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3,218,265

MONOVALENT BIS(AROMATIC HYDROCARBON)CHROMIUM CATIONS AS CORROSION INHIBITORS

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10 Claims. (Cl. 252—389)

This application is a continuation-in-part of copending application Serial No. 749,643, filed July 21, 1958, now abandoned.

This invention relates to new liquid compositions for use in fluid heat transfer, hydraulic and lubrication systems, and the like. It is particularly concerned with new and useful inhibitors for preventing corrosion of metals in contact with such systems.

Fluid heat transfer, hydraulic and lubrication systems often utilize liquids which are inherently corrosive, or liquids in which a corrosive action is induced, and the term "ordinarily corrosive liquid medium," as used herein, refers to either type of liquid. For example, either water or aqueous solutions are usually inherently corrosive because of the presence of the bicarbonates, sulfates or chlorides of calcium and magnesium. Pure alcohols or glycols are not considered to be inherently corrosive to metals, but under conditions of their use in the above-mentioned systems numerous factors are encountered through which a corrosive action may be induced. The fluid may be in circulation and diluted with water, and/or subjected to constant agitation in the presence of air. Such aeration, possible overheating, and leakage of foreign materials into the system all are conducive to reactions which may effect metal corrosion. It has therefore become customary to add inhibitors to both aqueous and non-aqueous systems for the purpose of preventing or counteracting inherent and/or induced corrosive conditions.

Numerous corrosion inhibitors have been proposed in the art, but many of them are only partially effective or subject of many other disadvantages in extensive use. For example, hexavalent chromium compounds have been used successfully to prevent corrosion in recirculated cooling water systems, but cause oxidation of glycols and thus are unsatisfactory for the most commonly used heat transfer media at the present time. Chromates have been shown to be particularly effective corrosion inhibitors in open systems because their effectiveness is not reduced by oxygenation. The most common method of using chromates for corrosion inhibition is to add a dichromate to water and subsequently treat the water-dichromate solution with NaOH to convert the dichromate to sodium chromate. This causes a change in pH from about 4.5 to that of a normal chromate solution, about 8.5, where it is most effective as a corrosion inhibitor. Unfortunately however, the chromates are readily reduced by organic compounds to the free chromic ion which has no inhibitor value. Consequently, dichromates cannot be used economically in the presence of more than a small amount of organic reducing matter. For example, it has not been possible to use chromates in glycol solutions containing greater concentrations than about 5% glycol since the latter causes reduction of the chromate which leaves a sludge in the system and impairs the corrosion protection by the chromate.

It is a primary object of this invention to provide an improved corrosion inhibitor composition for use in ordinarily corrosive liquid media, which will effectively protect all metals contacted by such media in fluid heat

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transfer, hydraulic, or lubrication systems. Another object of this invention is to provide a method for inhibiting atmospheric corrosion of metals. These and other objects and advantages of the invention will become apparent from the following description and appended claims.

It has been found that a soluble salt of monovalent bis (aromatic hydrocarbon)chromium cations will afford excellent protection for all solid metals and alloys in such systems when added in minor quantities to the ordinarily corrosive liquid medium. Such a resulting non-corrosive liquid medium will further provide resistance to corrosion over extended periods of use of the liquid and under all normal operating conditions. The medium to which these corrosion inhibitors are added can be either polar or non-polar.

The metals which can be protected from corrosion by the method of this invention includes magnesium and all solid metals below magnesium in the electromotive series of the chemical elements as well as alloys of two or more of such metals, for example iron, aluminum, brass, hard and soft solders, copper, and the like. The term "electromotive series of the chemical elements" as used herein refers to the table of oxidation potentials of elements set forth on page 1733 of the "Handbook of Chemistry and Physics," 40th Edition.

The salts of monovalent bis(aromatic hydrocarbon)chromium cations which are useful in the present invention can be represented by the formula



wherein each Ar represents an aromatic hydrocarbon compound having an unfused benzene ring and free of aliphatic unsaturation, X is an anion, and n is the ionic charge of the anion X and is an integer having a value from one to four, inclusive. Of course n also represents the number of monovalent Ar_2Cr^+ cations associated with each anion in order to provide a salt in which the cationic and anionic charges are equal.

The aromatic hydrocarbon compound Ar cannot be a fused ring compound such as naphthalene or anthracene or a compound containing aliphatic unsaturation such as phenyl acetylene or divinyl benzene.

