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ALKALINE LIQUIDS FOR CLEANING METALS
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8 Claims

ABSTRACT OF THE DISCLOSURE

Grain-refining pretreatment liquids for ferrous or zinc-containing metal surfaces, which have a pH of at least 4.5 and contain a titanium grain-refining compound are stabilised by the addition thereto of a soluble copolymer of maleic acid (anhydride), fumaric acid or citraconic acid and ethylene or a methyl, ethyl or cyclohexyl vinyl ether. The copolymers must have a viscosity as a 4% by weight solution in water of pH 9 of at least 3.5 centipoise at 25° C. A process of zinc phosphating in which the grain-refining liquid so-stabilised in a water-rinse immediately preceding a phosphating liquid is also disclosed.

This invention relates to aqueous grain-refining metal pretreatment process and liquids, to stabilisers for use therein and to aqueous metal pretreatment liquids so-stabilised.

By metal pretreatment liquids we mean liquids which are used to treat metal surfaces so as to present a favourable substrate to which a protective and/or decorative coating, for example a paint oil or wax film, may be subsequently applied. In the present context we are referring in particular to aqueous liquids which are used in conjunction with and preceding a zinc phosphate coating step in a metal pretreatment process.

It is known that the corrosion resistance of ferrous and zinc based (e.g. zinc or galvanised) metal surfaces can be usefully improved by depositing on them a crystalline zinc phosphate coating, which is then sealed with an appropriate top-coat. Before the application of the zinc phosphate coating, the metal surface must be cleaned to remove contaminants such as oil, grease and dirt, for which purpose an aqueous cleaning liquid is commonly used. Unless special precautions are taken to avoid it, the phosphate coating deposited on the metal surface so-cleaned tends to form as a mass of relatively coarse, loosely packed crystals. Coatings with these characteristics have been found to show poor flexibility and adhesion to the metal. They also have a further disadvantage in that they will disrupt and mar the surface appearance of an otherwise glossy paint film applied over them.

It has been proposed that if certain complex titanium/phosphate compounds known broadly in the art as titanium grain-refining compounds are added to aqueous liquid used to clean the metal, the subsequently applied zinc phosphate coatings will be denser, more finely crystalline and more tightly adhered to the metal substrate. The corrosion resistance of such surfaces is also considered to be superior to that of a metal surface coated with a coarser, less dense zinc phosphate film.

Titanium grain-refining compounds of this class are typified by the so-called "Jernstedt" salts described, for example, in Australian patent specification No. 224,761 and U.S. patent specification No. 2,310,239. While the precise nature of these salts is not known they would appear to be titanium/phosphate complexes present in the pretreatment solution as finely dispersed solids, possi-

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bly of colloidal dimensions, which supply titanium ions to the liquid.

We have observed that although the usefulness of an aqueous metal pretreatment liquid decreases predictably as active constituents are exhausted from it, the effectiveness of a titanium grain-refining compound present in the liquid is also time-dependent. That is, although the cleaning or other function of the liquid is usually unaffected by storage, its grain-refining capacity can diminish markedly with time, even when the liquid is not being used; that is the grain-refining capacity may decay quite rapidly. Furthermore, the rate of decay of grain-refining capacity is significantly dependent on the pH of the liquid. If the liquid is mildly alkaline, e.g. pH 8-9, its grain-refining capacity may remain at a useful level for hours or even days. On the other hand, if the liquid is acidified or its pH is increased above about pH 10 the grain-refining properties may, for all practical purposes, be destroyed. Thus there has been an inherent limitation on the pH of the aqueous liquid in which a titanium grain-refining compound can be used. For example, for some purposes mildly acidic cleaning baths are particularly effective cleaning or etching agent for metal surfaces, but in these media titanium grain-refining compounds usually decay too rapidly to be commercially useful.

In order to appreciate some of the limitations which the pH dependent decay of grain-refining capacity may have in metal pretreatment processes, it is useful to consider a typical industrial process for the cleaning and zinc phosphating of metal articles.

