. The mixture was extruded using an extrusion machine at 180-190°C to produce a mono-layered film of thickness 100µm.

### Film 10

[0069] In this example, the protection components are VCI, oxygen scavenger, desiccant, and cathodic protection, consisting of ammoniated phosphate ester, caprylic acid, isononanoic acid, AMP 95, triazole, Vulkasil, and zinc oxide compound.

[0070] 77g of PAE was placed in the mixing vessel. The PAE was ammoniated at 50 PSI for 1 hour. 18g of caprylic acid and 10g of isononanoic acid were added to the ammoniated PAE and heated to 100°C. 27g of AMP95 was then added to the mixture and heated to 100°C. 5g of sodium benzoate and 9g of triazole was then added to the mixture.

[0071] In a separate mixing vessel 114g of Vulkasil and 40g of calcium stearate were blended for 5 minutes using the high speed mixer. The amine salt mix was added to the blend and mixed for 2 minutes using the high speed mixer until a fine powder was attained. 100g of wax, 100g of calcium carbonate, 308g of MF22, 164g of MF08 and 36g of hybrid of sacrificial anode (zinc oxide compound) was added to 310g of the fine powder. This was blended for 3 minutes using the high speed mixer.

[0072] The resulting powder was then put through a twin screw extruder, producing a single strand which was then pelletized.

[0073] 18g of the resulting pellets were added to 282g of polyethylene to make a 6% concentration. The mixture was extruded using an extrusion machine at 180-190°C to produce a mono-layered film of thickness 100µm.

[0074] The thickness of all of the films was in the range of 100 - 140 µm.

### Tests

[0075] Steel panels and blades were used as metal samples for each test. The specimens were washed in tap water, followed by drying with a paper towel. Immediately before use the plates are wiped with Toluene.

### Types of tests

[0076] Table 2 presents tests carried out.

[0077] All the test results are based on visual inspection of rates of the corrosion on the metal panels compared against rates of controls.

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Table 2

| Tests                                                                                                               | CONDITIONS                                                   |                                |              |              |                                                           |               |          |                   |
|---------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------|--------------------------------|--------------|--------------|-----------------------------------------------------------|---------------|----------|-------------------|
|                                                                                                                     | Test According to Standard                                   | Medium                         | Equalib Time | Temp Changes | Duration of Temp Changes                                  | No. of Cycles | Humidity | Duration. of Test |
| A                                                                                                                   | Modified German Military Standard TL-8135                    | De-ionized water               | -            | 55°C/RT      | RT for 1 hour<br>55°C for 1 hour                          | 5             | 100%     | 10 hours          |
| B                                                                                                                   | Modified German Military Standard TL-8135                    | De-ionized water               | -            | 40°C         | -                                                         | 1             | 100%     | 1-2 hours         |
| C                                                                                                                   | BFSV - German Military Standard TL-8135-0002                 | Glycerine & de-ionized water   | 22 hours     | RT/40°C      | RT for 22 hours<br>40°C for 2 hours                       | 1             | 90°C     | 1 day             |
| D                                                                                                                   | German Military Standard TL-8135                             | De-ionized water               | 24 hours     | 10°C/40°C    | 10°C for 6 hours<br>40°C for 6 hours,<br>2 cycles per day | 20            | 100°C    | 10 days           |
| E                                                                                                                   | Modified German Military Standard TL-8135                    | De-ionized water               | 1 hour       | RT/ 55°C     | RT for 1 hour<br>55°C for 1 hour                          | 5             | 100°C    | 10 hours          |
| F                                                                                                                   | Extracted from Corporate Corrosion Testing Manual ES-688-021 | Acetic Acid & de-ionized water | -            | 55°C         | -                                                         | 1             | 100°C    | 3 days            |
| No. of cycles refers to the number of cycles of temperature change the sample is subjected to in a climatic chamber |                                                              |                                |              |              |                                                           |               |          |                   |

## Test Results

## Reference Films

**[0078]** Film No. 1 failed all of the tests. Film No. 2 failed half of the tests. Good results were achieved on D, E and F tests, which could indicate inhibiting properties of Film No. 2. Film No. 3 (having only a hybrid sacrificial anode), failed all of the tests. Film No. 4 (having only ZnO), failed most of the tests, even though good results were achieved on the B and D tests. Film No. 5 (having VCI and desiccant), passed most of the tests, giving very good results. This indicates good corrosion protection performance when these two components are used.

