Oct. 16, 1973 P. A. ARGABRIGHT ET AL 3,766,086

POLYISOCYANURATE-BIURET SURFACTANTS

Filed June 28, 1971 2 Sheets-Sheet 1

Fig.1

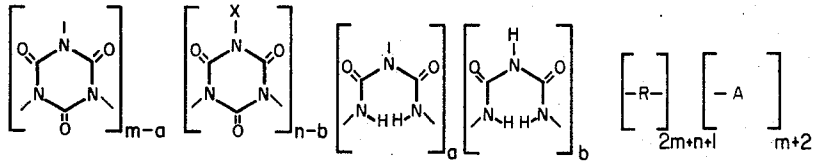
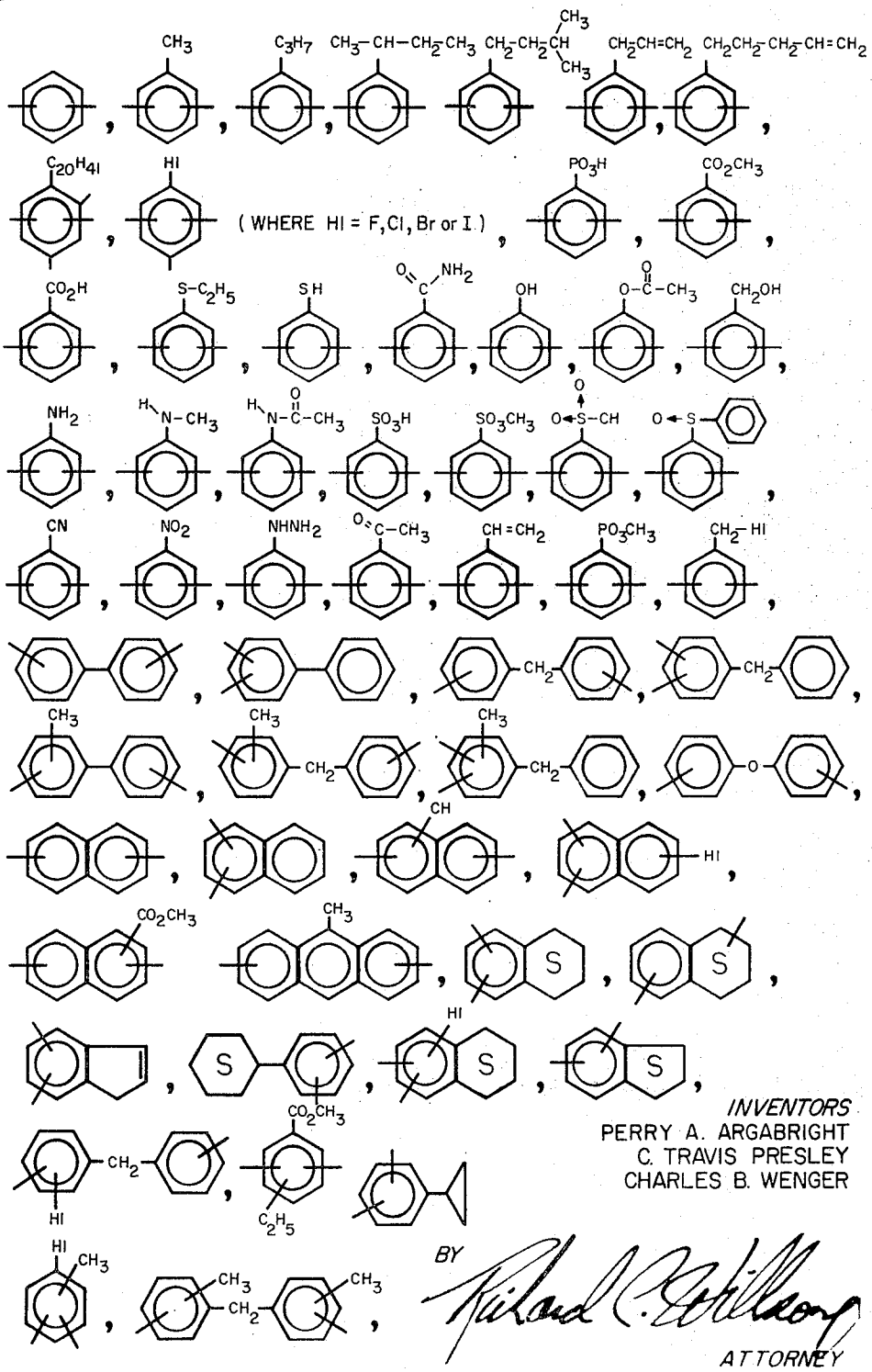