The metal is conveyed mechanically through a series of adjoining dip or spray stages which successively drench the metal with a series of liquids, forming in combination what is essentially a single continuous metal treatment unit. When spray stages are used it is the normal practice to collect run-off from the treated metal in a sump at the bottom of each stage and for economy to re-cycle it to the sprays. Because of the close proximity of adjacent stages, splash-back of liquid from one stage to the next is usually encountered so that there is a gradual build-up of contamination in the liquid of each stage. In a typical installation there may be present in sequence the following stages; alkaline metal cleaner, one or more water rinses, zinc phosphating solution and final water rinse.

It is a common practice to incorporate titanium grain-refining compound in the alkaline cleaning liquid, which is then, however, limited to a maximum pH of about 8-9, as mentioned above.

An alternative proposal to avoid this pH limitation is to omit titanium grain-refining compound from the cleaning stage and to introduce it into a water rinse stage immediately preceding the phosphating stage. Provided an adequate water rinse is interposed between the cleaning and grain-refining stages, alkali contamination of the titanium grain-refining compound is thereby avoided. One objection to this proposal is, however, that splash-back of acidic phosphating solution can quickly destroy the effectiveness of the titanium compound in the grain-refining stage. While this could presumably be prevented by interposing an additional rinse stage immediately prior to the phosphating stage, this is an economically unattractive solution.

We have now found that the time-dependent loss of grain-refining capacity of a liquid comprising titanium grain-refining compound may be inhibited over a wide pH range by adding to it certain polymeric materials as hereinunder defined. The polymeric materials when used in cleaning and rinse liquids as described above have no grain-refining function per se and as an apt description of their effect, but without ascribing any particular mech-

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anism to their function we refer to them hereinunder as grain-refiner stabilisers.

According to the present invention we provide an aqueous grain-refining pretreatment liquid for ferrous and zinc-containing metal surfaces the said liquid having a pH of at least 4.5 and comprising titanium grain-refining compound together with a soluble grain-refiner stabiliser consisting of an addition copolymer of monomer (a) and monomer (b) in essentially equimolar ratios wherein monomer (a) is at least one unsaturated polycarboxylic acid or acid anhydride selected from the group consisting of maleic acid, maleic anhydride, fumaric acid and citraconic acid, and monomer (b) is at least one unsaturated monomer selected from the group consisting of ethylene, methyl vinyl ether, ethyl vinyl ether and cyclohexyl vinyl ether, and further characterised in that the copolymer shall have a viscosity of at least 3.5 centipoise at 25° C. when tested as a 4% by weight solution in an aqueous sodium hydroxide solution at a pH of 9.

It is a particular and unexpected advantage of this invention that titanium grain-refining compounds may be stabilised in this way in aqueous liquids having a pH of from 4.5 to greater than 12. Thus the invention is applicable not only to conventional mildly alkaline pretreatment liquids but to both acidic and relatively strongly alkaline metal pretreatment liquids as well.

The aqueous metal pretreatment liquid may be an acidic or mildly alkaline cleaning or etching liquid having a pH of at least 4.5. In one particular embodiment of this invention in which full advantage can be taken of the vigorous cleaning action of strongly alkaline liquids, the aqueous metal pretreatment liquid has a pH of at least 9 and comprises titanium grain-refining compound together with polymeric grain-refiner stabiliser as hereinabove defined.

Alternatively, the aqueous metal pretreatment liquid may be a water rinse consisting essentially of water together with grain-refiner stabiliser and titanium grain-refining compound. In this embodiment of our invention, the liquid can be used satisfactorily as a final grain-refining water rinse stage immediately preceding a zinc phosphate coating stage. For purely economic reasons, splash-back from the adjacent acidic zinc phosphate stage is unlikely to lower the pH of the water rinse to 4.5 and under such mildly acid conditions the stabiliser of our invention resists grain-refining decay to an acceptable degree.

When the aqueous metal treatment liquid is an alkaline cleaning liquid it may consist essentially of an aqueous solution of alkali, for example, sodium and potassium carbonates, bicarbonates and hydroxides, at the concentration necessary to provide the desired pH. Other materials, for example, polyphosphates (e.g. alkali metal pyrophosphates and tripolyphosphates), alkali metal silicates and anionic or non-ionic surface active agents are commonly added to the liquid, for example to enhance its detergent action.

