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**(54) Title:** METHOD FOR INHIBITING OXIDATION OR ACID ATTACK OF FERROUS METALS UTILIZING GLYCOSIDES AND CLEANING COMPOSITIONS FOR FERROUS METALS

**(57) Abstract**

Glycosides and polyglycosides having the formula: $R(OG)_x$, wherein R is an aliphatic hydrocarbon radical having from 1 to 25 carbon atoms or is a radical with the formula $R_1(OR_2)_n$ which does not have more than 25 carbon atoms and wherein n = 0 to 24 and $R_1$ and $R_2$ are aliphatic hydrocarbon radicals, G is the residue of a saccharide moiety selected from the group consisting of fructose, glucose, mannose, galactose, talose, gulose, allose, altrose, idose, arabinose, xylose, lyxose, ribose or alkoxylated derivatives thereof and x is 1 to 30, which glycosides and polyglycosides inhibit oxidation and acid attack of ferrous metals.

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# METHOD FOR INHIBITING OXIDATION OR ACID ATTACK OF FERROUS METALS UTILIZING GLYCOSIDES AND CLEANING COMPOSITIONS FOR FERROUS METALS

This application relates to the inhibition of oxidation of ferrous metals. More particularly, this invention relates to the use of alkyl glycosides, alkyl polyglycosides (APGs) or mixtures thereof to inhibit the oxidation of ferrous metals and acid attack of ferrous metals.

Ferrous metals when soiled frequently are the subject of cleaning with cleaning compositions. Acid cleaning compositions often are used for the removal of soil such as iron oxides in a process known as pickling. More broadly, however, acid is used for the removal of mill scale (hot-rolled scale) developed during hot forming of metal; scale developed during welding; scale developed during heat treating; superficial oxide which interferes with painting, porcelain enameling, tinning, galvanizing, or electroplating; rust and corrosion products; proteinous deposits; hard water scale; and products of reaction of hard water with soil, especially protein. Acids commonly used for cleaning ferrous metals include, but are not limited to, sulfuric acid, hydrochloric acid, phosphoric acid, nitric acid, hydrofluoric acid and organic acids such as oxalic acid, trichloracetic acid, citric acid, formic acid and acetic acid.

Acid cleaning action is enhanced by the use of surfactants especially when a soil such as an oxide is combined with another soil such as oil. Hence, surfactants form an important part of cleaning compositions for the removal of soil from ferrous metals by acid cleaners. Surfactants have the property of concentrating at the surface to be cleaned to facilitate cleaning. Further, surfactants facilitate cleaning in

various other ways which include, but are not limited to, the neutralization of forces which attract soil to the surface to be cleaned and the retention of soil in suspension after its removal to prevent its redeposition on the cleaned surface.

Moreover, with acid cleaning it is often desirable to have minimal acid attack on the base metal. Excessive reaction with the metal consumes acid, creates fumes, enhances hydrogen embrittlement, produces smut, and may remove enough metal to affect tolerances.

After cleaning a moist clean ferrous metal surface, such as steel, with a mildly acidic residue rerusts very rapidly. Rerusting can be minimized by rapid dry-off and by maintaining the part submerged in cool water prior to a rapid dry-off. If the water is alkaline, oxidation may be inhibited; soda ash or lime is often used in the final rinse to prevent rusting during handling. Sodium nitrite solutions of from 0.1 to 10% concentration, depending on the time of storage, are often used as a final rinse (and can be quite effective) for those cases where the parts should not be covered with an oily rust preventive. Sodium nitrite, however, leaves a surface deposit which sometimes is considered undesirable in metal working. Moreover, because the salt tends to break up emulsions it causes problems in the formulation of metal cleaners.

As used throughout this application, oxidation means the alteration of a ferrous metal by the formation of oxides which include but are not limited to rust and mill scale. As used throughout this application, acid attack means the reaction of an acid with a ferrous metal. Ferrous metal means iron or an alloy of iron

containing more iron than any other metal, the most common iron alloy being steel.