Fig. 2



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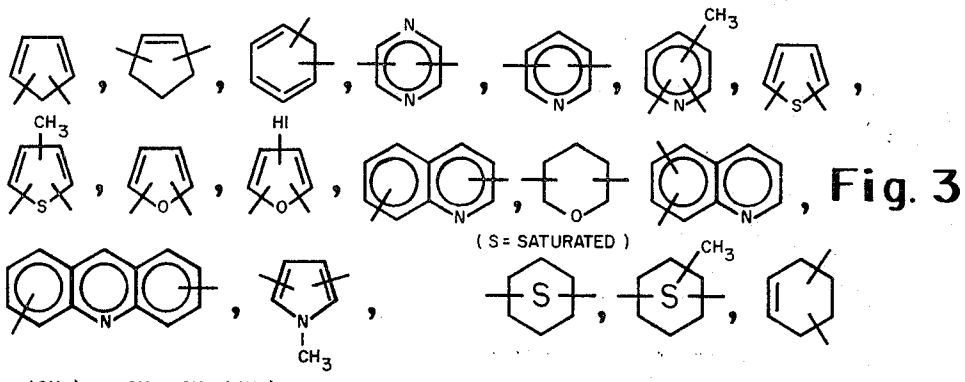
POLYISOCYANURATE-BIURET SURFACTANTS

Filed June 28, 1971 2 Sheets-Sheet 2

CYCLOHEPTATRIENE



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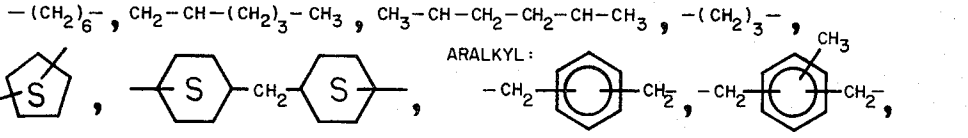

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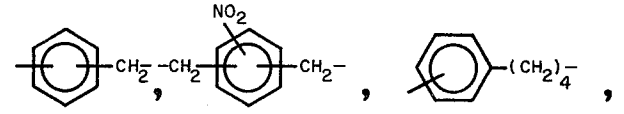

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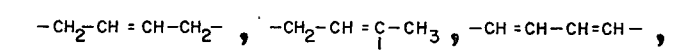

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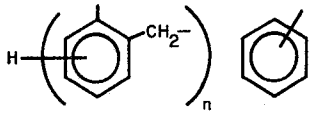

(WHERE n MAY BE FROM 1 to 50)

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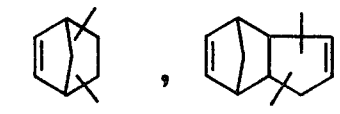
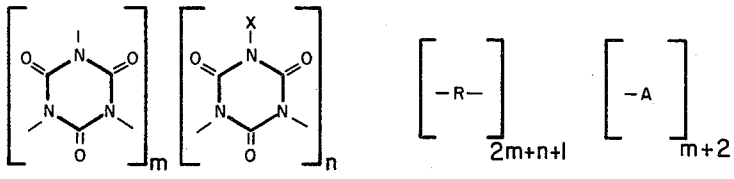


Fig. 3

Fig. 4



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Patented Oct. 16, 1973

3,766,086

POLYISOCYANURATE-BIURET SURFACTANTS

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Filed June 28, 1971, Ser. No. 157,236
Int. Cl. C08g 22/00
U.S. Cl. 252—312 7 Claims

ABSTRACT OF THE DISCLOSURE

A mixture of molecules containing all of the following groups show emulsifying ability: isocyanurate, metal isocyanurate and biuret.

CROSS-REFERENCES TO RELATED APPLICATIONS

The following U.S. patent applications relate to compounds and uses which are generally related to the present invention: Ser. No. 224,905, filed Feb. 9, 1972; Ser. No. 224,904, filed Feb. 9, 1972; Ser. No. 715,199, filed Mar. 28, 1968; Ser. No. 89,883, filed Nov. 16, 1970; Ser. No. 72,388, filed Sept. 15, 1970; Ser. No. 72,288, filed Sept. 15, 1970.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates generally to the field of isocyanurate-containing organic compounds generally classified within Class 260, subclasses —248 and —88.3 of the United States Patent Office.

