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2,850,453

CORROSION INHIBITED OIL COMPOSITIONS

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This invention relates to improved compositions which are effective corrosion inhibitors, particularly with respect to silver and/or copper and which are effective anti-oxidants, and more particularly the invention pertains to lubricating oil compositions, and non-viscous liquid hydrocarbon compositions such as motor fuels, fuel oils, naphthas, etc. containing such inhibitors.

To meet the increased demands upon engine lubricants, many types of lubricant additives have been developed to obtain certain desired characteristics thereof. Among the more effective addition agents which have been developed for compounding with lubricants are many sulfur-containing organic compounds, such as by way of example, sulfurized terpenes, sulfurized hydrocarbon oils, vegetable oils or animal oils, xanthate esters, organic polysulfides, particularly polyalkyl polysulfides, etc., which contain active-sulfur or sulfur compounds which are corrosive to silver, copper, etc.

Recent increased use of silver and similar metals in the construction of improved internal combustion engines has created new problems in the use of sulfur-containing additives in lubricants for such engines; the primary problem created being the corrosion of such silver parts of the engine by the sulfur-containing additives. While such corrosion can be eliminated by avoiding the use of sulfur-containing additives in lubricants for such engines, this solution of the problem is accompanied by the loss of the highly desired beneficial effects of the additives of this type.

It is an object of the present invention to provide a non-corrosive composition. Another object of the invention is to provide a composition non-corrosive to silver, copper and similar metals. A still further object of the invention is to provide a composition which will inhibit the corrosion of silver, copper and similar metals by sulfur and/or organo sulfur-containing compounds. A still further object of the invention is to provide a lubricant composition which is non-corrosive. Still another object of the invention is to provide a lubricant composition containing an addition agent which will inhibit the corrosion of silver, copper and similar metal by sulfur and/or organo sulfur-containing compounds. A further object of the invention is to provide a method of inhibiting the corrosion of silver, copper and similar metal. Another object of the invention is to provide a non-corrosive hydrocarbon motor fuel containing corrosive sulfur compounds. Still another object of the invention is to provide a method of lubricating internal combustion engines containing silver and similar metal parts and inhibiting the corrosion of such metals by lubricants which contain sulfur and/or organo sulfur-containing compounds.

In accordance with the present invention, the foregoing objects can be attained by employing in oleaginous materials of the type hereinafter mentioned small amounts, viz., from about 0.0001% to about 10%, and preferably from about 0.001% to about 5% by weight, of the oil-soluble reaction product obtained by reacting 2,5-di-

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mercapto-1,3,4-thiadiazole, an aldehyde and an alcohol or an aromatic hydroxy compound in the molar ratio of from 1:2:1 to 1:6:5 respectively, at a temperature within a range of from about 25° C. to about 15° C. Reaction times of from about 0.5 hour to about 48 hours can be employed. The reaction can be conducted in the presence or absence of a suitable solvent by (a) mixing all the reactants together and heating, (b) by first reacting the aldehyde with the alcohol or the aromatic hydroxy compound, and then reacting the resultant product with the thiadiazole, or (c) by reacting the aldehyde with the thiadiazole first and the resultant product with the hydroxy compound. Examples of suitable solvents are dioxane, ethylene glycol, di-methyl ether, di-ethyl ether, diethylene glycol, etc. At the completion of the reaction period the solvent and water produced in the reaction are removed from the reaction product by suitable well-known means, preferably by stripping in a vacuum, and the stripped product filtered, if necessary.

The aldehyde employed can be an aliphatic aldehyde containing 1 to about 20 carbon atoms or an aromatic or heterocyclic aldehyde containing from about 5 to 30 carbon atoms. The aldehydes may contain substituents such as alkoxy, hydroxy, mercapto, nitro or halogen groups. Examples of suitable aldehydes are: formaldehyde, acetaldehyde, benzaldehyde, 2-ethyl hexyl aldehyde, butyraldehyde, caprylic aldehyde, acrylaldehyde, crotonaldehyde, vinyl acetaldehyde, phenyl acetaldehyde, nitrobenzaldehyde, salicylaldehyde, furfural, chloral, etc.