Films of the Invention

**[0079]** Film No. 6 (having three aspects of corrosion control, VCI, desiccant and oxygen scavenger), passed all of the tests except F, giving excellent corrosion protection. Film No. 7, being Film No. 6 modified by addition of zinc oxide at the last stage of production (extrusion), did not give excellent results. It failed A and C tests. This demonstrates that it is advantageous to mix the ingredients homogeneously, so that they are dispersed throughout the mixture, prior to film extrusion in order to achieve optimum corrosion protection. Film No. 8 (having desiccant, oxygen scavenger, VCI and zinc oxide added at the mixing stage), was able to protect the metal panels on all tests except C and F tests. Film No. 9 received very good results, with the exception that it failed test F. No evidence of corrosion and very good results were observed during the test on film No. 10. As for films 7 to 9, film No. 10 also contains all four aspects of corrosion control. The hybrid sacrificial anode of film No. 10 was added at the mixing stage.

**[0080]** Figs. 1 to 7 present the results of the tests carried out on all of the films. Films: No. 1, No. 2, No. 3 and No. 4 each with a single type of corrosion protection failed all 6 tests. They did not provide any protection against corrosion, as illustrated in Figs. 2 and 4. There was a slight difference between the films No. 5 & No. 6 comparing B and D test results (see Figs. 3 and 5). No. 5 which did not contain an oxygen scavenger gave a little bit worse results than No. 6. Four films: No. 7, No. 8, No. 9 and No. 10 contain cathodic protection. It was found that, when the cathodic protection element was added at the mixing stage of formulation, (No. 8 and No. 10), these films provided better corrosion protection than films where the cathodic protection element was added at extrusion stage. Film No. 10 provided the best results among all films (see Figs. 4, 6, and 7).

**[0081]** Addition of desiccant and oxygen scavenger to the VCI formulation causes a major improvement in results. If a fourth aspect of corrosion protection, cathodic protection, is included in film formulations, this brings about further improvement of corrosion protection.

**[0082]** The tests demonstrate that there is a synergistic mechanism of volatile corrosion inhibitors in conjunction with desiccants, oxygen scavenger and cathodic protectors. A combination of all four types of corrosion inhibition provides the optimum corrosion protection in packing.

**[0083]** Fig. 8 illustrates the protection mechanism. In the left diagram Fe dissolves and releases electrons where there is a conventional PE film with a VCI protection component. Basically, the iron dissolves at the anode and releases electrons which are subsequently consumed by oxygen at the cathode, and so the metal corrodes.

**[0084]** However, with a film of the invention as shown on the right, the cathodic protection element, in this case a sacrificial anode of ZnL (wherein L indicates a ligand, for example oxygen) dissolves. There are four protective components incorporated in the film layer, film no. 10. They can be represented as four barriers working together against unfavourable conditions which can cause the corrosion. A 1<sup>st</sup> barrier provided by the oxygen scavenger component does not allow oxygen from outside to penetrate through the film. Oxygen which is already contained in the packaging is trapped inside and neutralized by the oxygen scavenger. A 2<sup>nd</sup> barrier is provided by the desiccant of the packaging material. It provides an alternative for corrosion protection by water absorption. A desiccant is a hygroscopic substance that draws and retains moisture from its environment. Different desiccant products have different properties, absorption rates, capacities and effective operating temperature ranges. They work by segregating the inside of the bag from the environment. Desiccants will absorb moisture until they are completely saturated. If new air is allowed to pass into the area to be protected, the desiccant will eventually become saturated, without some type of barrier (typically a polyethylene bag) to keep more moisture out.

**[0085]** A 3<sup>rd</sup> barrier is provided by the VCI component, which in the presence of moisture forms an invisible protective layer. In the presence of moisture, the VCI molecule becomes polarized and attracted to the anode and cathode of the metal. Once the VCI protective ions are adsorbed onto the surface, the electrochemical process of corrosion is interrupted as the ions create a protective barrier to contaminants such as oxygen, water and other corrosion accelerators. With the protective barrier in place the corrosion cell cannot form and corrosion is halted.

**[0086]** A 4<sup>th</sup> barrier is provided by the sacrificial anode, which may be considered as an organo-metallic compound once the zinc oxide compound has been mixed with wax which dissolves at the anode and releases electrons which are subsequently consumed by oxygen at the cathode, preventing dissolving of iron.