It is an object of this invention to provide a method for the inhibition of oxidation of ferrous metals.

It is another object of this invention to provide an oxidation inhibitor for ferrous metals which is stable in an acid medium.

It is still another object of this invention to provide a method for the moderation of acid attack on ferrous metals.

It is yet another object of this invention to provide a surfactant, oxidation inhibitor and additive for acid cleaning compositions for ferrous metals.

These and other objects of the invention will become more apparent with reference to the following detailed description.

According to the invention glycosides having the formula

$$R(OG)_x \qquad (I)$$

wherein

R is an aliphatic hydrocarbon radical having from 1 to 25 carbon atoms or is a radical having the formula $R_1(OR_2)_n$ which does not have more than 25 carbon atoms and wherein n = 0 to 24 and $R_1$ and $R_2$ are aliphatic hydrocarbon radicals,

G is the residue of a saccharide moiety selected from the group consisting of fructose, glucose, mannose, galactose, talose, gulose, allose, altrose, idose, arabinose, xylose, lyxose, ribose, alkoxylated derivatives of any of the

foregoing saccharide materials, or mixtures thereof, and x is 1 to 30

inhibit oxidation of ferrous metals, inhibit acid attack thereon and are stable in an acid medium. Preferably the glycosides used in the invention are alkyl glucosides (G is glucose). The degree of polymerization of the polyglycosides varies and is in the range of about 1 to 30 (x = 1 to 30). When the glycosides and polyglycosides are made or purchased they most often are mixtures comprising molecules of varying degrees of polymerization. Polyglycosides in these mixtures have a degree of polymerization as high as 30, most of the polyglycosides have a degree of polymerization of 10 or less and most of the latter group has a degree of polymerization of 1 to 4. Because the glycosides are often found as mixtures x may be expressed as an average degree of polymerization which includes fractional numbers. Recognizing that the glycosides used according to the invention are mixtures with varying degrees of polymerization, preferably the degree of polymerization of the polyglycosides is from about 1 to about 10 and most preferably is in the range of from about 1 to about 4. R is preferably at the $C_1$ position of the glycoside and is preferably an alkyl group which is straight chained or branched having 4 to 13 carbon atom and most preferably 9 to 13 carbon atoms.

The glycosides used in the invention inhibit oxidation within a pH range where oxidation occurs which includes a pH of 7 and below and up to a pH of about 9. They are stable in an acid medium and inhibit oxidation without leaving undesirable deposits which heretofore had been a problem. Moreover, the glycosides used in the invention inhibit acid attack of

metallic iron and alloys thereof. According to the method of the invention, solutions having less than two percent by weight on a dry basis of inorganic salts and comprising, on a total weight basis, from about 0.1 to about 50 percent by weight of the glycosides of the invention, preferably from about 1 to about 20 percent by weight and most preferably about 1 to about 10 percent by weight are applied to the ferrous metal to inhibit oxidation and acid attack thereof. The solutions may be made with any solvent which solvates the glycosides and which are compatible with ferrous metal such solvents including, but not limited to, water, glycol ether solvents including ethylene glycol monoethyl ether which is available as Cellosolve solvent, tetrahydrofurfuryl alcohol, butyl alcohol and mixtures thereof. Application of the solution may be any way of contacting the solution with the surface of the metal including, but not limited to, immersion, spraying or dipping. Thickeners, as are known, such as xanthan gum, polyacrylics or colloidal magnesium aluminum silicates which are available as Veegum may be included in the solutions of the glycosides as required. After application, the glycoside solution is permitted to evaporate or is dried from the surface of the metal.