The organic hydroxy compound employed in the reaction can be an aliphatic alcohol containing from about 4 to about 30 carbon atoms or an aromatic hydroxy compound containing 6 to about 40 carbon atoms such as phenols, naphthols, ar-hydroxy anthracenes, ar-hydroxy phenanthrenes, diphenols, etc.; the aromatic hydroxy compounds can have alkyl substituent groups. Examples of suitable aliphatic alcohols are butyl alcohol, amyl alcohol, octyl alcohol, nonyl alcohol, di-t-amyl cyclohexanol, 2-butyl actanol-1, etc. The alcohols may be mono- or polyhydroxy alcohols, and may contain aryl and heterocyclic groups as well as substituents such as alkoxy, nitro, cyano, and alkyl thio groups. Examples of suitable hydroxy aromatic compounds are nonyl phenol, 4-t-butyl-2-alpha-methyl benzyl phenol, and 3-pentadecyl phenol.

The preparation of the above described reaction products is illustrated by the following examples:

EXAMPLE I

To a solution of 16 cc. (0.2 mole) 37.5% aqueous formaldehyde in 100 cc. dioxane were added 15 grams (0.1 mole) 2,5-dimercapto-1,3,4-thiadiazole and the mixture stirred at room temperature (about 70° F.) for 15 minutes. To the mixture were added 50.8 grams (0.2 mole) of 4-t-butyl-2-alpha-methyl benzyl phenol, the mixture refluxed for 3 hours, then stripped in vacuo and filtered. The filtrate, amounting to 62 grams, was a viscous orange oil product containing 9.1% sulfur and 2.76% nitrogen.

EXAMPLE II

To a solution of 24 cc. (0.3 mole) 37.5% aqueous formaldehyde in 100 cc. dioxane were added 22.5 grams (0.15 mole) 2,5-dimercapto-1,3,4-thiadiazole and the mixture stirred at room temperature for 15 minutes. To the mixture were added 91.2 grams (0.3 mole) 3-pentadecyl phenol and the mixture refluxed for 4 hours, then stripped in vacuo and filtered. The filtrate, amounting to 108 grams, was a viscous red oil containing 11.7% sulfur and 3.45% nitrogen.

EXAMPLE III

A mixture of 220 grams (1 mole) nonyl phenol, 40

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grams (1 mole) sodium hydroxide in 250 cc. water, and 84.60 cc. (1 mole) 35.5% aqueous formaldehyde was allowed to stand at 25–27° C. for three days. The clear solution, substantially free of formaldehyde odor, was acidified with 60 cc. (1 mole) acetic acid and the organic layer taken up in ether. The ether layer was washed, dried over Drierite, filtered and the solvent evaporated off. The residue, nonyl hydroxy-methyl phenol was stirred at 110° C. for 2 hours with 75 grams (0.5 mole) 2,5-dimercapto-1,3,4-thiadiazole, while blowing a stream of nitrogen through the reaction mixture to remove the water formed. The recovered product (292 grams) was a viscous red oil containing 15.2% sulfur and 4.5% nitrogen.

EXAMPLE IV

To a mixture of 30 grams (0.2 mole) 2,5-di-mercapto-1,3,4-thiadiazole and 60 grams (0.4 mole) nonyl alcohol were added (at 60° C.) dropwise 32 cc. (0.4 mole) 37.5% aqueous formaldehyde. The mixture was stirred at 95° C. for 2 hours, the resultant organic layer taken up in benzene, and the benzene solution dried over Drierite, filtered and evaporated. The recovered product (64 grams) was a viscous yellow oil containing 21.6% sulfur and 6.39% nitrogen.

EXAMPLE V

Thirty-two cubic centimeters (0.4 mole) of 37.5% aqueous formaldehyde were added dropwise at 75° C. to a mixture of 30 grams (0.2 mole) 2,5-dimercapto-1,3,4-thiadiazole and 96 grams (0.4 mole) di-t-amyl cyclohexanol and the mixture stirred for one hour at 95° C. The reaction mass was then blown with nitrogen for 40 minutes at 120° C. and 119 grams of a bright yellow viscous product recovered by filtration. The reaction product analyzed 9.0% sulfur and 2.62% nitrogen.