**[0087]** It will be appreciated from the above that when the metal part is placed into a bag made from a film of the invention and sealed, changes in environmental conditions activate the four corrosion control mechanisms to create a synergistic effect for optimum corrosion protection. The desiccant prevents moisture from penetrating into the bag by water absorption, while the oxygen scavenger absorbs any oxygen that infiltrates through the seals or walls of packaging structures. The VCI and sacrificial anode are adsorbed onto the metal to jointly form a monomolecular layer on its surface. The oxygen scavenger and desiccant provide not only protection in how they operate individually, but also provide more freedom for the VCI and sacrificial anode to operate on the metal surface. In more detail, the latter two components can migrate from the film to the metal surface. In the presence of moisture, the VCI and sacrificial anode become polarized and attracted to the anode and cathode of the metal. Once the VCI protective ions are adsorbed onto the surface, the electrochemical process of corrosion is interrupted as the ions create a protective barrier to contaminants such as oxygen,

water and other corrosion accelerators. With the protective barrier in place the corrosion cell cannot form and corrosion is halted.

**[0088]** The invention is not limited to the embodiments described but may be varied in construction and detail.

## Claims

1. A packaging material comprising metal-protecting components including a volatile corrosion inhibitor, a desiccant, and an oxygen scavenger.
2. A packaging material as claimed in claim 1, wherein the metal-protecting components further comprise a cathodic protector.
3. A packaging material as claimed in claims 1 or 2, wherein the material comprises polyethylene as a bulk component, and the metal-protecting components are dispersed in said bulk component.
4. A packaging material as claimed in claim 1, wherein the volatile corrosion inhibitor is in the form of a mixed inhibitor.
5. A packaging material as claimed in claim 4, wherein the volatile corrosion inhibitor includes phosphate esters, acids, and amines.
6. A packaging material as claimed in claim 5, wherein said phosphate esters are ammoniated phosphate esters.
7. A packaging material as claimed in claim 5, wherein said acids are carboxylic acids.
8. A packaging material as claimed in any of claims 5 to 7, wherein said acids include caprylic acid and isononanoic acid.
9. A packaging material as claimed in any of claims 5 to 8, wherein said amines are primary amines.
10. A packaging material as claimed in any of claims 5 to 9, wherein the amines include amino-2methyl-1-propanol.
11. A packaging material as claimed in any preceding claim, wherein the desiccant comprises a silica gel.
12. A packaging material as claimed in any preceding claim, wherein the said oxygen scavenger comprises triazole.
13. A packaging material as claimed in claim 12 wherein the triazole is benzotriazole.
14. A packaging material as claimed in any of claims 2 to 12, wherein the said cathodic protector includes a sacrificial anode.
15. A packaging material as claimed in claim 13, wherein the sacrificial anode comprises a zinc oxide.
16. A packaging material as claimed in claims 13 or 14, wherein the sacrificial anode comprises a mixture of zinc oxide, titanium dioxide and silicon oxide.
17. A packaging material as claimed in any preceding claim, further comprising an organic salt.
18. A packaging material as claimed in any preceding claim, further comprising sodium benzoate.
19. A packaging material as claimed in any preceding claim, further comprising ammonia anhydrous.
20. A packaging material as claimed in any preceding claim, further comprising calcium carbonate.
21. A packaging material as claimed in any preceding claim, further comprising calcium stearate.
22. A packaging material as claimed in any preceding claim wherein the packaging material is in the form of a film.
23. A packaging material as claimed in claim 22 wherein the film has a thickness of between 100 $\mu$ m and 140 $\mu$ m.

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**24.** A method of manufacturing a packaging material of any preceding claim, comprising the step of mixing the protection components with a bulk material.

5 **25.** A method as claimed in claim 24, wherein the bulk material is a plastics material and the protection components and the plastics material are mixed, heated, and extruded.

**26.** A method as claimed in claim 25, wherein the plastics material is polyethylene.

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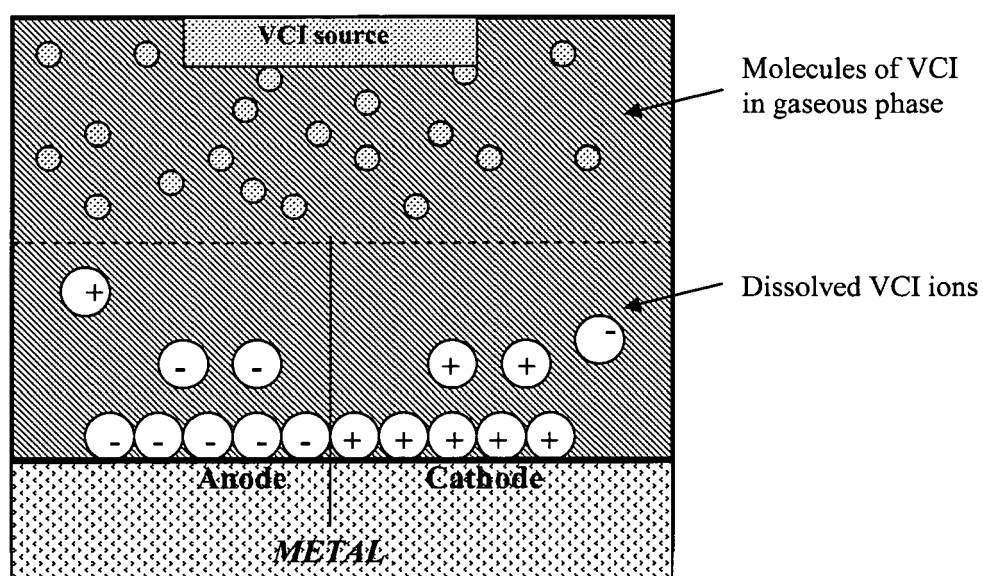