Description of the prior art

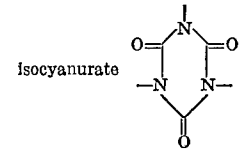
The present invention is concerned with a new class of emulsifying agents. The prior art which might be generally relevant is U.S. 3,072,654 which teaches calcium di(dichloroisocyanurate) in bleaching and cleaning compositions at its col. 1, lines 9–32; U.S. 3,272,813 which complexes chloroisocyanurates with potassium to make bleaching compositions at its col. 16, lines 63–70; U.S. 3,489,696 which forms polyamides from isocyanurates and polycarboxylic acids and mentions use of biuret triisosyanate at col. 5, line 62; on the basic hydrolysis of disubstituted isocyanurates, Argabright and Phillips, Journal of Heterocyclic Chemistry, 7, 999 (1970) which teaches formation of relatively simple biurets. Prior art of lesser interest includes U.S. 3,150,132, U.S. 3,251,818, U.S. 3,252,942, U.S. 3,275,630. None of the aforementioned prior art teaches the compounds of the present invention or in any way discloses their use as surfactants.

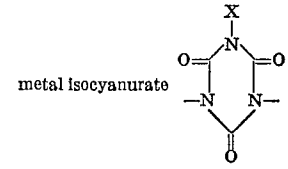
SUMMARY OF THE INVENTION

General Statement of the invention

The present invention relates to a new class of compounds which are useful as emulsifying agents, e.g., in forming dispersions and emulsions. These compounds are

characterized by containing in a single molecule all of the following groups:





and biuret, (—NHCONH—CO—NH— and —NHCON(—CONH—)).

The compounds of the present invention have the general structure shown in FIG. 1;

where:

R=divalent hydrocarbon or substituted hydrocarbon radical, as described below and exemplified in FIG. 2.

X=a metal, or hydrogen or quaternary ammonium (which, for the purposes of this invention, acts like a metal) or a combination thereof. Particularly preferred are hydrogen, quaternary ammonium and metals selected from the following groups of the Periodic Table; *Ia*, *Ib*, *IIa*, *IIb*, *IIIa*, *IIIb*, *IVa*, *IVb*, *Va*, *Vb*, *VIa*; including such meals as Li, Na, K, Rb, Cs, Ca, Ag, Au, Be, Mg, Ca, Sr, Ba, Ra, Zn, Cd, Hg, B, Al, Sc, Y, La, and the other rare earths, Ac, Ga, In, Tl, Ti, Zr, Hf, Ge, Sn, Pb, V, Nb, Ta, Sb, Bi, Cr, Mo, W, Mn, Fe, Ru, Co, Ni, Rh, Pd, Os, and Ir.

A=a monovalent organic radical selected from the following: isocyanate urethane (—$NHCO_2R'$), urea (—NHCONHR'), amino (—NH_2), —NHR' or —NR_2')

R'=monovalent hydrocarbon or substituted hydrocarbon radical, as discussed below;

m-a=average number of trisubstituted isocyanurate rings and is a positive integer from 0 to about 400, and most preferably from 0 to about 200.

n-b=average number of isocyanuric acid and/or isocyanurate salt groups and is a positive integer from 1 to about 10,000, more preferably from 2 to about 1000, and most preferably from 3 to about 100.

a=average number of trisubstituted biuret groups, as described below, and is a positive integer from 0 to about 2000, more preferably from 0 to about 400, and most preferably from 1 to about 200.

b=average number of disubstituted biuret groups, as described below, and is a positive integer from 1 to about 9000, more preferably from 2 to about 5000 and most preferably from 3 to about 1000.

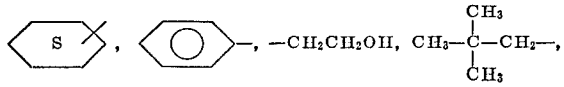
$2m+n+1$=average number of divalent R groups and is a positive integer from 2 to about 11,000, more preferably from 3 to about 1,100 and most preferably from 4 to about 140.

$m+2$=average number of A groups and is a positive integer from 2 to about 2000, more preferably from 2 to about 400 and most preferably from 2 to about 200;

and wherein there are no N-to-N bonds and no A-to-N bonds and no A-to-A bonds and no R-to-R bonds.

R preferably contains 2 to 40, more preferably 2 to 30, and most preferably 2 to 18 carbon atoms.

R' preferably contains 1 to 40 carbon atoms, more preferably 1 to 20 carbon atoms and most preferably 1 to 10 carbons, for example —CH_3, —C_2H_5, —C_3H_7, i-C_3H_7,



R and/or R' can be substituted with groups that do not interfere in the products' subsequent utility or in its preparation. Examples of such non-interfering groups are: —NO_2, Cl, F, Br, I, CN, —CO_2R'', —CO—R'', —O—R'', —SR'', NR_2'', —$CONR_2''$, —SO_3R, —SO_2—, —SO—, phenyl naphthyl, alkyl (1–40 carbon atoms), PO_3R'', cyclohexyl, cyclopropyl, polymethylene (e.g., tetramethylene), —OCOR'',

etc. where R'' may be hydrogen, lower alkyl (e.g., ethyl, hexyl) or aryl (e.g. monovalent radicals corresponding to the aryl radicals described in FIG. 2. The examples of R (shown in FIG. 2) are set forth for purposes of elucidation, not restriction.

It will be recognized that the values of *m* and *n* described above are on the basis of the integers which will be used to describe a single molecule. In actual practice, the invention will involve mixtures of molecules of the general form described above. Thus, the average value of *m–a* for the mixture may be from about 1 to about 2000, more preferably from about 1 to 400, and most preferably from about 1 to 200; the average value of *n–b* may be from about 0.5 to 10,000, more preferably from about 0.5 to 1000, and most preferably from about 0.5 to 100; the value of *a* may be from about 0 to 2000, more preferably from 0 to 400, and most preferably from 2 to 200.

The present invention relates to a new class of emulsifying agents, their preparation, and processes for their use. For example, the compounds of the present invention may be added to immiscible mixtures of water and organic compounds, e.g., equal parts by volume of water and a hydrocarbon and the resulting mixture agitated to form emulsions. This result is all the more surprising as many of the compounds are only very slightly soluble, and some are insoluble, in either phase.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows the general formula of the products of the present invention.

FIGS. 2 and 3 exemplify some of the possible structures of R groups of the starting materials and products of the present invention.

FIG. 4 shows the general formula of the organic starting materials of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Starting materials

The starting materials for the present invention are salts of polyisocyanuric acids produced according to the techniques taught in copending U.S. patent application S.N. 715,199, filed Mar. 22, 1968, now U.S. Pat. 3,573,259, by reacting a metal cyanate and an organic diisocyanate in the presence of an aprotic solvent to form isocyanurate-containing polyisocyanate metal salts.

It has been discovered that aqueous solutions of the aforementioned polyisocyanurate salts, of the general formula shown in FIG. 4 (where the lettered groups are as described above under "Summary of the Invention"), under basic conditions (i.e., pH in excess of 7) gives the biuret product shown in FIG. 1. The product is dramatically less soluble in water than is the polyisocyanurate salt reactant. Suitable bases include alkali metal or alkaline earth metal hydroxide.

Reaction media.—Water or mixtures of water and an alcohol, ketone, ester, amide, sulfoxide, sulfone, etc.

Temperature.—While not narrowly critical, temperatures in the range from 10 to about 200° C. are preferred, with 15–150° C. being more preferred and 20–120° C. being most preferred. The lower limit is generally the freezing point of solution and the upper limit is generally the boiling point of the solution at the reaction pressure.

Pressure.—While not narrowly critical, the reaction can be carried out at pressures of from 0.5 to 100, with 0.6 to 50 being more preferred, and 0.7 to 10 atmospheres being most preferred.

Time.—The reaction time, of course, is dependent on the initial concentration of the starting materials and the temperature. The preferred time is from 0.01 to 4500 hours, more preferred 0.05 to 350 hours, and most preferred from 0.06 to 200 hours.

Examples:

EXAMPLE I

Preparation of polyisocyanurate salt

To a stirred slurry of 82.4 KOCN (1.02 mole) in 2000 ml. of dimethylformamide (DMF) at 75° C., 183 g. of tolylene diisocyanate (1.05 mole) is added at a rate of 0.85 ml./min. by means of a syringe pump.

The entire operation is carried out in a nitrogen atmosphere. Following the addition, the reaction mixture is stirred an additional 5 minutes, dry methanol added (large excess) and allowed to react for an additional hour to insure complete quenching. The major product is insoluble in DMF and thus readily separated by a single filtration. A trace DMF soluble product is obtained after solvent stripping the filtrate. After vacuum drying at 80° C. to remove residual DMF and methanol, the following yield and analytical data are obtained:

Product	Percent yield [1]	Aryl/end group [2] ratio ($2m+n+1/m+2$)	Average mol. wt. (minimum)
DMF insoluble [3]	96.5	21.2	10,000
DMF soluble	Trace	1.5	750

[1] Corrected for residual DMF.
[2] Measured by nuclear magnetic resonance spectroscopy.
[3] Contains 20.9% DMF of solvation.

EXAMPLE II

Preparation of polyisocyanurate biuret

The polyisocyanurate product (DMF insoluble) of Example I is dissolved in water to give a 10% (by weight) solution. To this solution is added an equal volume of aqueous 8% NaOH. After standing at 25° C. for 4 hours, the hydrolysis is essentially complete. The desired product is a water-insoluble solid in the form of a colloidal suspension. Aliquots of this suspension are used for testing without further purification.

EXAMPLE III

The utility of the polyisocyanurate biuret as an emulsifying agent is demonstrated in the following manner.

To a graduate, containing 10 ml. of n-heptane and 9 ml. of water (deionized and distilled) is added 2 ml. of the crude suspension of Example II. Subsequent shaking provides a stable emulsion having a volume of approximately 16 ml.

EXAMPLE IV

In a manner similar to Example III, 10 ml. of n-heptane, 10 ml. of water and 0.5 ml. of the suspension prepared in Example II on shaking, gives approximately 11 ml. of emulsion, which remains stable.

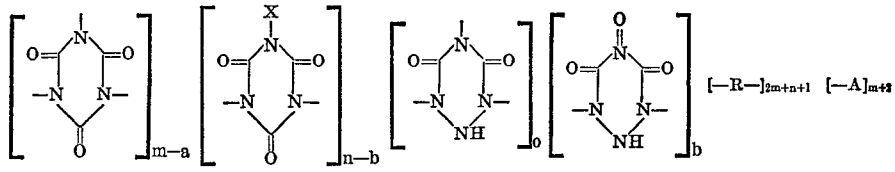
Modifications of the invention

It should be understood that the invention is capable of a variety of modifications and variations which will

be made apparent to those skilled in the art by a reading of the specification and which are to be included within the spirit of the claims appended hereto.

What is claimed is:

1. A composition comprising a mixture of compounds containing in a single molecular isocyanurate, metal isocyanurate and biuret groups, and having the structure:



wherein

R=divalent hydrocarbon or substituted hydrocarbon radical, containing 2 to about 40 carbon atoms,

X is selected from the group consisting of metals, hydrogen, or quaternary ammonium radicals,

A is a monovalent organic radical selected from the group consisting of $—NHCO_2R'$, —NHCONHR', $—NH_2$, —NHR' and $—NR_2'$, wherein

R' is a monovalent hydrocarbon radical or substituted hydrocarbon radical containing from 1 to about 40 carbon atoms, wherein

m-a is the average number of trisubstituted isocyanurate rings per molecule and is a positive integer from zero to about 400,

n-b is the average number of isocyanurate acid and/or isocyanurate salt groups and is a positive integer from 1 to about 10,000, wherein

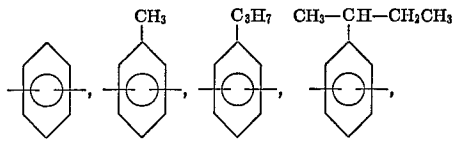
a is the average number of trisubstituted biuret groups, and is from about 0 to about 2,000, wherein

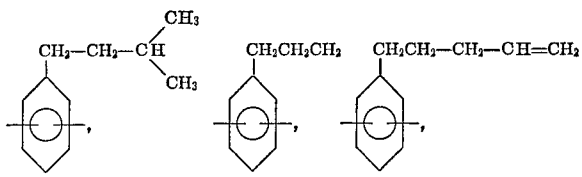
b is the average number of disubstituted biuret groups and is from about 1 to about 9000,

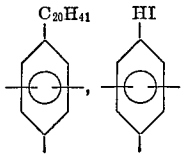
$2m+n+1$=the average number of divalent R groups and is a positive integer from 2 to about 11,000, and wherein

$m+2$ is the average number of A groups and is a positive integer from 2 to about 2,000, and wherein there are no N-to-N bonds and no A-to-N bonds, and no A-to-A bonds and no R-to-R bonds.