The aromatic hydrocarbon compound Ar can be benzene, alkyl-substituted benzenes such as toluene, xylene, mesitylene, hexamethylbenzene, cumene, t-butylbenzene and n-hexylbenzene, alkylene-substituted benzenes such as tetrahydronaphthalene and octahydroanthracene, and aryl-substituted benzenes such as diphenyl and p,p'-dimethyldiphenyl. Preferably, each Ar moiety contains from 6 to about 14 carbon atoms.

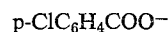
The Ar moiety in the cationic portion of the salts useful in this invention can be the same or different as, for example, in the salts bis(benzene)chromium hydroxide and (toluene) (tetrahydronaphthalene)chromium chloride.

The anions which X can represent are exemplified by the following:

(1) Inorganic anions such as AlY_4^- , wherein Y is halogen, F^- , Cl^- , Br^- , I^- , Br_3^- , I_3^- , ClO_3^- , ClO_4^- , NO_2^- , NO_3^- , BrO_3^- , IO_3^- , CN^- , SCN^- , OCN^- , SO_3^{--} , SO_4^{--} , $S_2O_3^{--}$, PO_4^{--} , $H_2PO_4^-$, HPO_4^{--} , CO_3^{--} , BO_3^{--} , HBO_3^- , $H_2BO_3^-$, $[Fe(CN)_6]^{--}$, $[Fe(CN)_6]^{--}$, MoO_4^{--} , WO_4^{--} , VO_4^{--} , MnO_4^- , S^{--} and OH^- .

(2) Organic anions:

(a) Aliphatic, aromatic, substituted aliphatic and substituted aromatic carboxylate anions such as CH_3COO^- , $C_6H_{17}COO^-$, $C_6H_5COO^-$, CF_3COO^- , and



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(b) Alkyl, aryl, substituted alkyl, and substituted aryl sulfonate anions such as CH_3SO_3^- , $\text{C}_6\text{H}_5\text{SO}_3^-$, CF_3SO_3^- and $\text{p-ClC}_6\text{H}_4\text{SO}_3^-$.

(c) Alkoxides, aryloxides, substituted alkoxides and substituted aryloxides such as $\text{C}_2\text{H}_5\text{O}^-$, $\text{C}_6\text{H}_5\text{O}^-$,



$\text{p-ClC}_6\text{H}_4\text{O}^-$, $\text{CH}_3\text{C}_6\text{H}_4\text{O}$ and $\text{C}_{10}\text{H}_7\text{O}^-$ (naphthoxide).

(d) Alkyl and aryl mercaptides such as $\text{C}_2\text{H}_5\text{S}^-$, $\text{C}_6\text{H}_5\text{S}^-$, $\text{CF}_3\text{CH}_2\text{S}^-$, and $\text{p-ClC}_6\text{H}_4\text{S}^-$.

(3) Organo-metallic anions:

(a) $\text{C}_5\text{H}_5\text{M}(\text{CO})_3^-$ where M is Cr, Mo and W.

(b) Metal carbonyls such as $\text{Fe}(\text{CO})_4^-$ and



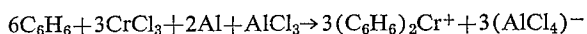
(c) Diarylborinate: $(\text{C}_6\text{H}_5)_2\text{BO}^-$.

(d) Aluminum tetraalkoxide and aluminum tetraaryloxide, e.g., $(\text{RO})_4\text{Al}^-$, wherein R represents alkyl and aryl hydrocarbon radicals.

A preferred class of inorganic anions are the hydroxide, dihydrogen borate, monohydrogen borate, borate, monohydrogen phosphate, dihydrogen phosphate and phosphate ions, and a preferred class of aryloxide anions are the phenoxide, cresoxide and naphthoxide ions. For these preferred anions, the value of n in formula A is from 1 to 3, inclusive.

The anions set forth above which are least preferred are the haloaluminates (AlY_4^-) , Cl^- , Br^- , I^- , Br_3^- , I_3^- , BrO_3^- , IO_3^- , SO_4^{--} , $\text{S}_2\text{O}_3^{--}$, $[\text{Fe}(\text{CN})_6]^{--}$, $[\text{Fe}(\text{CN})_6]^{--}$ and the aliphatic carboxylate ions containing less than about 6 carbon atoms, such as acetate and trifluoroacetate.