Fig. A Prior Art

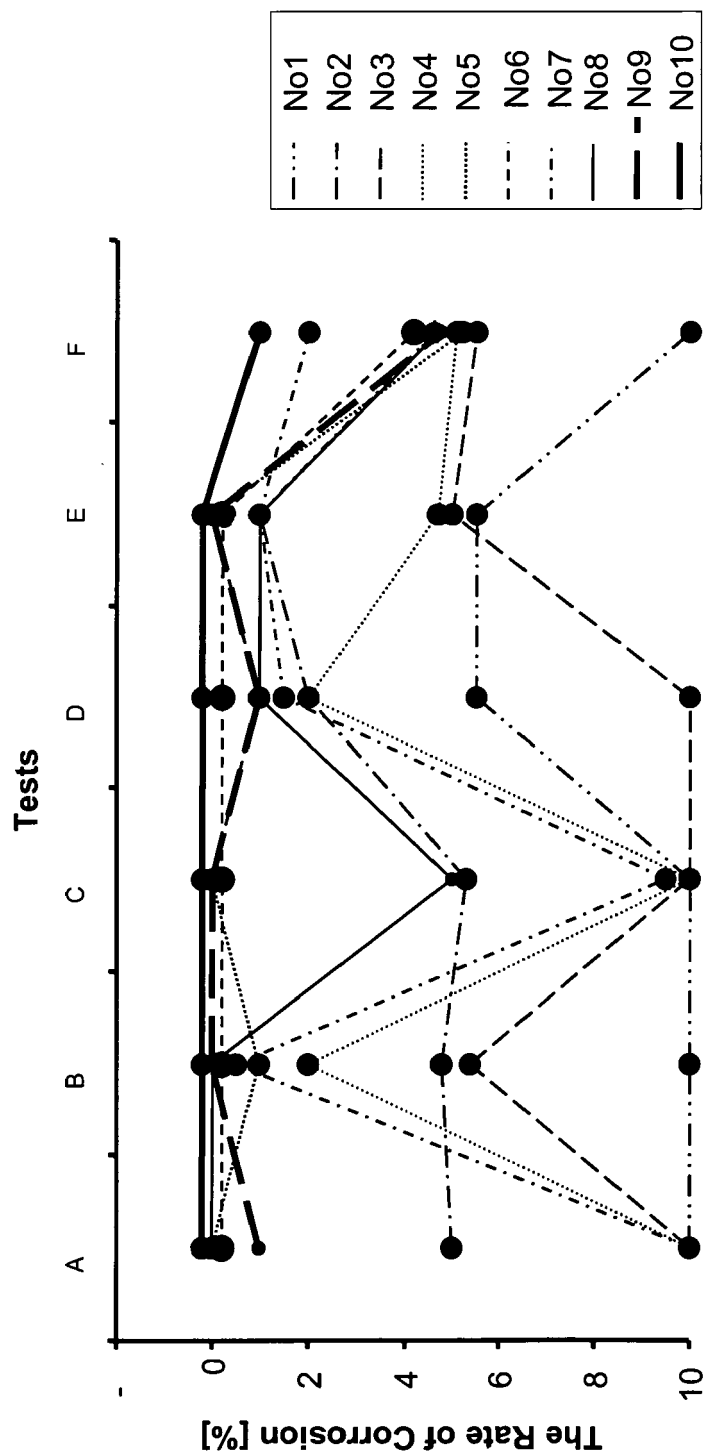


Fig. 1

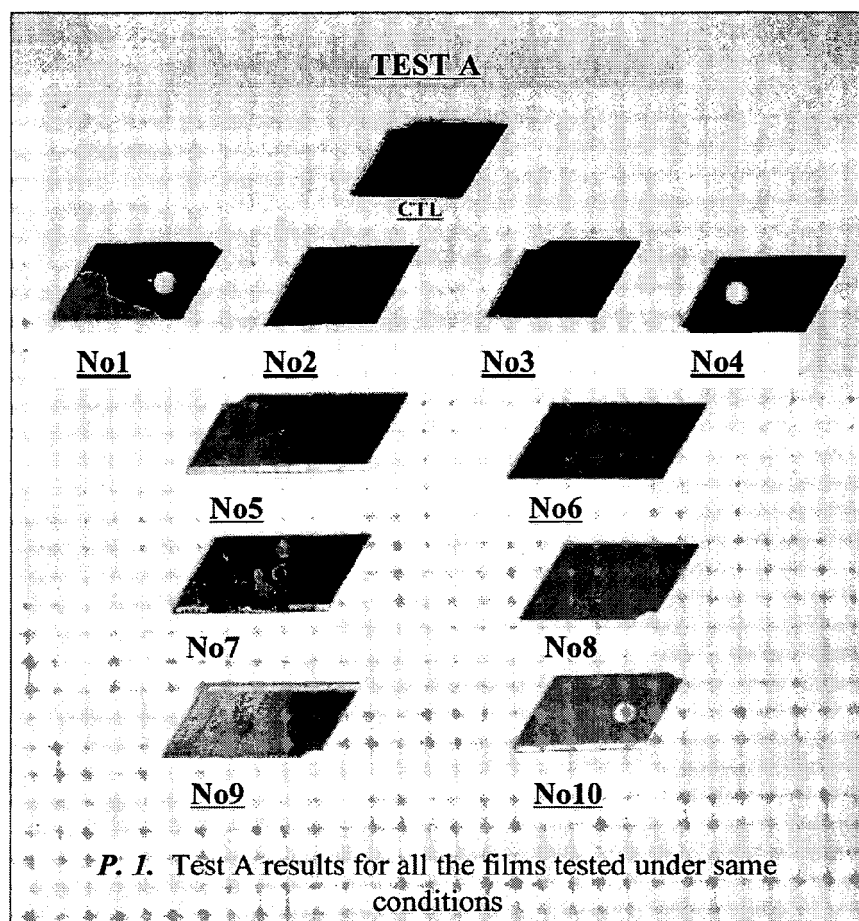