The method of the invention is particularly pertinent to the acid cleaning of ferrous metals with acids such as sulfuric, hydrochloric, phosphoric, nitric, hydrofluoric and organic acids such as oxalic, trichloroacetic, formic, citric or acetic acid, when the latter acids are combined with aqueous solutions of the glycosides of the invention to provide ferrous metal cleaning compositions. The glycosides not only act as a surfactant to assist cleaning, but also inhibit oxidation

of the cleaned surface and acid attack on the base metal. Hence the cleaning compositions which include the glycosides not only clean the surface of the metal without undesirable acid attack of the base metal, but also have the unexpected property of inhibiting oxidation on cleaned surface of the metal. It has been found that glycosides of formula I have excellent stability under highly acid conditions. The glycosides which are excellent surfactant materials provide sufficient foaming in hard surface cleaners so that the acid component of the composition does not merely run off of the surface being cleaned. The aqueous acidic cleaning compositions, on a total weight basis, have from 0.1 to about 50 percent by weight of the glycosides described herein, preferably about 1 to about 20 percent by weight and most preferably about 1 to about 10 percent by volume. The aqueous cleaning compositions should preferably have a pH in the range of about 0.1 to about 4.0 and less than about two percent by weight, on a total weight basis, on a dry basis of inorganic salts for the cleaning composition to exhibit oxidation inhibition. Other ingredients such as thickeners and organic solvents as previously described may be optionally added to the cleaning composition. The acids suitable for use in the present invention include relatively strong acids such as sulfuric, hydrochloric, gluconic, nitric, sulfamic, oxalic, phosphoric, phosphorous or any other strong acid. Such acids may conveniently have a dissociation constant $K_1$ at 25°C of equal to or greater than $2.5 \times 10^{-4}$; preferably equal to or greater than $1 \times 10^{-4}$; more preferably equal to or greater than $5 \times 10^{-3}$; most preferably $1 \times 10^{-3}$ or greater. Such strong acids, when employed at 0.1N in distilled water at 25°C, will

typically give a pH of 1.8 or less; preferably 1.6 or less. The cleaning compositions of the invention may be applied to the metal surface to be cleaned by dipping, spraying or immersion with contact times being a function of the application method, temperature and pH of the composition.

The various glycoside and polyglycoside compounds and processes for making them are disclosed in U.S. Patent Nos. 2,974,134; 3,219,656; 3,598,865; 3,707,535; 3,772,269; 3,839,318; 3,974,138; and 4,223,129. Alkoxylated glycosides, such as those disclosed in U.S. Patent 3,640,998, are also useful herein. All of the indicated patents are incorporated by reference herein. Moreover, a mixture of alkyl glucosides and alkyl polyglycosides which may be used in the method of the invention are commercially available as Triton BG-10 from the Rohm and Haas Company.

Where an acid is present in the solution used in the method of the invention it is typically employed at from about 5% to about 70% by weight of the actual acid species, e.g. 37% hydrochloric acid is expressed as a 100% HCl basis. Thus the amount of acid utilized is conveniently from about 6% to about 50%; and most preferably from about 8% to about 45% by weight.

The acid and the glycoside may be mixed to the desired proportions in any convenient manner. It is desired however that when mixing the glycoside and the acid, a minimal amount of agitation be employed as this tends to cause the glycoside to foam which is not particularly desirable during preparation of the compositions of interest. As the glycoside and the acid are both compatible liquid materials, it is possible to

form a simple mixture or upon careful agitation to obtain a true solution of the glycoside and acid.

As most of the acids employed herein are obtained in their concentrated aqueous form. it is a further desirable variable herein that the solutions used in the method of the invention be aqueous with the amount of water employed typically being from about 10% to about 95%; and preferably from about 15% to about 75%.

Other materials which may be incorporated within the treatment solutions and/or acidic cleaning compositions hereof include an anionic surfactant such as an alkylsulfate, paraffin sulfate, paraffin sulfonate, olefin sulfonate, alkylether sulfate, or an alkylbenzene sulfonate. These anionic surfactants are typically found in the form of their sodium, potassium or ammonium salt, however, it is noted herein that due to the high degree of acidity in the present compositions the anionic surfactants will typically be in their acid form to a substantial degree notwithstanding the cationic salt species employed.