The polymeric stabilisers are, in general, readily soluble in alkaline liquids, with which they are reactable to form soluble alkaline salts. In acid solutions or solutions likely to become contaminated with acidic liquids it is necessary to select for use as stabilisers those compositions as defined above which are soluble in the liquid at the required pH and working concentration.

The required concentration of stabiliser to give a useful grain-refining life to a liquid is related to the nature and concentration of the titanium grain-refining compound used therein. The effectiveness of the titanium complex in turn appears to depend to a degree on the method by which it has been manufactured and while concentrations as low as 0.0005% by weight in the liquid (expressed as titanium ions) may be effective, the more useful working concentrations are of the order of 0.005% to 0.05% by weight. In general, we have found that a weight of sta-

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biliser equal to that of the total weight of titanium in the grain-refining compound is the minimum amount which can confer the benefits of the invention although higher concentrations of stabiliser can be used in the liquid. Our usual practice is to prepare a series of aqueous liquids of increasing stabiliser contents but of otherwise identical formulae and then check their active grain-refining lives. When this is done it is usually found that for a particular grain-refining compound there is a definite stabiliser concentration at which the liquid displays its maximum grain-refining life; which is not prolonged by the use of higher concentrations of stabiliser. To achieve a useful working life for the liquid we prefer that it should contain at least 0.005% by weight of stabilizer, the most useful working concentration range under normal working conditions being 0.01 to 0.02% by weight. When, for example, a cleaning liquid comprising a titanium grain-refining compound is to be used industrially on heavily soiled metal it may be found necessary to use even higher concentrations of stabiliser, presumably because of the adverse effect on the stabiliser of the contaminants.

The degree of improvement which can be achieved in the useful active life of the metal pretreatment liquid depends on a number of factors which are characteristic of the particular liquid to be stabilised. For example, when the liquid is mildly alkaline, that is below about pH 9.5-10, the achievable improvement is useful but often relatively small; for example it may extend the active life by a few hours only. However, at pH values of 11 and over or when the liquid is acidic the liquid may have virtually no useful grain-refining action at all in the absence of the grain-refiner stabiliser, whereas in the presence of the stabiliser of the invention a pronounced grain-refining capacity may persist for more than 72 hours. We have observed that the maximum achievable grain-refining capacity of a particular liquid can vary according to the source of the titanium grain-refining compound contained therein. Although these materials as a class are well-known in the art the nature of individual compounds appears to vary somewhat and this is reflected in their performance in grain-refining liquids. In particular, we have observed that when the titanium grain-refining compound is to be used in an aqueous pretreatment liquid which has a pH of greater than about 9, some titanium compounds which otherwise perform satisfactorily as grain-refining materials appear to lose their activity completely if the liquid comprises alkali metal polyphosphates, e.g. alkali metal pyrophosphates and tripolyphosphates. We have observed that this loss of grain-refining activity is associated with an apparent complete solubility of the titanium compound in the liquid. For example, the addition of a titanium grain-refining compound to an aqueous pretreatment liquid normally imparts a slight turbidity to the liquid, whereas in the above cases a clear liquid is usually formed. Although we are not able to ascribe any particular mechanism to this observed effect, it does appear that in relatively strongly alkaline solutions and in the presence of alkali metal polyphosphates certain materials which are broadly accepted by the art as titanium grain-refining compounds react with such liquids and can not then be comprehended as titanium grain-refining compounds. It is our understanding that a titanium/phosphate complex which the art recognises as a grain-refining compound is at least partially insoluble in the liquid in which it is to be used. Because of this dependence of the life of an unstabilised liquid comprising a titanium grain-refining compound on the pH of the liquid and the variation in nature of the grain-refining compound itself and bearing in mind that the purpose of the stabiliser is to prolong the active life of a grain-refining liquid and not to accelerate or otherwise increase its activity, any improvement brought about in the liquid by the use of the stabiliser of the invention must be related to the performance of the particular liquid in the

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absence of stabilizer and not to that of another pretreatment liquid.