Fig. 2

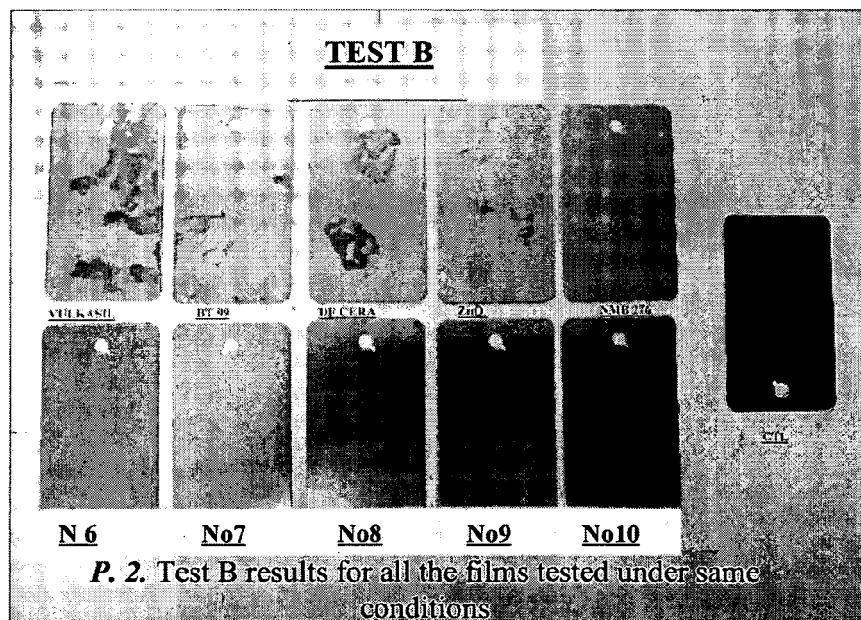


Fig. 3

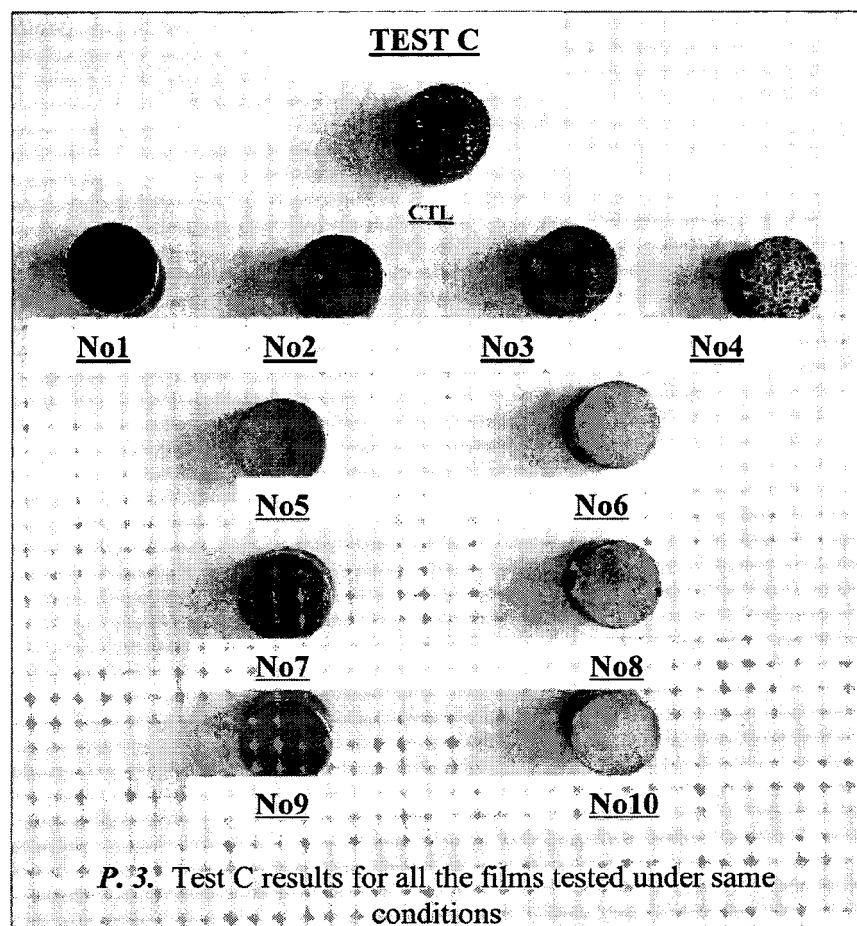