EXAMPLE VI

To a mixture of 45 grams (0.3 mole) 2,5-dimercapto-1,3,4-thiadiazole and 111.6 grams (0.6 mole) 2-butyl octanol-1 were added dropwise at 75° C. 48 cc. (0.6 mole) 37.5% aqueous formaldehyde and the mixture stirred at 95° C. for 1.5 hours. The reaction mass was then blown with nitrogen at 120° C. for 1.5 hours to remove water, and the product filtered through Celite. The recovered product, 129 grams, was a viscous dark yellow liquid having 10.2% sulfur and 2.98% nitrogen.

The above-described reaction product can be used in amounts of from about 0.0001% to about 10%, and preferably from about 0.001% to about 5% in oil compositions containing elemental sulfur and/or organic sulfur-containing compounds normally corrosive to silver, copper and similar metals. Such oil compositions can be lubricant compositions, heater fuels, motor fuels, etc. The lubricant compositions can contain as base oils hydrocarbon oils, synthetic hydrocarbon oils, such as those obtained by the polymerization of hydrocarbons, such as olefin polymers, for example, polybutenes, polypropylene and mixtures thereof, etc.; synthetic lubricating oils of the alkylene-oxide type, for example, the "Ucon oils," marketed by Carbide and Carbon Corporation, as well as other synthetic oils, such as the polycarboxylic acid ester-type oils, such as the esters of adipic acid, sebacic acid, maleic acid, azelaic acid, etc. Concentrates of a suitable oil base containing more than 10%, for example, up to 50% or more, of the herein described reaction product, alone or in combination with other additives, can be used for blending with other oils in the proportions desired for the particular conditions of use to give a finished product containing from about 0.0001% to about 10% of said reaction product.

Under certain conditions, it is desirable to use in combination with the herein described reaction products oils containing from about 0.05% to about 10% elemental

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sulfur or an organic sulfur-containing compound, such as sulfurized terpenes, sulfurized hydrocarbon oils, sulfurized vegetable oils, sulfurized animal oils, sulfurized marine oils, xanthate esters, organic polysulfides, etc., which contain active sulfur. Effective sulfur-containing organic compounds are sulfurized terpenes, including monocyclic, bicyclic, acyclic terpenes, as well as polyterpenes. Examples of such terpenes are pine oil, turpentine, cymene, alphapinene, beta-pinene, allo-ocimene, fenchenes, bornylenes, menthadienes, limonene, dipentene, terpinene, di-terpene and polyterpenes; mixtures of such terpenes can also be sulfurized. Sulfurization of the terpenes can be accomplished by the usual manner of adding sulfur to the terpene and heating to the sulfurization temperature or they can be prepared by the methods of U. S. 2,445,983 issued to R. W. Watson July 27, 1948.

Frequently, such sulfur-containing organic compounds are used in lubricant compositions in conjunction with from about 0.05% to about 5%, other additives for example, neutralized sulfur- and phosphorus-containing reaction products of a phosphorus sulfide and a hydrocarbon, for example, polyolefins, such as polybutenes, polypropylene, etc. Suitable phosphorus sulfide-hydrocarbon reaction products are those described in U. S. 2,316,080 and U. S. 2,316,082 issued to C. M. Loane et al. April 6, 1943. The combination of such phosphorus and sulfide-hydrocarbon reaction products and sulfur-containing organic compounds of the type above described in lubricant compositions is described in U. S. Reissue 22,464 issued to Kelso et al. April 4, 1944, and U. S. 2,422,585 issued to Rogers et al. June 17, 1947.

While the sulfur-containing organic compounds impart highly desired properties to lubricant, they are corrosive to silver, copper and similar metals, particularly when they contain active sulfur, as evidenced by the darkening of the metal.

In accordance with the present invention, the incorporation in such lubricant compositions of from about 0.001% to about 5%, and preferably from about 0.01% to about 2.5% of the reaction product herein described effectively inhibits the corrosion of copper, silver and similar metals.