Amines may be included in the acidic cleaning compositions herein at from 0% to 50% by weight to further inhibit acid etching of the metal surface. Preferably, the amines will be nonaromatic materials. The amines should be used at less than a 10:1 ratio to the glycoside. Quaternary compounds may be included, if desired.

Additional ingredients which may be employed in the treatment solutions and acidic cleaning compositions hereof include materials such as detergent builders and abrasive materials. Certain abrasive materials, such as calcium carbonate, would tend to

decompose and liberate carbon dioxide. Thus it is more preferred that a material such as a silica be employed as the abrasive to avoid having the abrasive material decompose upon storage. The amount of detergent builder or abrasive which may be included in the acidic cleaning compositions is typically from about 2% to about 40%; preferably from about 3% to about 30% by weight. Suitable builders include the phosphates, nitrilotriacetic acid (NTA), aluminosilicates and the builders disclosed EP-A-150930.

EXAMPLE I

The oxidation inhibition capabilities of the glycosides of the invention were evaluated by the following test. Water with 100 ppm hardness is prepared. The material to be tested for its rust inhibition capabilities is added. Three grams of degreased cast iron chips of 15 to 40 mesh are placed on #1 filter paper having an area of one square inch and 3 ml of the test solution are added to the metal chips which then are dried for 16 hours. After drying chips and filter paper are evaluated for rust and are rated on a scale from 1 to 10 with 10 indicating no rust. In the test results shown in Table I, hard water with no additives and a solution of sodium nitrite were used as controls. Igepal CO630, Neodol 25-3S, Biosoft D-62 and Dowfax 2A1 are known surfactants. APG stands for glycoside compounds of the Formula I above.

TABLE I

RUST INHIBITION CAPABILITIES FOR FERROUS METALS OF AQUEOUS SOLUTIONS OF GLYCOSIDES, POLYGLYCOSIDES AND OTHER SURFACTANTS

| a) | % Salt on dry basis | SURFACTANT CONCENTRATION 0% | 1% | 5% | 20% |
|---|---|---|---|---|---|
| | | | weight % | | |
| Water (Control) | --- | 5.0 | | | |
| $NaNO_2$ (Control) | --- | | 5.0 | 9.0 | 10.0 |
| Methyl Glucoside | <1.0 | | 5.7 | 5.5 | 5.5 |
| Ethyl Glucoside | <1.0 | | 5.7 | 5.6 | 5.2 |
| Butyl Glucoside | <1.0 | | 5.0 | 5.7 | 7.3 |
| 2-Ethyl Hexyl Glucoside | <1.0 | | 4.0 | 8.0 | 8.0 |
| APG where x averages 1.5 and G is derived from glucose and R is derived from $C_9$ to $C_{11}$ alcohols sold by Shell Oil Company under the name Neodol 91. | <1.0 | | 6.3 | 8.0 | 8.5 |
| APG where x averages 1.5, G is glucose and R derived from Neodol 91. | 4.1 | | 4.8 | 4.8 | 4.8 |
| APG where G is glucose, x averages about 1.8 to 3 and R is derived from Neodol 91. | 11.9 | | 6.0 | 5.5 | 4.0 |
| APG where G is glucose, x averages about 3 and R is derived from $C_{12}$ to $C_{13}$ alcohols sold by Shell Oil Company under the name of Neodol 23. | <1.0 | | 5.6 | 5.7 | 5.7 |
| APG where G is glucose, | | | | | |