Fig. 4

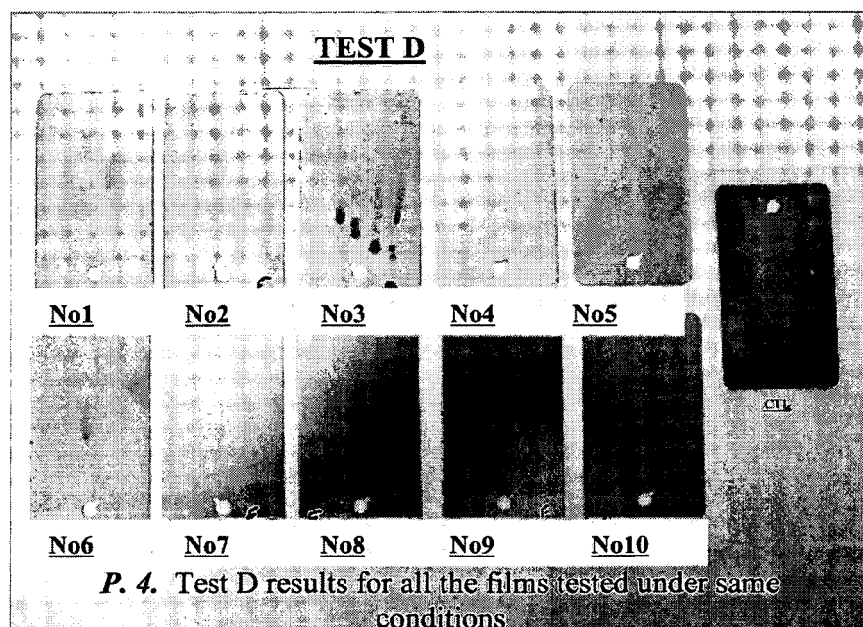


Fig. 5

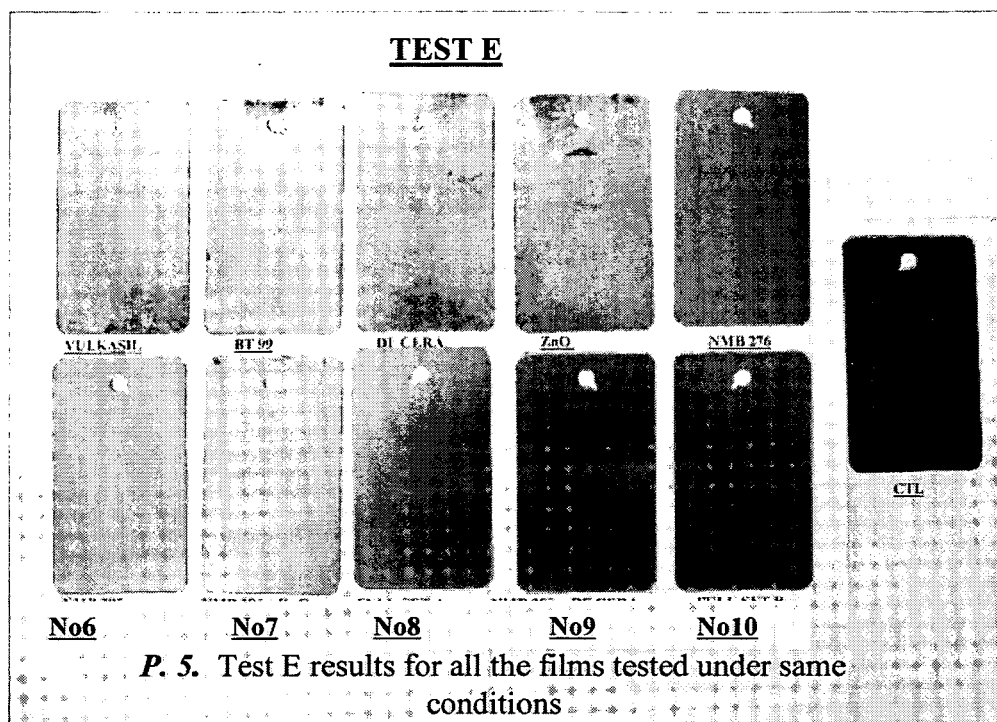