Aqueous cleaning liquids according to this invention are prepared by stirring into a conventional cleaning liquid, or in the case of a water rinse, to a rinse liquid, the required amount of titanium grain-refining compound and grain-refiner stabiliser. In the case of alkaline liquids it may be necessary to add an amount of additional alkali to compensate for a drop in pH as the stabiliser dissolves. Alternatively, and especially in the case of an alkaline cleaner, all of the solid components of the cleaner may be premixed as a dry powder and the grain-refining liquid is then prepared by dissolving the powder in water, which optionally contains pre-dissolved components, e.g. conventional surface-active agents, which may assist in the rapid wetting out and dispersion of the powder.

As mentioned above, the ability to maintain grain-refining capacity for a useful practical life in a mildly acid liquid permits of the use of a grain-refining rinse before zinc phosphate coating independent of the means employed to pre-clean the metal to be phosphated. For the best results it is preferable to rinse cleaning liquid from the metal before it enters the grain-refining rinse stage. Accordingly, in a preferred embodiment of our invention we provide a process of zinc phosphating steel or zinc-based metal surfaces wherein the metal is sequentially subjected to an aqueous cleaning liquid, at least two water rinses and a zinc phosphating liquid and characterised in that the water rinse immediately preceding the zinc phosphating liquid comprises a titanium grain-refining compound and a grain-refiner stabiliser as hereinabove defined and has a pH of at least 4.5.

Zinc phosphating liquids are well known in the art and no special requirements must be met in selecting a suitable phosphating liquid for performing the process of our invention. They are broadly recognised as essentially acid solutions of zinc orthophosphates.

The invention is illustrated by the following examples in which all parts are expressed by weight.

EXAMPLE 1

Effect of an acidic cleaning liquid containing no polymeric stabiliser according to the invention, as a pretreatment for zinc phosphated steel.

A bath of acid cleaning liquid was prepared by dispersing in water to a weight concentration of 0.4% the following mixture:

	Parts
Monosodium orthophosphate	77.00
Disodium orthophosphate	9.00
Diatomaceous earth	2.00
Anionic surfactant	4.00
Non-ionic surfactant	8.00

The non-ionic surfactant used was a commercial octyl phenol/ethylene oxide condensate and the anionic surfactant a commercial aryl sulphonate.

The solution had a pH of 5.8. The bath was heated to 140° F. and a steel panel which had been given a preliminary pre-washed with hydrocarbon cleaning solvent was sprayed with the solution for one minute. The panel was then rinsed free of this solution by spraying with clean water for 30 seconds then zinc phosphate coated in a commercial zinc phosphate coating bath. A light, fluffy relatively coarse, discontinuous coating of zinc phosphate was formed on the steel.

Additions of a polymeric stabiliser as hereinabove defined, a poly (maleic anhydride/methyl vinyl ether) of viscosity 200 centipoise at 25° C. (4% solution in aqueous sodium hydroxide, pH 9), to the cleaner without titanium grain-refining compound had no visible effect on the nature of the zinc phosphate coating formed on the steel.

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EXAMPLE 2

Effect of polymeric stabiliser and a titanium grain-refining compound according to the invention on the action of an acid cleaning bath.

An acid cleaning bath was prepared according to Example 1 but containing additionally 0.01% by weight of stabiliser according to Example 1 and 0.025% by weight of titanium grain-refining compound (as Ti). The titanium grain-refining compound was prepared by heating 24 parts of water to 94° C. and adding to it with continuous mechanical agitation 95 parts of anhydrous disodium hydrogen phosphate. The mixing was continued while 5 parts of anhydrous potassium fluo-titanate were added to the batch in small increments over a period of 30 minutes. Mixing and heating were continued until a dry mass was formed, which was the ground to less than 60 mesh, to provide a titanium grain-refining compound of approximately 1% by weight titanium.

When testing was carried out according to Example 1 on steel panels, a dense, even, fine-grained coating of zinc phosphate formed on the steel.

The example was repeated using titanium grain-refining compound but omitting the stabiliser. A relatively coarse, discontinuous coating of zinc phosphate formed on the panel, thus demonstrating the effectiveness of the combination of titanium grain-refining compounds and stabiliser according to the invention.