The aromatic hydrocarbon chromium salts which are used as corrosion inhibitor additives by the method of this invention are preferably prepared by the reaction of an aromatic hydrocarbon with a chromium halide in the presence of a reducing metal and an aluminum halide, as described more completely in United States Patent No. 2,953,586. This reaction is represented by the following equation:



The product, bis(benzene)chromium tetrachloroaluminate, can then be converted to the neutral compound, bis(benzene)chromium by reduction of the cation with sodium hydrosulfite and subsequently oxidized to yield the hydroxide salt of monovalent bis(benzene)chromium. Any salt of monovalent bis(aromatic hydrocarbon)chromium cations which is soluble in the liquid medium can be used as the corrosion inhibitor of the present invention, as for example the chloride, borate, and monohydrogen phosphate salts. The term "salt," as used in this specification and the appended claims refers to a compound of a positive radical and a non-metal or negative radical, as defined on page 753 of "Hack's Chemical Dictionary," 3rd Edition, and as represented by Formula A hereinabove. The previously described neutral bis(aromatic hydrocarbon)chromium can be oxidized

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to yield the hydroxide and then converted into such salts by means well-known to those skilled in the art.

If the inherently corrosive liquid medium is nonpolar, a solvent soluble salt containing the aforescribed bis(aromatic hydrocarbon)chromium cation can be formed by the reaction of a monovalent bis(aromatic hydrocarbon)chromium salt with a phenolic compound to form a bis(aromatic hydrocarbon)chromium aryloxide. Bis(aromatic hydrocarbon)chromium aryloxides which can be prepared by this method include bis(toluene)chromium phenoxide, bis(mesitylene)chromium cresoxide, bis(octahydroanthracene)chromium naphthoxide, and bis(toluene)chromium di-tertiary butyl cresoxide. These organic-solvent soluble compounds can be employed to impart corrosion resistance to metals in organic solutions such as mineral oils, drying oils, resins and the like.

By the method of this invention, corrosion of metals by an ordinarily corrosive liquid medium in contact therewith is inhibited by dissolving in such liquid medium one or more of the aforementioned soluble salts of a monovalent bis(aromatic hydrocarbon)chromium cation. The salt, and preferably the hydroxide, can be added to the liquid medium in concentrations of about 0.1% to 10% by weight, and preferably in concentrations of about 0.25% to 2.0% by weight, based on the weight of the liquid medium.

The liquid medium, which may be used for heat exchange, hydraulic, or lubricating purposes, can contain as the major ingredient, water, or other polar solutions such as aqueous and non-aqueous alcohol, diesters and dimethyl sulfoxide. The alcohols can be lower monohydroxy alcohols such as methanol, ethanol and propanol; lower aliphatic glycols such as methylene glycol, ethylene glycol and propylene glycol; and polyalkylene glycols such as dimethylene glycol, diethylene glycol and dipropylene glycol. The diesters, referred to previously, can be compounds such as dioctylphthalate, dibutylterephthalate and dihexylisophthalate. The invention is also applicable to non-polar liquid media such as mineral oil, drying oils and resins, as well as silicone oils and other synthetics. The normally corrosive liquid media to which the method of the present invention is applicable are those having a pH value of from about 7 to about 12.5. The pH value of the liquid solution after dissolution of the bis(aromatic hydrocarbon)chromium cation salt is also in the range from about 7 to about 12.5.

The following tests illustrate the remarkable and unexpected advantages of the present invention:

A small amount (2 to 3 grams) of neutral bis(aromatic hydrocarbon)chromium was added to about 100 ml. of a corrosive water (i.e., water containing 100 p.p.m. each of chloride, sulfate, and bicarbonate ions) and vigorously aerated to form the hydroxide. Tared pieces of ordinary carbon steel were then added to these solutions and aeration was continued for 24 hours. Table I sets forth the results of this series of tests which demonstrate the effectiveness of the hydroxide salt of monovalent aromatic hydrocarbons in inhibiting corrosion of steel in corrosive water.