The silver corrosion-inhibiting properties of the above described reaction products is determined by the following test; this test is frequently referred to as a modified EMD test:

A silver strip 2 cm. x 5.5 cm. with a small hole at one end for suspension, is lightly abraded with No. 0 steel wool, wiped free of any adhering steel wool, washed with carbon tetrachloride, air-dried and then weighed to 0.1 milligram. 300 cc. of the oil to be tested is placed in a 500 cc. lipless glass beaker, the oil heated to a temperature of 300° F. (+2° F.), and the silver test strip suspended in the oil so that the strip is completely immersed therein. The oil in the beaker is stirred by means of a glass stirrer operating at 300 R. P. M. At the end of twenty-four hours, the silver strip is removed and while still hot, rinsed thoroughly with carbon tetrachloride and air-dried, then immersed in a 10% potassium cyanide solution at room temperature until the silver surface assumes its original bright or silver appearance. The silver strip is then washed successively with distilled water and acetone, air-dried and weighed.

The following compositions were subjected to the above test and the data obtained are tabulated in Table I:

Sample A.—Control (Solvent-extracted SAE 30 oil +3.3% barium-containing neutralized reaction product of P_2S_5 and a polybutene of about 1000 molecular weight +0.75% sulfurized dipentene).

Sample B.—A+0.15% product of Example I.

Sample C.—A+0.15% product of Example IV.

Sample D.—A+0.15% product of Example V.

Sample E.—A+0.15% product of Example VI.

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Table I

Sample:	Silver corrosion (wt. losses mg.)
A -----	110
B -----	7
C -----	4
D -----	7
E -----	8

For comparison purposes, lubricant compositions containing 3.3% neutralized reaction products of P_2S_5 and a polybutene but containing no sulfurized dipentene will give a weight loss of 20 milligrams in the silver corrosion test in the absence of the herein described reaction products and usually a weight loss of zero milligrams in the presence of such reaction products.

As indicated by the above data, the reaction products of this invention effectively inhibit the corrosion tendencies of active sulfur-containing organic compounds towards silver. Such reaction products are also effective in inhibiting the active corrosion of copper and/or lead. This is demonstrated by subjecting lubricant compositions containing such additives to the following test:

A copper-lead test specimen is lightly abraded with steel wool, washed with naphtha, dried and weighed to the nearest milligram. The cleaned copper-lead test specimen is suspended in a steel beaker, cleaned with a hot tri-sodium phosphate solution, rinsed with water, acetone, and dried, and 250 grams of the oil to be tested, together with 0.625 gram lead oxide and 50 grams of a 30-35 mesh sand, charged to the beaker. The beaker is then placed in a bath or heating block and heated to a temperature of 300° F. ($\pm 2^\circ$ F.) while the contents are stirred by means of a stirrer rotating at 750 R. P. M. The contents of the beaker are maintained at this temperature for twenty-four hours, after which the copper-lead test specimen is removed, rinsed with naphtha, dried and weighed. The test specimen is then replaced in the beaker and an additional 0.375 gram of lead oxide added to the test oil. At the end of the additional twenty-four hours of test operation, the test specimen is again removed, rinsed and dried as before, and weighed. The test specimen is again placed in the beaker together with an additional 0.250 gram of lead oxide and the test continued for another twenty-four hours (seventy-two hours total). At the conclusion of this time, the test specimen is removed from the beaker, rinsed in naphtha, dried and weighed.

The loss in weight of the test specimen is recorded after each weighing.

This test, known as the Sand Stirring Corrosion Test, is referred to hereinafter as "S. S. C. T."

The following compositions were subjected to the above test, and the data obtained are tabulated in Table II:

Sample A'.—Control (Solvent-extracted oil+3.3% barium-containing neutralized reaction product of P_2S_5 and a polybutene of about 1000 molecular weight).

Sample B'.—A'+0.75% product of Example I.

Sample C'.—A'+0.75% product of Example II.

Sample D'.—A'+0.75% product of Example IV.

Sample E'.—A'+0.75% product of Example V.

Sample F'.—A'+0.75 product of Example VI.

Table II

Sample	S. S. C. T. (mg. wt. loss)		
	24 hrs.	48 hrs.	72 hrs.
A'-----	305	580	850
B'-----	10	95	158
C'-----	4	69	129
D'-----	7	21	82
E'-----	13	155	293
F'-----	7	50	97

Since weight losses of 200 milligrams in 48 hours and 500 milligrams in 72 hours are passing, the copper-lead

corrosion inhibiting properties of the herein-described reaction products is clearly demonstrated by the above data.