EXAMPLE 3

Comparative tests of strongly alkaline grain-refining metal-cleaning liquids showing the benefit of including therein the grain-refiner stabiliser of the invention.

The following mixtures were prepared by dry blending:

Component	Mixture No. (parts by wt.)		
	1	2	3
Sodium hydroxide.....	25	25	25
Sodium carbonate.....	60	60	60
Non-ionic surfactant.....	8	8	8
Commercial titanium grain-refining compound.....	7	7	8
Grain-refiner stabiliser.....		0.5	3

The non-ionic surfactant was an octyl phenol/ethylene oxide condensate containing approximately 11 ethylene oxide units per phenol group. The grain-refiner stabiliser was a poly (maleic anhydride/methyl vinyl ether) of approximately 1:1 molar ratios which had a viscosity as a 4% by weight solution in aqueous sodium hydroxide solution of pH 9 of 200 centipoise at 25° C.

Each dry mix was stirred into water heated to 160° F. at a concentration by weight of 0.4% to give alkaline cleaning liquids of pH greater than 12.

Cleaning liquid 3 (based on mixture No. 3) was a liquid according to the invention, comprising about 0.00056% by weight of titanium grain-refining compound (as Ti ions) and 0.012% by weight of stabiliser.

The cleaning liquids were tested by the following method. Rolled sheet steel panels coated with a heavily soiled oily film were sprayed with cleaning liquid at a pressure of 20 p.s.i. for one minute, rinsed with a spray of clean water for one minute, then sprayed for one minute with a commercial zinc phosphating solution of the type described in, for example, Australian patent application No. 9478/66. The panels were then air dried and examined visually for cleanliness and by microscopy to determine the nature of the coating found on them.

In order to compare the useful grain-refining life of the liquids they were tested after the following stipulated time intervals, measured from the time when the dry powders were stirred into the water. During the holding periods the liquids were held at 160° F. unless otherwise

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stipulated to simulate industrial practice. The results were as follows:

Liquid No.	Time interval	Cleaning power	Coating
1-----	Tested immediately-----	Excellent..	Fine-grained, even, continuous.
1-----	4 hours-----	do-----	Thin, coarsely crystalline, powdery.
2-----	Tested immediately-----	do-----	Fine-grained, even, continuous.
2-----	8 hours-----	do-----	Thin, coarsely crystalline, powdery.
3-----	Tested immediately-----	do-----	Fine-grained, even, continuous.
3-----	4 hours-----	do-----	Do.
3-----	8 hours-----	do-----	Do.
3-----	8 hrs. plus over-night cooling, re-heated to 160° F.	do-----	Do.

The limited useful life of the stabiliser-free composition is apparent from the above results when compared with cleaning liquid No. 3. Cleaning liquid No. 2 which contained less than the recommended concentration of stabiliser (0.002% by wt.) was also inferior after 8 hours storage to the composition according to the invention.

EXAMPLE 4

Preparation of silicate-containing alkaline grain-refining metal-cleaning liquids according to the invention.

By the general method of Example 3 an alkaline liquid cleaner was prepared from a dry mix of the following materials:

	Parts
Sodium orthosilicate -----	43
Tetra sodium pyrophosphate -----	22
Sodium carbonate -----	16
Non-ionic surfactant (As Example 3) -----	8
Commercial titanium grain-refining compound -----	8
Grain-refiner stabiliser (as Example 3) -----	3

The cleaning liquid, which had a pH of 12, comprised about 0.00064% by weight titanium grain-refining compound (as Ti ions) and 0.012% by weight of stabiliser, was slightly turbid.

The liquid was tested by the method of Example 3 for cleaning and grain-refining capacity after time intervals from preparation of zero, 8 hours, 16 hours and 72 hours (the last periods including over-night cooling followed by re-heating).

In all tests the liquid showed excellent cleaning ability and there was no obvious fall-off in grain-refining capacity even at the 72 hour test. The phosphate coating was dense, finely crystalline and tightly adhered to the metal surface.

EXAMPLE 5

Comparison of the effectiveness of relatively low pH alkaline cleaning liquids with and without stabiliser according to the invention.