| | | | | |
|---|---|---|---|---|
| x averages about 3 and R is derived from Neodol 23. | 9.2 | 3.5 | 4.2 | 2.5 |
| APG where G is glucose, x averages 3 and R is derived from Neodol 23. | <1.0 | 6.5 | 7.2 | 7.2 |
| APG where G is Glucose, x averages 3 and R is derived from Neodol 23. | 12.7 | 3.5 | 3.5 | 3.5 |
| $C_{12}$ to $C_{15}$ ethoxylated alcohols sold by Shell Chemical Company under the name of Neodol 25 which is the reaction product of alcohol with seven moles of ethylene oxide. | | 4.2 | 3.5 | 1.0 |
| Nonylphenol ethoxylate sold by GAF under the name of Igepal which is the reaction product of 9-1/2 moles of ethylene oxide with phenol. | | 3.0 | 2.5 | 1.0 |
| Alkyl ether sulfate sold by Shell Chemical Company under the name of Neodol 25-3S. | | 2.0 | 2.0 | 1.5 |
| Sodium linear alkyl benzene sulfonate which is an anionic surfactant sold by Stephan Chemical Company under the name of Biosoft D-62. | | 2.0 | 1.5 | 1.0 |

| | | | | |
|---|---|---|---|---|
| A branched $C_{12}$ alkylated diphenyl oxide disulfonate some of which is a sodium salt and which is an anionic surfactant sold by The Dow Chemical Company under the trademark Dowfax 2A1. | 2.0 | 1.5 | 1.0 |

Higher Number represents better results.

10 = No Rust 1 = Very Heavy Rust

EXAMPLE II

The capabilities of solutions of the glycosides of the invention to inhibit the acid attack of a ferrous metal surface were tested in various acids as indicated below. In each case the glycoside was a glucoside. The test was conducted by first recording the weight of a piece of galvanized steel (3" x 1/2" x 1/8"), then heating the steel in the acid for six hours and then measuring and recording the weight loss of the steel. The experiment then was repeated using the acid and APG combination. The weight loss with the APG acid solution divided by the weight loss with the acid alone yields the percent corrosion inhibition data illustrated in Table II.

TABLE II

APG AS A CORROSION INHIBITOR

% CORROSION INHIBITION IN ACID

| SURFACTANT 0.1% | ALKYL GROUP | AVERAGE DP | 5% HCL | 10% SULFURIC | 10% SULFAMIC | 10% PHOSPHORIC | 10% CITRIC | 10% FORMIC |
|---|---|---|---|---|---|---|---|---|
| APG, R is derived from Neodol 91 | $C_{9, 10, \& 11}$ | 1 | 19.3 | 35.8 | 54.3 | 20.9 | 8.5 | 31.5 |
| APG, R is derived from Neodol 91 | " | 3.0 | 23.8 | 41.7 | 63.3 | 27.8 | 6.1 | 22.18 |
| APG, R is derived from Neodol 23 | $C_{12, \& 13}$ | 3.0 | 16.9 | 38.6 | 51.1 | 17.7 | 13.4 | 23.9 |
| APG, R is a straight chain | $C_8$ | 3.3 | 27.5 | 66.4 | 72.5 | 57.6 | 59.8 | 39.1 |
| APG, R is a straight chain | $C_{10}$ | 3.4 | 41.8 | 45.0 | 54.0 | 34.8 | 23.2 | 43.5 |
| APG, R is a straight chain | $C_{14}$ | 5.7 | 41.7 | 62.5 | 60.5 | 44.3 | 36.6 | 25.0 |
| APG, R is a straight chain | $C_{16}$ | 4.2 | 25.5 | 53.7 | 54.6 | 24.1 | 24.1 | 28.3 |
| *Dowfax 2A1 | | | 7.1 | 39.4 | 52.7 | 20.3 | 20.3 | 13.0 |

*Trademark of The Dow Chemical Company.

## EXAMPLE III

The following compositions useful in the method of the invention and listed in Table III below are prepared by obtaining a glycoside of the average degree of polymerization (DP) and having an alkyl chain length shown as carbon chain. The acids are presented on an active "solids" basis. The stability of the glycosides in the acidic medium of the composition is shown by the maintenance of the surface tension after 7 days storage at 49°C.