The herein-described reaction products are effective corrosion inhibitors for hydrogen motor fuels which contain sulfur compounds corrosive to copper and silver. In certain equipment having copper and/or silver parts associated with fuel systems of engines it is essential that the fuel used be substantially free of compounds which are corrosive to such metals. For example, certain types of fuel pumps are submerged in the fuel tank to circumvent vapor lock difficulties. Such pumps are operated by electric motors provided with silver commutators and armatures. The presence of free sulfur and/or active sulfur compounds in motor fuels causes corrosion to such equipment. The addition of very small amounts, namely 0.0001% to 0.2% of the reaction products of this invention effectively inhibits such corrosion. This is demonstrated by the data in Table III which were obtained by immersing copper test strips in a hydrocarbon solvent and an aviation gasoline, each of which contained small amounts of the reaction product of Example III, maintaining the samples at 212° F. for three hours and noting the staining of the copper test strips; the lower the number rating of the copper strip, the less is the corrosion caused by sulfur.

Table III

Sample No.	Composition	Copper strip rating
A''-----	Hydrocarbon solvent ¹ -----	12
B''-----	A'' + .01% product of Example III-----	2
C''-----	Aviation gasoline-----	7
D''-----	C'' + 0.01% product of Example III-----	0
E''-----	C'' + 0.001% product of Example III-----	1

¹ The hydrocarbon solvent used above had a distillation range about 210° F. to about 240° F. and a kauri butanol value of about 90.

The herein-described reaction products of the present invention are also effective antioxidants as evidenced by the data in Table IV which were obtained by subjecting a turbine oil base with and without the additive to the following test:

A mixture of 300 cc. oil plus 60 cc. water is immersed in a bath at 95° C. The catalyst, which consists of a coil containing 3 meters 14 gauge copper wire and 3 meters 14 gauge iron wire, is added, and the mixture is blown with pure oxygen at the rate of 3 liters per hour. The oxidation life of the oil is the time in hours till it reaches a neutralization number of 2 (2 mg. KOH/g. oil).

Table IV

Sample:	Hours to acidity of 2 mg. KOH/g. sample
Control (no additive)-----	50-75
Control +0.1% product of Example III-----	600

These data demonstrate the effectiveness of the reaction products of this invention as anti-oxidants.

While this invention has been described in connection with the use of the herein-described polysulfides in lubricant compositions and motor fuels containing free sulfur and/or active sulfur-containing organic compounds, their use is not limited thereto, but the same can be used in other products, such as for example, fuel oils, insulating oils, greases, non-drying animal and vegetable oils, waxes, etc., which contain corrosive sulfur.

Percentages given herein and in the appended claims are weight percentages unless otherwise stated.

Although the present invention has been described with reference to specific preferred embodiments thereof, the invention is not to be considered as limited thereto, but includes within its scope such modifications and variations as come within the spirit of the appended claims.

I claim:

1. A composition having corrosion and oxidation in-

hibiting properties comprising a major proportion of an oil and from about 0.0001% to about 10% of an oil-soluble reaction product obtained by reacting at a temperature of from 25° C. to about 150° C. 2,5-dimercapto-1,3,4-thiadiazole, an aldehyde containing from 1 to 30 carbon atoms and an organic hydroxy compound having the general formula ROH in which R is a hydrocarbon radical selected from the group consisting of an aliphatic radical containing from about 4 to 30 carbon atoms and an aromatic radical containing from about 6 to 40 carbon atoms, said reactants being used in the molar ratio of from 1:2:1 to 1:6:5 respectively.

2. A composition having corrosion and oxidation inhibiting properties comprising a major proportion of an oil and from about 0.0001% to about 10% of the oil-soluble reaction product obtained by reacting at a temperature of from about 25° C. to about 150° C. 2,5-dimercapto-1,3,4-thiadiazole, formaldehyde and an aliphatic alcohol having from about 4 to about 30 carbon atoms, said reactants being used in the molar ratio of 1:2:2.