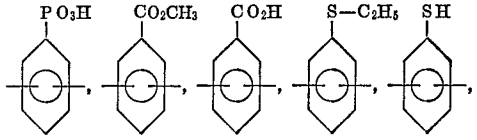
2. A process according to claim **1** wherein R is selected from the group of organic radicals consisting of:

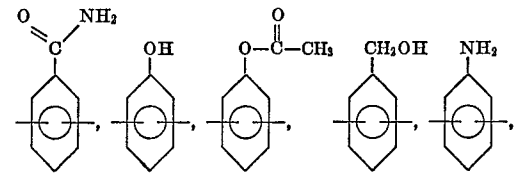


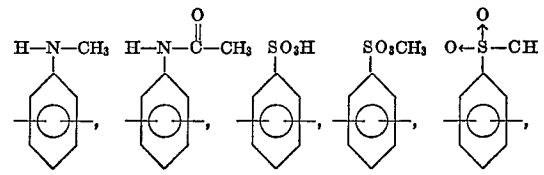


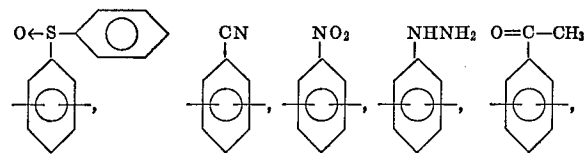


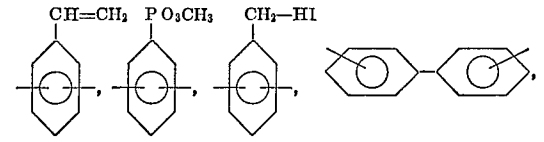
(Where HI=F, Cl, Br or I),

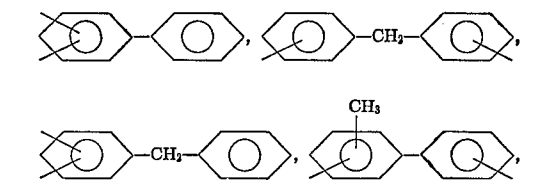


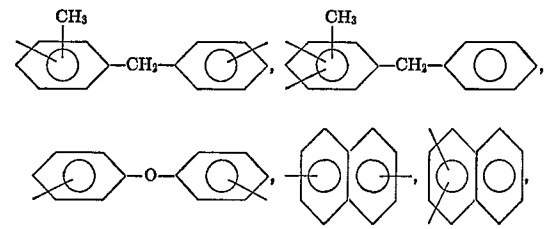


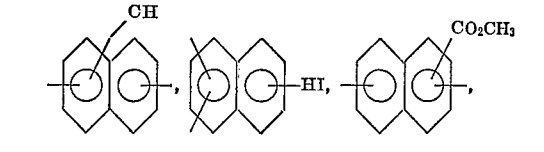


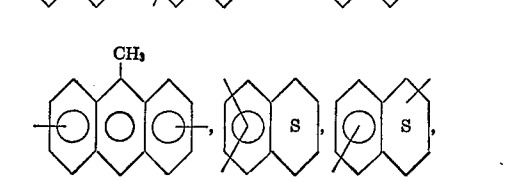


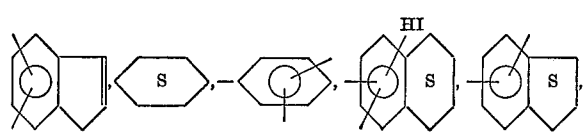


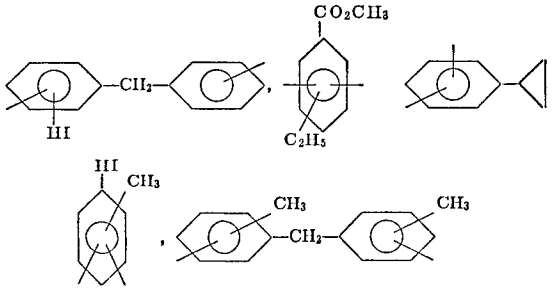








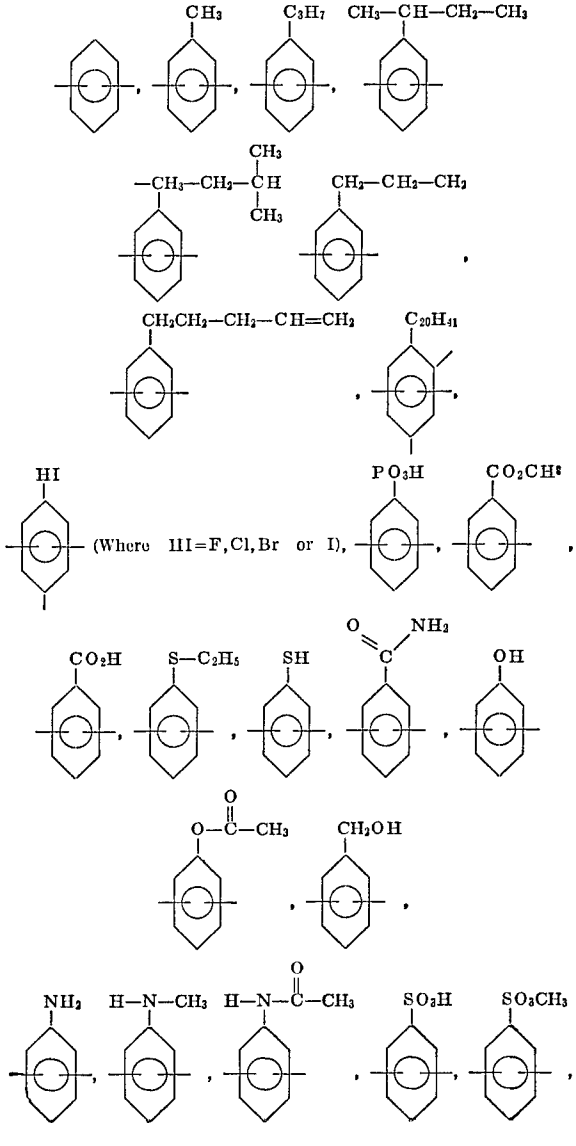


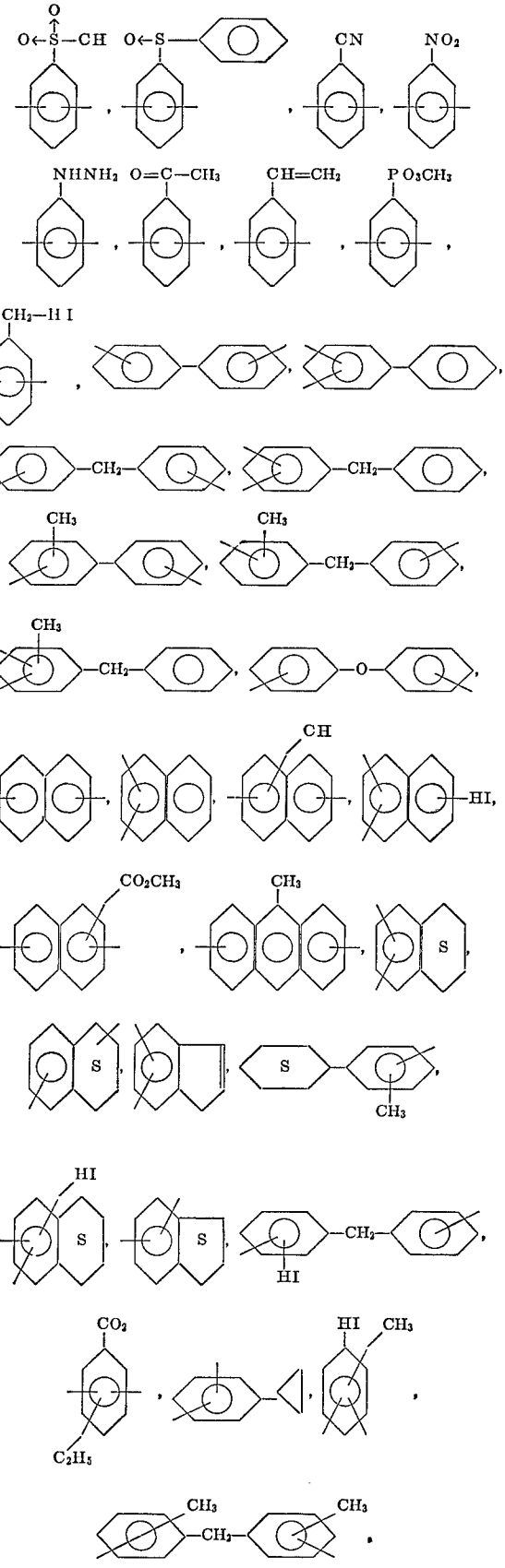


3. Compositions according to claim **1** wherein X is selected from the group consisting of hydrogen, quaternary ammonium radicals and metal radicals selected from the following groups of the Periodic Table; I*a*, I*b*, II*a*, II*b*, III*a*, III*b*, IV*a*, IV*b*, V*a*, VI*a*.

4. Compositions according to claim **1** wherein *m*–a is a positive integer from 0 to about 200, wherein *n*–*b* is a positive integer from 3 to about 100, wherein *a* is a positive integer from 1 to about 200, and wherein *b* is a positive integer from 3 to about 1,000, and wherein $2m+n+1$ is a positive integer from 4 to about 140, and wherein $m+2$ is a positive integer from about 2 to about 200.