Fig. 6

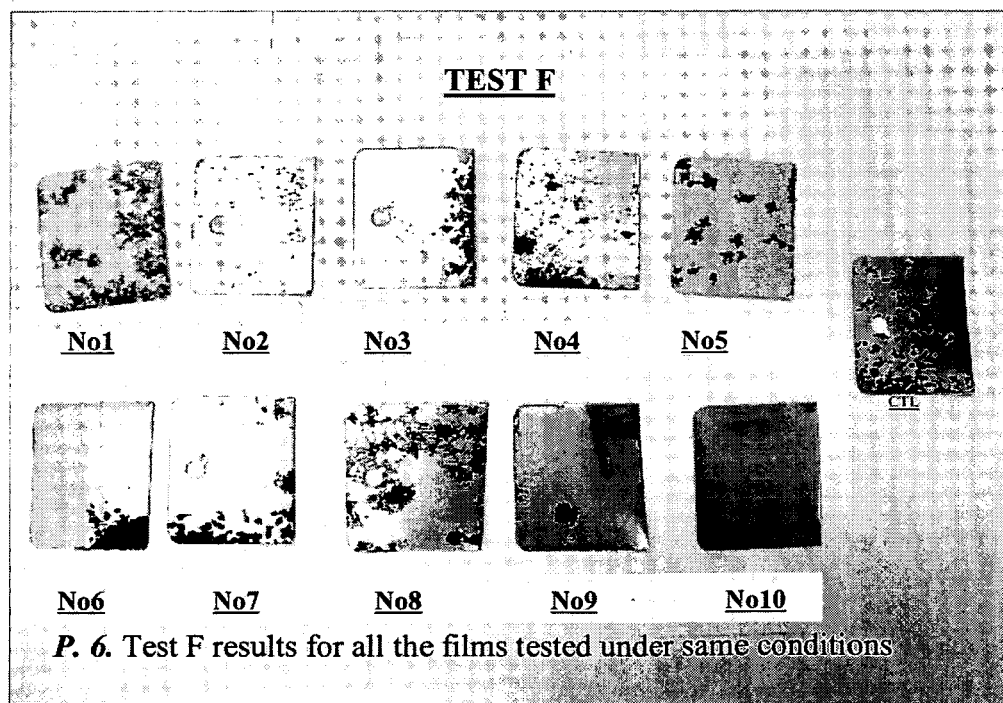
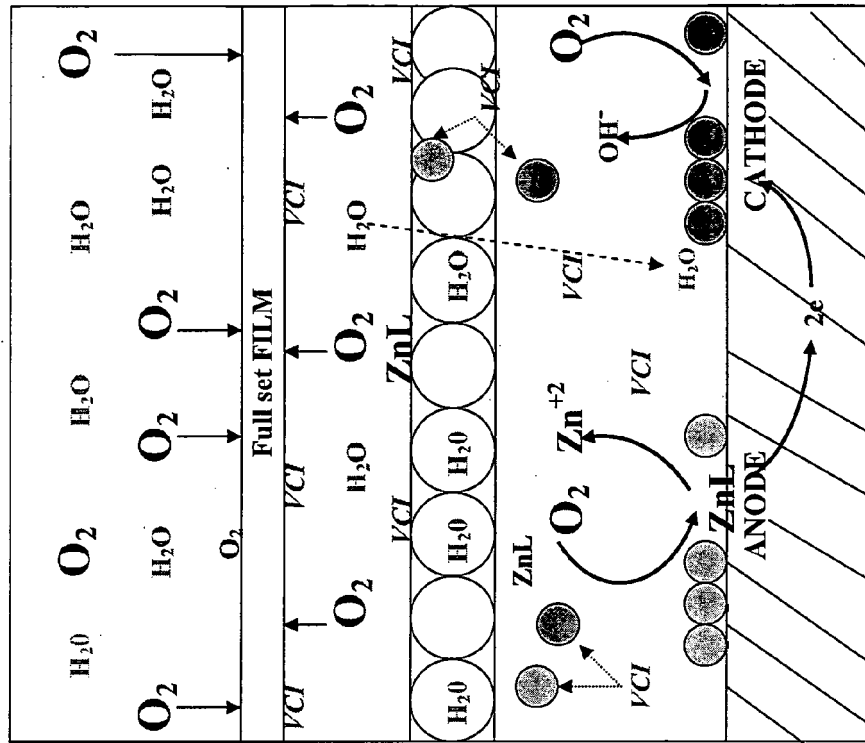