3. The composition as described in claim 2 in which the aliphatic alcohol is nonyl alcohol.

4. The composition as described in claim 2 in which the aliphatic alcohol is 2-butyloctanol-1.

5. The composition comprising a major proportion of an oil and from about 0.0001% to about 10% of the oil-soluble reaction product obtained by reacting at a temperature of from about 25° C. to about 150° C. 2,5-dimercapto-1,3,4-thiadiazole, formaldehyde and an organic hydroxy compound having the general formula ROH wherein R is an aromatic radical containing from about 6 to about 40 carbon atoms, said reactants being used in the molar ratio of from 1:2:1 to 1:6:5 respectively.

6. The composition as described in claim 5 in which the organic hydroxy compound is phenol.

7. The composition as described in claim 5 in which the organic hydroxy compound is nonyl phenol.

8. The composition as described in claim 5 in which the organic hydroxy compound is 4-t-butyl-2-alpha-methylbenzyl phenol.

9. The composition described in claim 5 in which the organic hydroxy compound is 3-pentadecyl phenol.

10. A lubricant composition comprising a major proportion of a lubricating oil, from 0.001% to about 10% of the oil-soluble reaction product obtained by reacting at a temperature of from 25° C. to about 150° C. 2,5-dimercapto-1,3,4-thiadiazole, an aldehyde containing from 1 to 30 carbon atoms, and an organic hydroxy compound having the general formula ROH wherein R is a hydrocarbon radical selected from the group consisting of an aliphatic radical containing from 4 to about 30 carbon atoms and an aromatic radical containing from about 6 to about 40 carbon atoms, said reactants being used in the molar ratio of from 1:2:1 to 1:6:5 respectively, and from about 0.001% to about 10% of a phosphorus- and sulfur-containing detergent-type lubricant additive.

11. The composition as described in claim 10 in which the aliphatic alcohol is nonyl alcohol.

12. The composition as described in claim 10 in which the aliphatic alcohol is 2-butyl octanol-1.

13. The composition as described in claim 10 wherein the organic hydroxy compound is a phenol.

14. The composition as described in claim 10 in which the organic hydroxy compound is nonyl phenol.

15. The composition as described in claim 10 in which the aromatic hydroxy compound is 4-t-butyl-alpha-methylbenzyl phenol.

16. The composition as described in claim 10 in which the phosphorus- and sulfur-containing detergent-type additive is a neutralized reaction product of a phosphorus sulfide and a hydrocarbon.

17. A lubricant composition as described in claim 10 which contains from about 0.05% to about 10% of a sulfurized terpene normally corrosive to silver.

18. The composition of claim 16 in which the hydrocarbon is an olefin polymer.

19. The composition of claim 18 in which the olefin polymer is a polybutene.

20. An addition agent for oils comprising a concentrated solution of an oil containing more than 10% of an oil-soluble reaction product obtained by reacting at a temperature of from 25° C. to about 150° C. 2,5-dimercapto-1,3,4-thiadiazole, an aldehyde containing from 1 to 30 carbon atoms and an organic hydroxy compound having the general formula ROH in which R is a hydrocarbon radical selected from the group consisting of an aliphatic radical containing from about 4 to 30 carbon atoms and an aromatic radical containing from about 6 to 40 carbon atoms, said reactants being used in the molar ratio of from 1:2:1 to 1:6:5 respectively, said solution being capable of dilution with an oil to form a homogeneous mixture containing from about 0.0001% to about 10% of said oil-soluble reaction product.

21. An internal combustion engine motor fuel comprising a major proportion of a sulfur-containing hydrocarbon distillate in the gasoline distillation range normally corrosive to silver and from about 0.0001% to about 0.2% of an oil-soluble reaction product obtained by reacting at a temperature of from 25° C. to about 150° C. 2,5-dimercapto-1,3,4-thiadiazole, an aldehyde containing from 1 to 30 carbon atoms and an organic hydroxy compound having the general formula ROH in which R is a hydrocarbon radical selected from the group consisting of an aliphatic radical containing from about 4 to 30 carbon atoms and an aromatic radical containing from about 6 to 40 carbon atoms, said reactants being used in the molar ratio of from 1:2:1 to 1:6:5 respectively.

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CERTIFICATE OF CORRECTION

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Ellis K. Fields

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 4, for "15° C." read -- 150° C. --.

Signed and sealed this 2nd day of December 1958.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents

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