STABILITY OF GLUCOSIDE IN ACID MEDIUM

| | Carbon Chain | DP | % Glucoside | % Acid | Surface tension (25°C) Initial (Dynes/cm) | Surface tension (25°C) After 7 Days At 49°C (Dynes/cm) |
|---|---|---|---|---|---|---|
| 1. | *91 | 3.0 | 1.0 | 10% HCl | 27.5 | 23.7 |
| 2. | 91 | 3.0 | 1.0 | 5% HCl | 27.2 | 25.4 |
| 3. | **23 | 3.0 | 0.1 | 10% HCl | 27.3 | 23.5 |
| 4. | 23 | 3.0 | 1.0 | 20% HCl | 27.3 | 23.4 |
| 5. | 23 | 3.0 | 1.0 | 20% $H_2SO_4$ | 27.4 | 25.4 |
| 6. | 23 | 3.0 | 0.1 | 10% $H_2SO_4$ | 27.4 | 25.6 |
| 7. | 23 | 3.0 | 1.0 | 40% $H_3PO_4$ | 27.8 | 26.7 |
| 8. | 23 | 3.0 | 0.1 | 40% $H_3PO_4$ | 29.1 | 21.0 |

* 91 is a mixture of nonyl, decyl and undecyl, i.e. R derives from the alcohol mixture sold by Shell Oil Company under the name Neodol 91.

** 23 is a mixture of dodecyl and tridecyl, i.e. R derives from the alcohol mixture sold by Shell Oil Company under the name Neodol 23.

It should be understood that while certain preferred embodiments of the present invention have been illustrated and described, various modifications thereof will become apparent to those skilled in the art. Accordingly, the scope of the present invention should be defined by the appended claims and equivalents thereof.

Various features of the invention are set forth in the following claims.

WHAT IS CLAIMED IS:

1. A method for inhibiting oxidation or acid attack of a ferrous metal comprising:

contacting the surface of the ferrous metal with a solution which has less than about two percent by weight inorganic salts and which solution includes, on a total weight basis, from about 0.1 to about 50 percent by weight of a glycoside having the formula

$$R(OG)_x$$

wherein

R is an aliphatic hydrocarbon radical having from 1 to 25 carbon atoms or is a radical with the formula $R_1(OR_2)_n$ which does not have more than 25 carbon atoms and wherein n = 0 to 24 and $R_1$ and $R_2$ are aliphatic hydrocarbon radicals,

G is the residue of a saccharide moiety selected from the group consisting of fructose, glucose, mannose, galactose, talose, gulose, allose, altrose, idose, arabinose, xylose, lyxose, ribose, alkoxylated derivatives of any of the foregoing saccharides, or mixtures thereof, and x is 1 to 30.

2. A method as recited in Claim 1 wherein G is glucose, the solution is an aqueous solution and R is an aliphatic hydrocarbon radical.

3. A method as recited in Claim 2 wherein the glycoside comprises, on a total weight basis, from about 1 to about 20 percent by weight of the solution.

4. A method as recited in Claim 2 wherein the glycoside comprises from about 1 to about 10 percent by volume of the solution.

5. A method as recited in any of Claims 2, 3 or 4 wherein R is an alkyl group which is a straight chain or branched having 4 to 13 carbon atoms and x = 1 to 10.

6. A method as recited in any of Claims 2, 3 or 4 wherein R is an alkyl group which is a straight chain or branched having 9 to 13 carbon atoms and x = 1 to 4.

7. A method as recited in any of Claims 2, 3, 4, 5 or 6 wherein said method is for inhibiting oxidation.

8. A method as recited in any of Claims 1 - 7 wherein the solution has a pH of about 7 or below.

9. An aqueous acidic cleaning composition, which has less than about two percent by weight inorganic salts, for ferrous metals comprising;

an acid; and, on a total weight basis,

from about 0.1 to about 50 percent by volume of the composition of a glycoside having the formula

$$R(OG)x$$

wherein

R is an aliphatic hydrocarbon radical having from 1 to 25 carbon atoms or is a radical with the formula $R_1(OR_2)_n$ which does not have more than 25 carbon atoms

and wherein n = 0 to 24 and $R_1$ and $R_2$ are aliphatic hydrocarbon radicals,

G is the residue of a saccharide moiety selected from the group consisting of fructose, glucose, mannose, galactose, talose, gulose, allose, altrose, idose, arabinose, xylose, lyxose, ribose, alkoxylated derivatives of any of the foregoing saccharides, or mixtures thereof, and x is 1 to 30.