TABLE I

Media	Weight of Steel at Beginning, g.	Weight of Steel-Final, g.	Weight Loss, mg.	Weight Percent Loss
Corrosive water alone.....	4.7480	4.7274	20.6	0.43
Bis(toluene)chromium hydroxide.....	5.3079	5.3036	4.3	0.08
Bis(mesitylene)chromium hydroxide.....	4.7358	4.7320	3.8	0.08
Bis(octahydroanthracene)chromium hydroxide.....	3.9368	3.9313	5.5	0.14
Bis(tertiary butyl benzene)chromium hydroxide.....	4.4421	4.4390	3.1	0.07

In another series of tests, clean specimens of iron, aluminum, copper, brass and a 50:50 lead-tin solder spot on brass were immersed in test solutions with heating and aeration for a period of 200 hours. Each test unit consisted of a 600 ml. glass beaker equipped with a reflux condenser and a solution aeration tube. The specimens were cut from $\frac{1}{16}$ inch sheet stock and had a total surface of 9 square inches. The test temperature was 180° F. to correspond with automobile engine temperatures and the aeration rate was 0.028 cu. ft. per minute. The specimens were separated by glass insulators and covered with 300 ml. of solution. The corrosive water used contained 100 p.p.m. each of bicarbonate, chloride and sulfate ions. The results of these tests are set forth in Table II and also demonstrate the effectiveness of the new corrosion inhibitors in the media listed:

TABLE II.—BIS-TOLUENECHROMIUM HYDROXIDE IN VARIOUS MEDIA

Media	Conc. of (CH ₃ C ₆ H ₅) ₂ CrOH	pH		Res. Alk. ¹		Wt. Loss, mg./9 sq. in.				S.S. ²
		I	F	I	F	Fe	Al	Brass	Cu	
Corrosive water-----	0.33%-----	11.4	8.5	9.5	0.6	49	44	17	54	4
			9.1		0.5	56	51	11	50	4½
	None-----	8.6	8.4	0		1,527	228	18	15	3
			9.1	0		1,477	221	18	16	3
5% sodium chloride solution.	0.33%-----	10.9	8.1	0.5	0	454	138	38	158	4½
			7.7		0	884	142	56	119	4½
	None-----	7.2	9.4	0	0	348	884	63	372	4½
			9.9	0		249	477	174	482	4
27% methanol in corrosive water.	0.33%-----	11.5	10.1	0.5	0.3	33	46	30	27	5
			10.2	0	0	479	38	7	18	5
	None-----	8.2	9.5	0	0	393	8	15	87	4½
33% dimethylsulfoxide in corrosive water.	0.33%-----	12.4	9.2	0.5	0.2	27	46	17	34	5
			9.0		0.1	39	63	18	29	5
	None-----	8.2	5.7	0	0	568	42	85	87	4½
			5.8	0		606	42	75	51	4½
33% propylene glycol in corrosive water.	0.33%-----	11.3	8.9	0.5	0.4	38	86	19	32	4½
			9.2		0.2	29	118	25	32	4½
	None-----	8.2	5.7	0	0	700	51	166	144	4½
			5.7	0		1,247	103	308	285	4½
33% ethylene glycol in corrosive water.	0.33%-----	10.7	7.1	0.5	0	57	19	15	24	5
			7.2		0	50	26	15	25	5
	None-----	8.2	4.9	0	0	1,739	40	196	186	4½

¹ Reserve Alkalinity: ml. 0.1 N HCl per 10 ml. test solution.

² Solder Spot Rating: 6=excellent; 0=very poor.

From the concentration ranges (0.1 to 10% and 0.25 to 2% by weight) of the corrosion inhibiting compounds described hereinabove and the data set forth in Table II, the relative proportions of the previously corrosive organic compounds, i.e., methanol, dimethylsulphoxide, propylene glycol and the like, to the amount of corrosion inhibitor employed can be calculated. Thus, the weight ratio of organic compound to corrosion inhibitor employed can vary from a low of 2.7 to a high of 330 with a preferred range of about 13.5 to about 131.

Table III sets forth the results of a series of tests illustrating the effectiveness of bis(toluene)chromium borate and di-bis(toluene)chromium monohydrogen phosphate as corrosion inhibitors in 33% by weight ethylene glycol in corrosive water. The test procedure was similar to that described in relation to Table II.

