

PATENT SPECIFICATION

(11) 1 258 066

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NO DRAWINGS

- (21) Application No. 55492/68 (22) Filed 22 Nov. 1968
 (31) Convention Application No. 75454 (32) Filed 24 Nov. 1967
 (31) Convention Application No. 31410 (32) Filed 10 May 1968
 (31) Convention Application No. 47708 (32) Filed 8 July 1968
 (31) Convention Application Nos. 50309 and 50310
 (32) Filed 17 July 1968 in
 (33) Japan (JA)
 (45) Complete Specification published 22 Dec. 1971
 (51) International Classification C 23 f 11/08
 (52) Index at acceptance C7E 12B



(54) CORROSION INHIBITION

(71) We, KURITA WATER INDUSTRIES LIMITED, formerly Kurita Industrial Company Limited, a Japanese body Corporate of 1, 3-chome, Koraihashi, Higashi-ku, Osaka-shi, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to corrosion inhibition and inhibitors and provides a method for inhibiting the corrosion by water of steel, which is the major material from which equipment such as open type cooling water circulation systems are made.

Known corrosion inhibitors intended for use in systems such as the one described above comprised a mixture of chromates and/or bichromates and zinc salts, e.g. zinc sulphate. However such a corrosion inhibitor had the drawback that its corrosion inhibiting ability was mitigated by ineffective components contained therein. Thus, water treated with a corrosion inhibitor of the prior art which is a mixture of sodium bichromate and zinc sulfate contains SO_4^{2-} ions which serve to mitigate the corrosion preventing ability of the corrosion inhibitor. Therefore, in order to obtain the desired effect, in practice, from such a corrosion inhibitor, it was necessary to use it in a large quantity. However, the introduction of a large quantity of corrosion inhibitor was not desirable because in such an instance the treated water, e.g., cooling water, would come to contain, in solution, a large quantity of corrosion inhibiting components. These components would be eventually concentrated to a high degree as the treated water was circulated through the system, to form scale therein, and because the corrosion inhibitor-containing water would produce an environment suitable for bacteria to proliferate it would cause troubles attributable to slime. Also because the water containing a large amount of corrosion inhibitor components would lead to an increase

in the quantity of chromic acid ions dissolved in the cooling water, this would cause the discharged cooling water to become highly poisonous.

Moreover, zinc sulfate has a molecular formula of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, and therefore the weight of ineffective components of zinc sulfate becomes larger than that of zinc ions. Accordingly, it was inconvenient to handle since the total weight of a corrosion inhibitor necessary for use would be increased.

It is, therefore, an object of the present invention to provide, in water in contact with steel, a corrosion inhibitor which will produce an enhanced steel corrosion inhibiting effect by the use of a small amount of a corrosion inhibitor.

Another object of the present invention is to provide in the water a corrosion inhibitor which, owing to the employment of an additive or additives, permits a substantial reduction in the amount of highly poisonous chromate ions which are contained in the solution, and which also enhances the steel corrosion inhibiting effect.

The present invention provides a method of inhibiting the corrosion of steel objects by water, which comprises adding zinc chromate in solid form, or in the form of a concentrated aqueous solution made from solid zinc chromate, to the water to which the steel is exposed. The invention also provides certain novel corrosion inhibitors containing zinc chromate for use in the said process including inhibitors which contain both zinc chromate and an effective additive or additives.

Preferably the zinc chromate is added to the water in a concentration of at least 20 ppm.

Zinc chromate is a yellow pigment powder which is available in the market for use in industrial purposes.

Zinc chromate is expressed by the molecular formula ZnCrO_4 , and when added to water produces no ions that will promote the

[Price 25p]

corrosion of steel or reduce the corrosion inhibiting effect. This zinc chromate, when placed in water, will become dissociated into chromate ions and zinc ions, of which the former will serve as an anode type corrosion inhibitor, whereas the latter will function as a cathode type corrosion inhibitor.