10. A composition as recited in Claim 9 wherein G is glucose, the composition has a pH in the range of about 0.1 to about 4, x = 1 to 10 and R is an alkyl group which is a straight chain or branched having 4 to 13 carbon atoms.

11. A composition as recited in Claim 10 wherein the glycoside comprises, on a total weight basis, from about 1 to about 20 percent by weight of the acidic aqueous composition.

12. A composition as recited in Claim 10 wherein the glycoside comprises, on a total weight basis, from about 1 to about 10 percent by weight of the acidic aqueous composition.

13. A composition as recited in Claim 12 wherein R is an alkyl group which is a straight chain or branched having 9 to 13 carbon atoms.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/US86/00864

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL.4 C23F 11/04, 11/12; C23G 1/06, 1/08
U.S. CL. 252/146, 174.17; 422/12, 14

## II. FIELDS SEARCHED

Minimum Documentation Searched [4]

| Classification System | Classification Symbols |
|---|---|
| U.S. | 252/146, 174.17, 396, 407<br>422/12, 14; 134/41 |

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

## III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

| Category * | Citation of Document, [16] with indication, where appropriate, of the relevant passages [17] | Relevant to Claim No. [18] |
|---|---|---|
| Y | US,A, 2,977,315, PUBLISHED 28 MARCH 1961, See column 1, lines 50-62, column 2, lines 43-55, SCHEIB ET AL. | 1-13 |
| Y | US,A, 3,793,221, PUBLISHED 19 FEBRUARY 1974 See column 1, lines 65 through column 2, line 4, OTRHALEK ET AL. | 1-13 |
| Y | US,A, 3,653,095, PUBLISHED 4 APRIL 1972, See column 2, lines 20-63, DUPRE ET AL. | 1-7 |
| Y | US,A, 4,154,706, PUBLISHED 15 MAY 1979, See column 2, lines 33-35 and column 4, lines 42-66, KENKARE ET AL | 1-13 |
| Y | US,A, 4,359,391, PUBLISHED 16 NOVEMBER 1982, See column 5, line 46 and column 12, lines 20-35, SALATHIEL ET AL. | 1-13 |
| Y | US,A, 4,404,040, PUBLISHED 13 SEPTEMBER 1983, See column 4, lines 16-25 and Table I, WANG | 1-13 |

* Special categories of cited documents: [15]

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## IV. CERTIFICATION

| Date of the Actual Completion of the International Search [2] | Date of Mailing of this International Search Report [2] |
|---|---|
| 30 MAY 1986 | 27 JUN 1986 |
| **International Searching Authority [1]** | **Signature of Authorized Officer [20]** |
| ISA/US | DENNIS L. ALBRECHT |

**FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET**

| | | |
|---|---|---|
| X | US,A, 4,230,592, PUBLISHED 28 OCTOBER 1980, see column 2, lines 27-38 and column 3, lines 3-7, MILLER ET AL. | 1-7 |
| Y | US,A, 4,483,780, PUBLISHED 20 NOVEMBER 1984, See column 2, lines 30-62 and column 10, lines 10-13, LLENADO | |
| Y,P | US,A, 4,528,106, PUBLISHED 09 JULY 1985, see the abstract, GROLITZER | |
| Y,P | US,A, 4,536,318, PUBLISHED 20 AUGUST 1985 see column 4,356,318 PUBLISHED 20 AUGUST 1985. See column 5, lines 29-36, COOK ET AL. | |

**V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [10]**

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers....., because they relate to subject matter [12] not required to be searched by this Authority, namely:

2. ☐ Claim numbers....., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [13], specifically:

**VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [11]**

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.