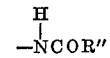
5. Compositions according to claim **1** wherein R is selected from the group of organic radicals as shown below:





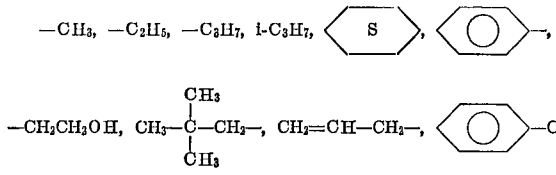
and the substitute derivatives thereof which are substituted with radicals selected from the group consisting of —NO, Cl, F, Br, I, CN, —CO_2R', —CO—R'', —O—R'', —SR'', NR_2'', —$CONR_2''$, —SO_3R, —SO_2—, —SO—, phenyl,

naphthyl, alkyl (1–40 carbon atoms), PO_3R'', cyclohexyl, cyclopropyl, -polymethylene —OCOR'',



where R'' may be hydrogen, lower alkyl or aryl.

6. A composition according to claim 1 wherein R' contains from 1 to 10 carbon atoms and is selected from the group consisting of



7. An emulsion comprising both water and at least one compound according to claim 1.

References Cited

UNITED STATES PATENTS

3,573,259 3/1971 Agabright et al. ..... 260—77.5 NC

OTHER REFERENCES

Noller: Chemistry of Organic Compounds, W. B. Saunders Co., Philadelphia, 1951, p. 186.

DONALD E. CZAJA, Primary Examiner

M. J. WELSH, Assistant Examiner

U.S. Cl. X.R.

252—356, 357; 260—29.2, TN, 77.5 NC, 248 NS.

UNITED STATES PATENT OFFICE

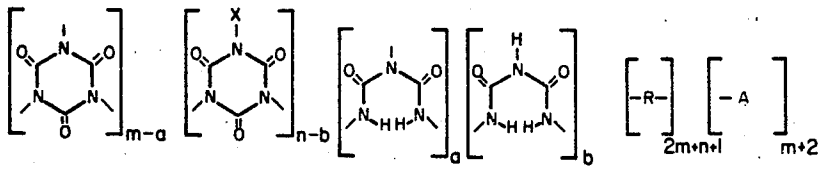
CERTIFICATE OF CORRECTION

Patent No. 3,766,086 Dated October 16, 1973

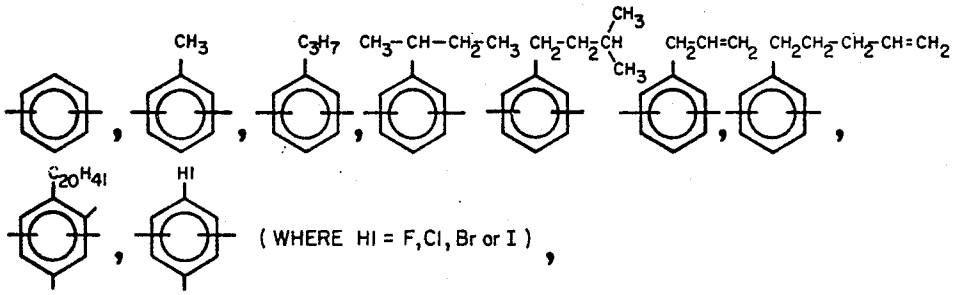
Inventor(s) Perry A. Argabright et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 5, structures of Claim 1 should read as follows:



Column 5, lines 46 through 65 should read as follows:



UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

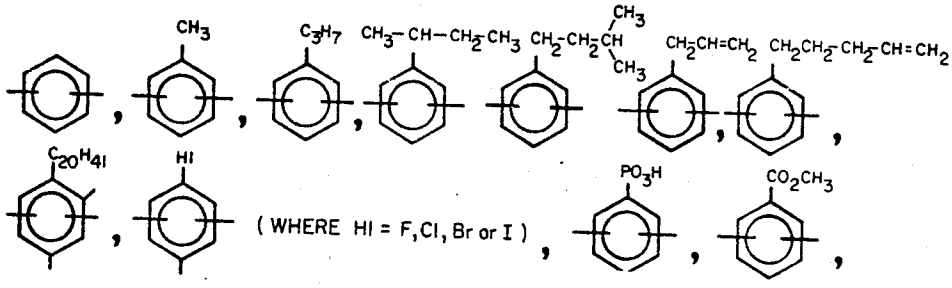
Patent No. 3,766,086 Dated October 16, 1973

Inventor(s) Perry A. Argabright et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 7, line 17 Following Va, add --Vb--

Column 7, lines 30 through 55 should read as follows:



Signed and Sealed this

Thirteenth Day of September 1977

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

LUTRELLE F. PARKER
Acting Commissioner of Patents and Trademarks