TABLE III.—BORATE AND PHOSPHATE SALTS OF BIS(TOLUENE)CHROMIUM

Media	pH		Res. Alk.		Wt. Loss mg./9 sq. in.				S.S.
	I	F	I	F	Fe	Al	Brass	Cu	
33% ethylene glycol in corrosive water-----	8.2	4.9	0	0	1,739	40	196	186	4½
33% ethylene glycol in corrosive water and 0.40% [(CH ₃ C ₆ H ₅) ₂ Cr]-H ₂ BO ₃ -----	7.7	6.9	7	1	66	5	11	9	4½
		6.8		1	78	6	13	13	4½
33% ethylene glycol in corrosive water and 0.38% [(CH ₃ C ₆ H ₅) ₂ Cr]-HRO ₄ -----	9.8	9.4	5	4	18	131	35	29	5
		9.2		3	20	67	35	27	4½

Although not essential for satisfactory corrosion inhibition, other known inhibitors may be added and mixed with the non-corrosive mixed liquid of the present invention. For example, an alkaline substance such as triethanolamine or sodium hydroxide can be used, if desired, to impart a reserve alkalinity to the liquid and thereby prolong the effective life of the essential inhibitor compound under conditions where severe acidity may be developed. Where the liquid media includes an alcohol to be used as a freezing point depressant in cooling fluids, minor quantities of soluble or emulsifiable oils may be also useful, particularly in their capacity to impart anti-leak properties to the fluid mixture. Anti-leak agents of the nature of gums, dyestuffs for coloring, and other additive materials heretofore employed in anti-freeze alcohols, may also be used in admixture.

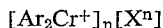
It is to be understood that certain modifications may be made to the specific forms of the invention as disclosed herein, without departing from the scope of such invention. For example, the organic solvent soluble bis(aromatic hydrocarbon)chromium aryloxides may be used as coating or components of coatings to protect metals from atmospheric corrosion. Such coatings could, for example, be applied to a metal surface by evaporating the organic solvent in which the surface is immersed. Furthermore, the chromium aryloxides of the present invention could be mixed with a variety of plastics such as polyvinylchloride, organopolysiloxanes, epoxides and acrylates to impart corrosion resistance to metals exposed to oxidizing atmospheres.

What is claimed is:

1. A method of inhibiting corrosion of metals by a cor-

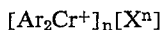
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rosive liquid solution having a pH value from about 7 to about 12.5 in contact with such metals which comprises dissolving in said liquid solution in an amount between about 0.1 percent by weight and about 10 percent by weight based on the weight of said liquid solution a salt of a monovalent bis(aromatic hydrocarbon)chromium cation represented by the formula



wherein each Ar represents an aromatic hydrocarbon compound having an unfused benzene ring and being free of aliphatic unsaturation and containing from 6 to about 14 carbon atoms, X is an anion capable of forming a salt with said monovalent bis(aromatic hydrocarbon)chromium cation which is soluble in said corrosive liquid solution, and n is the ionic charge of the anion X and is an integer having a value from one to four, inclusive.

2. A method of inhibiting corrosion of metals by a corrosive liquid solution having a pH value from about 7 to about 12.5 in contact with such metals which comprises dissolving in said liquid solution in an amount between about 0.1 percent by weight and about 10 percent by weight based on the weight of said liquid solution a salt of a monovalent bis(aromatic hydrocarbon)chromium cation represented by the formula

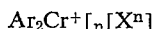


wherein each Ar contains from 6 to about 14 carbon atoms and is selected from the class consisting of benzene, alkyl-substituted benzenes and alkylene-substituted benzenes, X is an anion selected from the class consisting of hydroxide, dihydrogen borate, monohydrogen borate, borate, dihydrogen phosphate, monohydrogen phosphate and phosphate, and n is the ionic charge of the anion X and is an integer having a value from one to three, inclusive.

3. The method in accordance with claim 2 wherein the amount of said salt dissolved in said liquid solution is between about 0.25 percent by weight and about 2 percent by weight based on the weight of said liquid solution.

4. A method of inhibiting corrosion of metals by a corrosive aqueous solution having a pH value from about 7.2 to about 12.4 in contact with such metals which comprises dissolving bis(toluen)chromium hydroxide in said liquid solution in an amount between about 0.1 percent by weight and about 10 percent by weight based on the weight of said aqueous solution.