5 Zinc chromate may be introduced into the water to which the steel is exposed, e.g. cooling water, as a powder so that a required amount of zinc chromate is dissolved. Effecting a homogeneous dissolution of zinc chromate in the water will be simplified if there is prepared in advance a highly concentrated solution of zinc chromate by dissolving zinc chromate in a small amount of water so that this solution may serve as a stock solution which is used in such a way that a required amount of this solution is introduced in the make-up water of the cooling system. It is to be noted, however, that zinc chromate is a compound which has only a small solubility in water and that, accordingly, it is impossible to prepare a highly concentrated stock solution of zinc chromate if the latter is used alone. A highly concentrated stock solution of zinc chromate may, however, be conveniently prepared by the addition thereto of a small amount of inorganic acid, such as hydrochloric acid, to promote the dissolution of the zinc chromate. The pH at which the most satisfactory corrosion inhibiting effect is obtained from the zinc chromate is in the range of from 5 to 7, and therefore, the amount of the inorganic acid which is added for the purpose of promoting the dissolution of zinc chromate in water is desirably such that is sufficient for maintaining the pH of the make-up water in the aforesaid range when the stock solution is introduced into the make-up water. The minimum concentration, in water, of zinc chromate at which this compound exhibits an appreciable corrosion inhibiting effect is 20 ppm. However, a better effect will be obtained from a higher concentration. As has been stated above, the corrosion inhibitors of the present invention do not introduce into the water unnecessary and harmful ions such as were obtained from the corrosion inhibitors of the prior art, and therefore, a satisfactory corrosion inhibiting effect is obtained from the use of the corrosion inhibitors of the present invention in a small amount. When comparison is made between the method of the present invention and a method of the prior art using in each case the same zinc chromate contents, the method of the present invention provides much the greater corrosion inhibiting effect of the two.

60 Additives which are effective when employed jointly with zinc chromate include: hydroxycarboxylic acids, hydroxycarboxylates, chromates other than zinc chromate, bichromates and sulfamic acid. These additives are themselves corrosion inhibitors. However, in the method

of the invention, corrosion inhibitors which contain one or two kinds of these compounds as the additives provides a greater corrosion inhibiting effect than any of them used alone, so that not only is there obtained a considerable corrosion inhibiting effect from their use in a small amount, but also the amount of the poisonous chromate ions produced can be restricted.

Hydroxycarboxylic acids which serve as effective additives include, for example, tartaric acid, gluconic acid and citric acid. As for the hydroxycarboxylates, the employment of water-soluble salts such as the sodium salts of the acids enumerated above are suitable. The blending weight ratio of zinc chromate to the hydroxycarboxylic acids or their salts is preferably substantially 1:1. The amount of the corrosion inhibitors which may be introduced into the liquid to be treated and which are provided in the form of zinc chromate and the aforesaid additive or additives is preferably in the range of 10—30 ppm in terms of concentration in water. Although the hydroxycarboxylic acid is a weak acid, when used in conjunction with zinc chromate in the aforesaid blending ratio and introduced in the water to be treated so as to produce a concentration therein which is within the aforesaid range, no substantial change in the pH of the water which is being treated should result. Also, whether the hydroxycarboxylic acids are used as such, or in the form of acid or salts, should cause no substantial difference in their function as corrosion inhibitors.

When it is intended to use as corrosion inhibitor zinc chromate and a hydroxycarboxylic acid or its salts, these two components in admixture may be dissolved in the water to be treated, or alternatively, these two components may be introduced into the water separately. The aforesaid range of concentration of the corrosion inhibitor in the water may be produced by adding the corrosion inhibitor mixture directly to the water to be treated. Or, alternatively, a highly concentrated stock solution of corrosion inhibitor is prepared in advance by placing the corrosion inhibitor mixture and an inorganic acid such as hydrochloric acid in a small amount of water, and adding the stock solution so produced to the water to be treated so that this solution will be diluted therein down to the required concentration in the water. It is considered that the hydroxycarboxylic acid which is added to the water serves to assist the passivation of the surface of steel and also that the substances which are absorbed therefrom onto the surface of steel form a corrosion-protective film. However, the exact mechanism of the function of hydroxycarboxylic acids in water has not yet been elucidated.

Next, chromates other than zinc chromate which are also one of the group of effective additives in the present invention include, for

example, sodium chromate and potassium chromate. Bichromates which are also effective additives include sodium bichromate and potassium bichromate. Although zinc chromate is a compound which is hardly soluble in water, those corrosion inhibitors which are prepared in the form of zinc chromate together with this additive or additives will exhibit sufficient corrosion inhibiting effects owing to the action of the zinc chromate which is dissolved in a small amount in water. The amount of the aforesaid corrosion inhibitor which is sufficient for the attainment of the object of inhibiting the corrosion of steel is in the range of 10—30 ppm in terms of concentration in water. Also, an intensive corrosion inhibiting effect is obtained from a corrosion inhibitor having a zinc chromate to other chromate or bichromate blending weight ratio in the range 3:2 to 1:4. When these two compounds, namely, zinc chromate and other chromates or bichromates, are blended together in the aforesaid blending ratio, the corrosion inhibiting effect which is exhibited is enhanced markedly as compared with the effect which is obtained from the use of these two types of compounds independently, as will be understood from the Example which will be given later in this specification. Therefore, it is considered that this markedly enhanced steel corrosion inhibiting effect is attributed to a synergistic effect of zinc chromate together with other chromates or bichromates. The manner in which these corrosion inhibitors are used is the same as that described in connection with corrosion inhibitors where the additives consist of hydroxycarboxylic acids.

Description will next be directed to the corrosion inhibitors which contain sulfamic acid as an additive which is effective with zinc chromate. Sulfamic acid assists in the complete dissolution of zinc chromate in water, and besides, it enhances the corrosion inhibiting effect by virtue of a synergistic action with zinc chromate. The amount of these corrosion inhibitors which is sufficient in use is 10—30 ppm in terms of concentration in water. The desirable zinc chromate to sulfamic acid blending weight ratio is about 4:1. The following table shows the amounts of sulfamic acid which were required for the complete dissolution of a certain amount of zinc chromate in 100 ml of tap water, the zinc chromate being added to 100 ml of tap water and sulfamic acid being added little by little thereto while stirring.

Zinc chromate (gr/100 ml)	Sulfamic acid (gr/100 ml)
5	1.2
10	2.3
15	3.4

As will be understood from this table, in the preparation of a highly concentrated stock

solution of zinc chromate, this latter compound will completely dissolve when the zinc chromate to sulfamic acid blending weight ratio is about 4:1. Accordingly, this corrosion inhibitor which is a combination of zinc chromate and sulfamic acid will exhibit an effective steel corrosion inhibiting effect by the use of only a small amount of zinc chromate. Also, because this corrosion inhibitor is such that both of its two components are available in the form of powder, the corrosion inhibitor, which is a mixture of these two kinds of powder is easy to handle and has very little danger. Especially, highly concentrated aqueous solutions of this corrosion inhibitor may be prepared easily without the employment of hydrochloric acid which is used as the acid for promoting the dissolution of zinc chromate in the corrosion inhibitors of the type described earlier in this specification, and therefore, the corrosion inhibitors which are a combination of zinc chromate and sulfamic acid are very useful for industrial purposes.

Furthermore, a further mixture of this corrosion inhibitor and the aforesaid chromate other than chromate or bichromate is also effective as a corrosion inhibitor. In this instance, a sufficient amount of this corrosion inhibitor to use is in the range of 10—30 ppm in terms of concentration in water. An intensive steel corrosion inhibiting effect will be obtained from a zinc chromate to other chromate or bichromate blending weight ratio in the range of 3:2 to 1:4 and also from a zinc chromate to sulfamic acid blending weight ratio of about 4:1. While the amount of sulfamic acid employed need not be limited to 1 part against 4 parts of zinc chromate, it will be understood from the foregoing table that a highly concentrated aqueous solution of zinc chromate is obtained from this blending ratio.

The corrosion inhibitor of this last mentioned kind is highly effective in that sulfamic acid serves to improve the dissolution of zinc chromate and thereby to improve the effective concentration of zinc chromate and, accordingly, to enhance the steel corrosion inhibiting effect. At the same time, the synergistic effect exhibited by the chromates other than zinc chromate or bichromates with zinc chromate contributes to enhancement of the steel corrosion inhibiting effect. As with the corrosion inhibitors which are composed of zinc chromate and sulfamic acid, the corrosion inhibitors consisting of three types of components, namely, zinc chromate, other chromates or bichromates and sulfamic acid, are such that each of these components is provided in the form of powder, and accordingly, they are easy to handle and also permit the preparation of highly concentrated aqueous solutions without the use of hydrochloric acid.

Examples of corrosion inhibitors and

methods of corrosion inhibition will now be given:

EXAMPLE 1

5 A test piece (38 cm² in surface area and weighing about 14 g) of a mild steel (SS—41) immersed in tap water containing zinc chromate and held at 50°C, was rotated at 180

rpm for 24 hours to determine the amount of attrition due to corrosion. The result of this experiment is as shown in table 1. For comparison, the results of tests conducted under the same conditions but using conventional corrosion inhibitors and of a test wherein no corrosion inhibitor was introduced, are also shown.

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TABLE 1

Corrosion inhibitors and the concentration employed (ppm)			Amount of attrition (mg)
Zinc chromate 30.0 (10.8 as Zn, 19.2 as CrO ₄)			7.2
„ 40.0 (14.4 as Zn, 25.6 as CrO ₄)			6.5
„ 50.0			
Sodium bichromate			
24.3 + zinc sulfate 47.0 (10.8 as Zn, 19.2 as CrO ₄)			13.1
„ 32.4 + „ 62.5 (14.4 as Zn, 25.6 as CrO ₄)			10.3
„ 11.0 + „ 19.0			104.7
„ 15.0 + „ 25.0			25.0
„ 19.0 + „ 31.0			18.7
Where no inhibitor was used:			130.0
SS—41 refers to the rolled steel for general structures as is prescribed by JIS, the composition of this steel comprises 0.06% or less of both phosphorus and sulfur, and 0.04% or less of carbon.			

EXAMPLE 2

20 A mild steel test piece (38 cm² in surface area and weighing about 14 g, SS—41) immersed in tap water containing zinc chromate and a hydroxycarboxylic acid or its salt and held at 50°C, was rotated at 180 rpm to determine the amount of attrition due to corrosion

at the end of 24 hours. The result is shown in Table 2. For comparison, the results of tests conducted under the same conditions but using conventional corrosion inhibitors and that of a test wherein no corrosion inhibitor was introduced, are also shown.

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TABLE 2

Corrosion inhibitors and the concentration employed (ppm)	Amount of attrition (mg)
Zinc chromate 15 + tartaric acid 15	2.5
„ 15 + sodium tartarate 15	2.5
„ 15 + sodium gluconate 15	3.9
„ 15 + sodium citrate 15	5.1
„ 30	7.2
Tartaric acid 30	8.8
Sodium tartarate 30	8.8
Sodium gluconate 30	14.0
Sodium citrate 30	19.3
Sodium bichromate 24.3 + zinc sulfate 47.0 (30 ppm in terms of zinc chromate)	13.1
Where no inhibitor was used:	130.0

EXAMPLE 3

5 A mild steel test piece (SS—41, 38 cm² in surface area weighing about 14 g) immersed in tap water containing zinc chromate and sodium bichromate in predetermined amounts and held at 50°C, was rotated at 180 rpm to determine the amount of attrition due to corrosion at

the end of 24 hours. The result is shown in Table 3. For comparison, the results of a 10 test conducted under the same conditions but using conventional corrosion inhibitors and one without the use of a corrosion inhibitor, are also shown.

TABLE 3

Corrosion inhibitors and the concentration employed (ppm)	Amount of attrition (mg)
Zinc chromate 30 + sodium bichromate 0	7.2
„ 18 + „ 12	4.3
„ 15 + „ 15	4.2
„ 12 + „ 18	3.5
„ 6 + „ 24	2.9
„ 0 + „ 30	12.0
Where no inhibitor was used:	130.0

EXAMPLE 4

In a manner similar to that described in Example 3, a corrosion test was conducted

using zinc chromate and other chromates, the results are as shown in Table 4.

TABLE 4

Corrosion inhibitors and the concentration employed (ppm)			Amount of attrition (mg)
Zinc chromate	15 + sodium bichromate	15	4.2
„	15 + potassium bichromate	15	3.5
„	15 + sodium chromate	15	3.9
„	15 + potassium chromate	15	3.7
„	30		7.2
Sodium bichromate	30		12.0
Potassium bichromate	30		11.5
Sodium chromate	30		11.0
Potassium chromate	30		12.4

EXAMPLE 5

A mild steel test piece (SS—41, 38 cm² in surface area and weighing about 14 g) immersed in tap water containing zinc chromate and sulfamic acid in predetermined amounts

and held at 50°C, was rotated at 180 rpm and the amount of attrition due to corrosion at the end of 24 hours was determined. The result is as shown in Table 5.

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TABLE 5

Corrosion inhibitors and the concentration employed (ppm)			Attrition (mg)
Zinc chromate	30 + sulfamic acid	0	7.2
„	30 + „	5	6.0
„	30 + „	10	3.7
„	25 + „	5	5.5
Where no inhibitor was used:			130.0

EXAMPLE 6

A mild steel test piece (SS—41, 38 cm² in surface area and weighing about 14 g) immersed in tap water containing zinc chromate, other chromates or bichromates and sulfamic

acid in predetermined amounts and held at 50°C, was rotated at 180 rpm and the amount of attrition due to corrosion at the end of 24 hours was determined. The result is shown in Table 6.

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TABLE 6

Corrosion inhibitors and the concentration employed (ppm)				Amount of attrition (mg)
Zinc chromate	15 + sodium bichromate	15 + sulfamic acid	5	3.2
—ditto—	15 + potassium bichromate	15 + —ditto—	5	2.9
—ditto—	15 + sodium chromate	15 + —ditto—	5	2.7
—ditto—	15 + potassium chromate	15 + —ditto—	5	2.5
Zinc chromate	15 + sodium bichromate	15		4.2
—ditto—	15 + potassium bichromate	15		3.5
—ditto—	15 + sodium chromate	15		3.9
—ditto—	15 + potassium chromate	15		3.7
Zinc chromate	30 + sulfamic acid	5		6.0
—ditto—	30			7.2
Sodium bichromate	30			12.0
Potassium bichromate	30			11.5
Sodium chromate	30			11.0
Potassium chromate	30			12.4

WHAT WE CLAIM IS:—

1. A method of inhibiting the corrosion of steel objects by water, which comprises adding zinc chromate in solid form or in the form of a concentrated aqueous solution made from solid zinc chromate, to the water to which the steel is exposed. 30
2. A method according to claim 1, wherein there is also added to the water to which the steel is exposed a hydroxycarboxylic acid and/or a salt of a hydroxycarboxylic acid.
3. A method according to claim 1, wherein there is also added to the water to which the steel is exposed a chromate other than zinc chromate and/or a bichromate. 35
4. A method according to claim 3, wherein there is also added to the water to which the steel is exposed sulphamic acid.
5. A method according to claim 1, wherein the corrosion inhibiting material added to the water consists of zinc chromate and sulphamic acid. 40
6. A method according to claim 1, in which the zinc chromate is present in the treated water in a concentration of at least 20 ppm.
7. A method according to claim 2, in which the hydroxy carboxylic acid is tartaric acid, gluconic acid or citric acid, employed as such or in the form of a sodium salt. 45
8. A method according to claim 7 in which the weight ratio of zinc chromate to the hydroxycarboxylic acid or salt thereof is substantially 1:1.
9. A method according to claim 7 or 8 in which the zinc chromate and hydroxycarboxylic acid or salt thereof are together present in a concentration of 10 to 30 ppm. 50
10. A method according to claim 3 in which the corrosion inhibiting material added to the water consists of zinc chromate and sodium chromate, potassium chromate, sodium bichromate or potassium bichromate.
11. A method according to claim 10 in which the ratio of zinc chromate to other chromate or bichromate is in the range from 3:2 to 1:4 by weight.
12. A method according to claim 10 or 11, in which the zinc chromate and other chromate or bichromate are together present in a concentration from 10 to 30 ppm.
13. A modification of the method of any of claims 10, 11 or 12 wherein the corrosion inhibiting material added to the water includes sulphamic acid. 55

TABLE 6

Corrosion inhibitors and the concentration employed (ppm)				Amount of attrition (mg)
Zinc chromate	15 + sodium bichromate	15 + sulfamic acid	5	3.2
—ditto—	15 + potassium bichromate	15 + —ditto—	5	2.9
—ditto—	15 + sodium chromate	15 + —ditto—	5	2.7
—ditto—	15 + potassium chromate	15 + —ditto—	5	2.5
Zinc chromate	15 + sodium bichromate	15		4.2
—ditto—	15 + potassium bichromate	15		3.5
—ditto—	15 + sodium chromate	15		3.9
—ditto—	15 + potassium chromate	15		3.7
Zinc chromate	30 + sulfamic acid	5		6.0
—ditto—	30			7.2
Sodium bichromate	30			12.0
Potassium bichromate	30			11.5
Sodium chromate	30			11.0
Potassium chromate	30			12.4

WHAT WE CLAIM IS:—

1. A method of inhibiting the corrosion of steel objects by water, which comprises adding zinc chromate in solid form or in the form of a concentrated aqueous solution made from solid zinc chromate, to the water to which the steel is exposed.

2. A method according to claim 1, wherein there is also added to the water to which the steel is exposed a hydroxycarboxylic acid and/or a salt of a hydroxycarboxylic acid.

3. A method according to claim 1, wherein there is also added to the water to which the steel is exposed a chromate other than zinc chromate and/or a bichromate.

4. A method according to claim 3, wherein there is also added to the water to which the steel is exposed sulphamic acid.

5. A method according to claim 1, wherein the corrosion inhibiting material added to the water consists of zinc chromate and sulphamic acid.

6. A method according to claim 1, in which the zinc chromate is present in the treated water in a concentration of at least 20 ppm.

7. A method according to claim 2, in which the hydroxy carboxylic acid is tartaric acid,

gluconic acid or citric acid, employed as such or in the form of a sodium salt.

8. A method according to claim 7 in which the weight ratio of zinc chromate to the hydroxycarboxylic acid or salt thereof is substantially 1:1.

9. A method according to claim 7 or 8 in which the zinc chromate and hydroxycarboxylic acid or salt thereof are together present in a concentration of 10 to 30 ppm.

10. A method according to claim 3 in which the corrosion inhibiting material added to the water consists of zinc chromate and sodium chromate, potassium chromate, sodium bichromate or potassium bichromate.

11. A method according to claim 10 in which the ratio of zinc chromate to other chromate or bichromate is in the range from 3:2 to 1:4 by weight.

12. A method according to claim 10 or 11, in which the zinc chromate and other chromate or bichromate are together present in a concentration from 10 to 30 ppm.

13. A modification of the method of any of claims 10, 11 or 12 wherein the corrosion inhibiting material added to the water includes sulphamic acid.

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14. A method according to claim 4 or 13 in which the weight ratio of zinc chromate to sulphamic acid is substantially 4:1.
- 5 15. A method according to claim 13 or 14 in which the zinc chromate other chromate or bichromate and sulphamic acid are together present in a concentration from 10 to 30 ppm.
- 10 16. A method according to claim 5, in which the weight ratio of zinc chromate to sulphamic acid is substantially 4:1.
17. A method according to claim 5 or 16 in which the zinc chromate and sulphamic acid are together present in a concentration of from 10 to 30 ppm.
- 15 18. A method according to claim 1, substantially as herein described.
19. A method of inhibiting the corrosion of steel objects by water according to claim 1, substantially as described in any of Examples 1 to 6.
- 20 20. A method according to any of claims 1 to 17, in which the pH of the water is maintained within the range 5 to 7.
21. A method according to claim 20 in which the pH of the water is raised to within the said range by the addition of hydrochloric acid.
22. A corrosion inhibitor for use in the method of claim 1 said inhibitor comprising zinc chromate and sulphamic acid.
- 30 23. A corrosion inhibitor for use in the method of claim 1 said inhibitor comprising zinc chromate and hydroxy carboxylic acid and/or a salt thereof.
24. A corrosion inhibitor according to claim 22 and 23 which contains also a chromate or bichromate other than zinc chromate.
- 35 26. Corrosion inhibiting agents according to any of claims 22 to 24, substantially as described in any of the foregoing Examples 1 to 6.
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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1971.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