By the general method of Example 3 two cleaning liquids were prepared from the following dry mixes:

Component	Mixture No. (parts by wt.)	
	1	2
Sodium tripolyphosphate-----	60	60
Sodium carbonate-----	20	20
Non-ionic surfactant (as example 3)-----	10	10
Commercial titanium grain-refining compound-----	10	10
Grain-refiner stabiliser ¹ -----		3

¹ Copolymer 11 of Example 6.

The cleaning liquids so prepared, had a pH of about 9. Both liquids contained approximately 0.001% by weight of titanium grain-refining compound (calculated as Ti ions) and liquid No. 2 (derived from mixture No. 2) also contained 0.012% by weight of stabiliser.

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The liquids were tested by the method of Example 3 with the following results:

Liquid No.	Time interval	Cleaning power	Coating
1-----	Tested immediately-----	Very good..	Fine-grained, even, continuous.
1-----	8 hrs. plus over-night cooling, reheating to 160° F.	do-----	Thin, coarsely crystalline, powdery.
2-----	Tested immediately-----	do-----	Fine-grained, even, continuous.
2-----	8 hrs. plus over-night cooling, reheating to 160° F.	do-----	Do.

These results confirm the beneficial effect at pH 9 of the presence of stabiliser, according to the invention, in the liquid.

EXAMPLE 6

Comparison of polymeric stabilisers according to the invention with other polymeric materials in alkaline cleaning baths.

The polymers tested fell into two distinct classes. All of the polymers were soluble at the concentration at which they were tested in an alkaline cleaning liquid at a pH of about 12, but whereas one group was closely related structurally to and included within it the polymeric stabilisers of the invention, the other group was of chemically dis-similar polymers.

The chemically dis-similar polymers were hydroxyethyl cellulose, carboxy methyl cellulose and poly (acrylic acid).

Of the other group, all were copolymers of maleic anhydride and a comonomer (in approximately 1:1 molar ratio), which was either ethylene or a substituted ethylene. The composition of the comonomers is as follows:

Copolymer number	Comonomer	Viscosity (4% solu. pH 9) at 25° C.
1-----	Methyl vinyl ether-----	Less than 3 centipoise.
2-----	do-----	30 centipoise.
3-----	do-----	2,000 centipoise.
4-----	do-----	6,000 centipoise.
5-----	Ethyl vinyl ether-----	Greater than 3.5 centipoise.
6-----	Iso-butyl vinyl ether-----	Do.
7-----	Cyclohexyl vinyl ether-----	Do.
8-----	Styrene-----	Do.
9-----	Vinyl acetate-----	Do.
10-----	Acrylic acid-----	Do.
11-----	Ethylene-----	6 centipoise.
12-----	do-----	Approx. 10,000 centipoise.

The polymers were checked for their effectiveness as grain refiner stabilisers by incorporating them in the dry blend mixture of Example 3 as stabiliser component, using the formulation of mixture No. 3. This mixture was then compounded into a cleaning liquid and tested by the method of that example, the basis of selection of a suitable stabiliser being that it should provide a liquid retaining its grain-refining capacity for at least 8 hours. The results were as follows:

Polymer under test	Time to failure
Hydroxyethyl cellulose-----	Less than 1 hour.
Carboxy methyl cellulose-----	Do.
Poly (acrylic acid)-----	Do.
Copolymer No. 1 (above)-----	Do.
Copolymer No. 2-----	No failure at 72 hrs.
Copolymer No. 3-----	Do.
Copolymer No. 4-----	Do.
Copolymer No. 5-----	Do.
Copolymer No. 6-----	Less than 8 hours.
Copolymer No. 7-----	72 hours.
Copolymer No. 8-----	Less than 4 hours.
Copolymer No. 9-----	Less than 8 hours.
Copolymer No. 10-----	Do.
Copolymer No. 11-----	72 hours.
Copolymer No. 12-----	Do.

It will be seen that only polymers of the composition of the stabilisers according to this invention performed satisfactorily for 8 or more hours; that is for the span of a normal working shift.

Approx. equimolar copolymer of maleic acid/ethyl vinyl ether, fumaric acid/ethyl vinyl ether (viscosities of 4% solutions at pH 9 and 25° C. approximately 30 centipoise) were substituted on an equal weight basis in a further series of tests for the above copolymer No. 5 and gave an equivalent performance as grain-refiner stabilisers. A corresponding copolymer of citraconic acid/ethyl vinyl ether had a similar grain-refining action.

EXAMPLE 7

Metal pretreatment process comprising a titanium grain-refining wash stage according to the invention.

A simulated metal cleaning and phosphating line was assembled in which metal panels were sequentially cleared in an aqueous alkaline cleaning bath (mixture No. 1 of Example 4 but omitting the titanium grain-refining compound), water-rinsed to remove alkali, rinsed in a liquid consisting essentially of water together with 0.01% by weight of titanium grain-refining compound (calculated on titanium content) and 0.02% by weight of a grain-refiner stabiliser (copolymer 2 of Example 6) to which sufficient sodium hydroxide was added to form the sodium salt of the stabiliser, then coated with zinc phosphate in a conventional acid zinc phosphating bath.

Steel and galvanised steel panels passed through the line showed satisfactory fine and even phosphate coatings.

Acid phosphating solution was then added to the grain-refining rinse bath to bring the pH to 4.5 to simulate splash-back, and further panels passed through the line with satisfactory results. No significant fall-off in quality of the phosphating was evident when panels were passed through the line after aging the contaminated grain-refining rinse bath for up to 24 hours.

By way of comparison, the above trial was repeated but omitting the stabiliser from the final rinse bath. In this case, once the grain-refining cleaner rinse had been contaminated as above, there was a rapid decay (in less than 15 minutes) of the quality of the phosphate coating formed on the issuing panels. The coating became coarse and uneven.

We claim:

1. In an aqueous grain-refining pretreatment liquid for ferrous and zinc-containing metal surfaces which said liquid comprises a grain refining concentration of titanium grain-refining compound, the improvement wherein the liquid has a pH of at least 4.5 and comprises a grain-refiner stabilizer for the titanium grain-refining compound in an amount which is effective to reduce the time dependent loss of grain-refining capacity of said liquid, said grain-refiner stabilizer consisting of an addition copolymer of monomer (a) and monomer (b) in essentially equi-

molar ratios wherein monomer (a) is at least one unsaturated polycarboxylic acid or acid anhydride selected from maleic acid, maleic anhydride, fumaric acid and citraconic acid and monomer (b) is at least one unsaturated monomer selected from ethylene, methyl vinyl ether, ethyl vinyl ether and cyclohexyl vinyl ether, and further characterized in that the copolymer shall have a viscosity of at least 3.5 centipoise at 25° C. when tested as a 4% by weight solution in an aqueous sodium hydroxide solution at a pH of 9.

2. An aqueous grain-refining pretreatment liquid according to claim 1 in which the liquid is an alkaline cleaning liquid with a pH of at least 9.

3. An aqueous grain-refining pretreatment liquid according to claim 1 in which the liquid is a water rinse consisting essentially of water together with grain-refiner stabiliser and titanium grain-refining compound.

4. An aqueous grain-refining pretreatment liquid according to claim 1 in which the concentration of titanium grain-refining compound in the liquid is of the order of 0.005% to 0.05% by weight expressed as titanium ions.

5. An aqueous grain-refining pretreatment liquid according to claim 1 in which the concentration of grain-refiner stabiliser is at least equal to the total weight of titanium in the grain-refining compound present therein.

6. An aqueous grain-refining pretreatment liquid according to claim 1 in which the concentration of grain-refiner stabiliser is at least 0.005% by weight of the liquid.

7. An aqueous grain-refining pretreatment liquid according to claim 6 in which the concentration of grain-refiner stabiliser is at least 0.01% to 0.02% by weight of the liquid.

8. A process of zinc phosphating steel or zinc-based metal surfaces wherein the metal is sequentially subjected to an aqueous cleaning liquid, at least two water rinses and a zinc phosphating liquid and characterised in that the water rinse immediately preceding the zinc phosphating liquid comprises a titanium grain-refining compound and a grain-refiner stabiliser as defined in claim 1 and has a pH of at least 4.5.

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