Fig. 7



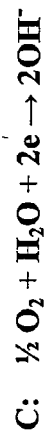
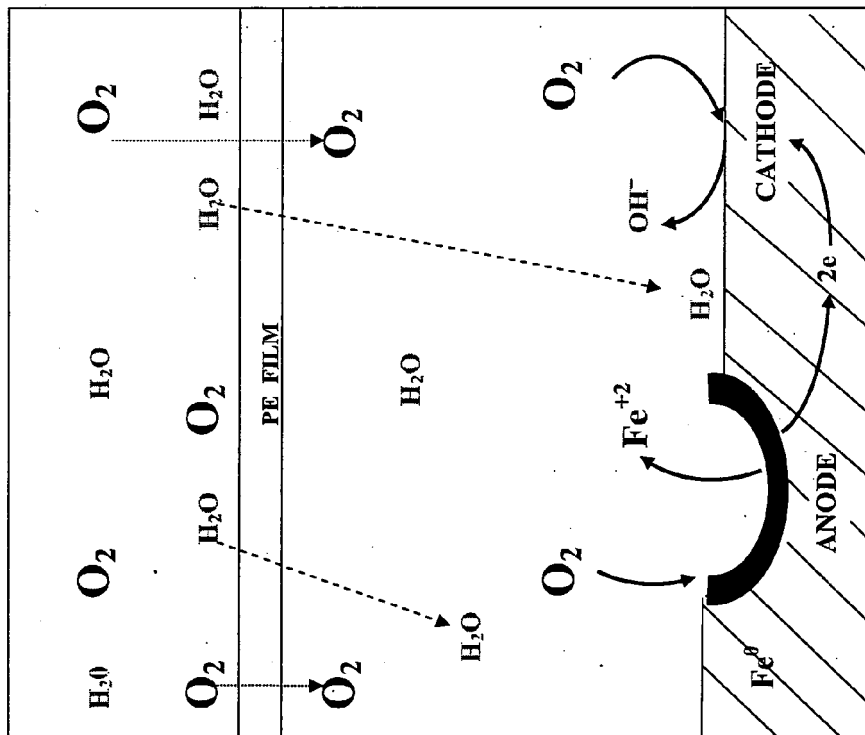
1<sup>st</sup> Barrier -  
Oxygen  
Scavenger  
active barrier

2<sup>nd</sup> Barrier -  
Desiccant  
active barrier

3<sup>rd</sup> Barrier -  
VCl active  
barrier &  
4<sup>th</sup> Barrier -  
Organometallic



Fig. 8





European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 07 39 4025

| DOCUMENTS CONSIDERED TO BE RELEVANT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                                                                                                                                                            |                                                             |                                                                  |
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| Place of search<br><b>Munich</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                                                                                                                                                                                            | Date of completion of the search<br><b>13 February 2008</b> | Examiner<br><b>Schütte, Maya</b>                                 |
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The members are as contained in the European Patent Office EDP file on  
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13-02-2008

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