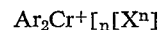
5. A liquid solution consisting essentially of an aqueous solution of organic compounds selected from the group consisting of lower monohydroxy alcohols, lower aliphatic glycols and polyalkylene glycols and dissolved in said aqueous solution a salt of a monovalent bis-aromatic hydrocarbon)chromium cation represented by the formula



wherein each Ar represents an aromatic hydrocarbon compound having an unfused benzene ring and being free of aliphatic unsaturation and containing from 6 to about 14 carbon atoms, X is an anion capable of forming a salt with said monovalent bis(aromatic hydrocarbon)chromium cation which is soluble in said corrosive liquid solution, and n is the ionic charge of the anion X and is an integer having a value from one to four, inclusive, said aqueous solution having a pH value from about 7 to about 12.5, said salt having a concentration of between about 0.1 percent by weight and about 10 percent by weight based on the weight of said aqueous solution, and the weight ratio of said organic compound to said salt being between about 2.7 and about 330.

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6. A liquid solution consisting essentially of an aqueous solution of organic compounds selected from the group consisting of lower monohydroxy alcohols, lower aliphatic glycols and polyalkylene glycols and dissolved in said aqueous solution a salt of a monovalent bis(aromatic hydrocarbon)chromium cation represented by the formula



wherein each Ar contains from 6 to about 14 carbon atoms and is selected from the class consisting of benzene, alkyl-substituted benzenes and alkylene-substituted benzenes, X is an anion selected from the class consisting of hydroxide, dihydrogen borate, monohydrogen borate, borate, dihydrogen phosphate, monohydrogen phosphate and phosphate, and n is the ionic charge of the anion X and is an integer having a value from one to three, inclusive, said aqueous solution having a pH value from about 7 to about 12.5, said salt having a concentration of between about 0.1 percent by weight and about 10 percent by weight based on the weight of said aqueous solution, and the weight ratio of said organic compound to said salt being between about 2.7 and about 330.

7. A liquid solution consisting essentially of an aqueous solution of ethylene glycol and bis(toluen)chromium hydroxide dissolved in said aqueous solution, said bis(toluen)chromium hydroxide having a concentration of between about 0.1 percent by weight and about 10 percent by weight based on the weight of said aqueous solution and the weight ratio of ethylene glycol to bis(toluen)chromium hydroxide being between about 2.7 and about 330.

8. A liquid solution consisting essentially of an aqueous solution of ethylene glycol and bis(toluen)chromium dihydrogen borate dissolved in said aqueous solution, said bis(toluen)chromium dihydrogen borate having a concentration of between about 0.1 percent by weight and about 10 percent by weight based on the weight of said aqueous solution and the weight ratio of ethylene glycol to bis(toluen)chromium dihydrogen borate being between about 2.7 and about 330.

9. A liquid solution consisting essentially of an aqueous solution of ethylene glycol and di-bis(toluen)chromium monohydrogen phosphate dissolved in said aqueous solution, said di-bis(toluen)chromium monohydrogen phosphate having a concentration of between about 0.1 percent by weight and about 10 percent by weight based on the weight of said aqueous solution and the weight ratio of ethylene glycol to di-bis(toluen)chromium monohydrogen phosphate being between about 2.7 and about 330.

10. A liquid solution consisting essentially of an aqueous solution of propylene glycol and bis(toluen)chromium hydroxide dissolved in said aqueous solution, said bis(toluen)chromium hydroxide having a concentration of between about 0.1 percent by weight and about 10 percent by weight based on the weight of said aqueous solution and the weight ratio of propylene glycol to bis(toluen)chromium hydroxide being between about 2.7 and about 330.

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JULIUS GREENWALD, *Primary Examiner*.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

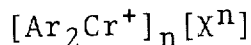
Patent No. 3,218,265

November 16, 1965

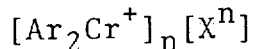
Donald R. Rink et al.

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

Column 1, line 19, for "hydraulic" read -- hydraulic --;
column 2, line 18, for "includes" read -- include --; lines 45
and 46, for "benbene" read -- benzene --; column 7, lines 53
and 54, for "bis-aromatic" read -- bis(aromatic --; lines 55
and 56, the structural formula should appear as shown below
instead of as in the patent:



column 8, lines 7 and 8, the structural formula should appear
as shown below instead of as in the patent:



same column 8, line 45, for "chormium" read -- chromium --.

Signed and sealed this 11th day of October 1966.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents