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# OIL SOLUBLE COPOLYMERS OF AZOMETHINES WITH UNSATURATED ORGANIC COMPOUNDS

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This invention relates to new and useful chemical compounds of a polymeric nature particularly adapted for use as additives of oils, particularly mineral lubricating oils, to which they impart desirable detergency properties.

Recent developments in the field of lubricants for internal combustion engines have led to the development of the so-called detergent oils. The purpose of detergent oils is to handle the products of combustion in an internal combustion engine. Such oils have the property of holding the carbonaceous degradation products of the lubricant or fuel in suspension in the lubricating oil rather than permitting the deposition of such products—"sludge"—on filters, oil jets or such other vital parts of the mechanism. Detergent oils also considerably reduce the deposits of varnish and carbonaceous matter on the piston skirts and like parts of the internal combustion engine.

Detergent oils have been previously suggested with a startling multiplicity of compositions. In the main, however, they have comprised conventionally refined mineral oils containing minor and functional proportions of metal soaps—usually Group I and Group II metals (including the sub-group). For examples, metal sulphonates such as calcium sulphonates have been used, alone and in combination with other compounds. Complex metal containing compounds—not always of certain composition—have also been suggested. These have also commonly been based on similar metals. Examples of such materials that have achieved considerable success are obtained by sulphurising or phosphosulphurising organic materials and then further reacting them with metal bases.

However, there has been one serious disadvantage attendant on the use of these metal containing compounds or complexes. This disadvantage has been that they inevitably increase, to some extent, the deposits laid down in the combustion chamber due to the combustion of the compounded oil.

It is the object of the present invention to provide a material that imparts detergent properties to lubricating oil compositions with which it is incorporated without adding any ash forming constituents thereto.

It has now been discovered and is the subject of this invention that certain polymeric materials based on anils (Schiff's bases) are effective in endowing oils with which they are incorporated with detergent properties without increased ashing tendencies.

Thus this invention comprises oil soluble polymers of anils or copolymers of such anils with other unsaturated organic compounds or mixtures of such polymers and/or copolymers. The invention also embraces oil compositions containing such polymers, copolymers, or mixtures.

Anils that are raw materials of this invention are obtained by condensing aldehydes and ketones with amines. The anils have the characteristic group >C=N—. Two types of anils may be used to produce the polymeric materials of this invention. In one type there is carbon to nitrogen unsaturation in the characteristic anil group, but



there is no olefinic unsaturation. In the other type olefinic unsaturation is also present. An example of the first type of anil is that obtained from aniline and benzaldehyde. Examples of the second type of anil are those obtained from aniline, and croton-aldehyde or acrolein.

In general the anils may be obtained by reacting an aromatic amine with a ketone or preferably an aldehyde. The aldehyde may be a saturated or unsaturated olefinic aldehyde or it may be an aromatic aldehyde. Although polymers of the anils alone, when they can be produced, are of some usefulness it is preferred to use copolymers of the anils with other unsaturated compounds containing a single olefinic unsaturated double bond i.e. the compound is mono-olefinic. Preferred optional comonomers are unsaturated hydrocarbons, esters, alcohols, ethers, halides and sulphides. It is, of course, also possible to form tripolymers or multipolymers, using an anil with two or more of the unsaturated comonomers herein mentioned.

The unsaturated comonomer is one in which a carbon atom adjacent to at least one of the unsaturated carbon atoms has a substituent group exerting an activating influence on the double bond, e.g. one exerting a negative I effect (Ingold). Thus suitable monomers include hydrocarbons such as styrene and alkylated styrene and analogous compounds. Suitable esters include esters of unsaturated alcohols and esters of unsaturated acids. It is preferred that the unsaturation be conjugated with the ester group or with some other active non-harmful group. Of course it may be preferred to use acids which may be esterified after polymerisation. Similar considerations apply to the alcohols, ethers, halides and sulphides. In all cases the monomers have from 2 to 24 carbon atoms. Examples of suitable esters are esters of acrylic, methacrylic and higher homologues. Of course, unsaturated dicarboxylic acids may be used, i.e. fumaric and maleic acid, as may be the corresponding esters, diesters, amides, etc. Suitable alcohols for esterification of such acids include the fatty alcohols, oxo alcohols or crude mixtures thereof.

Either monomer may contain substituent non-hydrocarbon groups but it must obviously be borne in mind that the substituent group should not interfere with the polymerisation reaction nor should it endow the finished polymer with properties that are undesirable in an oil additive, bearing in mind the purpose for which the compounded oil is intended. In this connection it will be obvious that the components will be selected bearing in mind that the finished polymer should be soluble in oil. The bases for such selection are well known in the art. An interesting aspect of this invention resides in the fact that by incorporating suitable groups, particularly straight chain groups—notably of 8–18 carbon atoms in at least one of the monomers—the resulting polymer imparts additional desirable properties such as improved viscosity index and pour point to oils with which it is incorporated.

The polymerisation or copolymerisation of unsaturated compounds of the types used in this invention is quite well known. Three types of polymerisation may be used.

(*a*) Free Radical—catalysed by materials such as organic peroxides (e.g. t-butyl hydroperoxide, benzoyl peroxide, 1-hydroxy cyclohexyl hydroperoxide-1 etc.) i.e. substance giving free radicals including redox systems.

(*b*) Anionic—catalysed by basic catalysts (e.g. sodiomalonic ester, sodium ethoxide, sodium ethyl magnesium bromide etc.) i.e. strong (Lewis) bases.

(*c*) Cationic—catalysed by acidic catalysts (e.g. stannic chloride, ferric chloride, sulphuric acid, etc.). That is strong (Lewis) acids including Friedel-Crafts catalysts.

Free radical polymerisation can also be initiated by

U.V. radiation and $\beta$ and $\gamma$ radiation—particularly useful where temperature must be kept low.

Any of the above types of polymerisation may be used, but the free radical type is preferred. In some cases the copolymerisation is very slow e.g. using benzoyl peroxide at 60 °C. A particularly useful catalyst is $\alpha\alpha$ azo di-isobutyronitrile. It is believed that polymerisation occurs at the carbon to nitrogen link.

The invention will be more readily understood by contemplation of the following example:

## PREPARATION OF BENZALANILINE

424 g. of aniline and 372 g. of benzaldehyde were refluxed with 750 mls. of toluene as water entrainer for 3 hrs., 72 mls. of water being collected.

The resulting crystalline mass was recrystallised from benzene or toluene to a constant melting point of 54° C.

## COPOLYMERISATION OF BENZALANILINE WITH LAURYL METHACRYLATE

### *Experiment I*

86.7% wt. of lauryl methacrylate was mixed with 12.3% wt. of benzalaniline using 1% wt. $\alpha\alpha$ azo di-isobutyronitrile as catalyst in a flask fitted with a stirrer and nitrogen bleed tube. After 1½ hrs. a thick oil insoluble mass was formed.

### *Experiment II*

86.3% wt. of lauryl methacrylate was mixed with 12.2 percent wt. benzalaniline and 2.0% wt. lauryl alcohol as modifier, 0.5% $\alpha\alpha$ azo-di-isobutyronitrile being used as catalyst. Using the same reaction conditions as above, an oil soluble polymer was formed. This was used for the Phorone tests given below.

The following Phorone Test data illustrate the detergency of the benzalaniline co-polymer of Experiment II when used in a 5% wt. blend in a refined paraffinic S.A.E. 30-grade lubricating mineral oil (U.S. Essolube HD–30 base).

| Volume 10% sulphuric acid (mls): | Wt. deposits (mg) |
|---|---|
| 7 | 0.1 |
| 10 | 0.3 |

The Phorone No. is obtained from the following test:

The Phorone is intended to evaluate the performance of lubricating oils in automotive engines, in particular diesel engines. It is carried out by stirring the lubricant compositions with an oxygenated easily polymerised material such as Phorone in the presence of aqueous sulphuric acid of fixed concentration. Under these conditions using standard fixed quantities of lubricant and Phorone and carrying out the test at a fixed temperature in the range 100° F. to 400° F. and a fixed time between 0.5 hour and 6 hours, a deposit is formed whose amount is a function of the volume of aqueous sulphuric acid used. Thus it is found that the best detergent oils are those which give the lowest deposits for a given volume of acid. In practice it is found more convenient to carry out a series of tests at gradually increasing volumes of aqueous sulphuric acid and note the volume of acid required to produce 10 mg. of deposits (by interpolation if necessary). This is called the Phorone No. of the lubricating oil composition. The greater the Phorone No. of the lubricating oil composition the better its detergency. It is also possible to correlate the Phorone Nos. of lubricating oils with engine cleanliness ratings by performing a series of engine tests on oils of known Phorone Numbers.



The proportion of anil of the polymerisation feed may vary between 1% and 30% by weight, particularly useful products being those containing about 10% to 15% by weight of the anil.

It will be understood that a primary purpose of the polymers and co-polymers of this invention is to provide additives for lubricating oils, particularly mineral lubricating oils. Care must, therefore, be taken in choosing the constituents so that the product is soluble in the desired base stock in appropriate proportions. Generally speaking, the proportion of polymer used in the oil composition will vary with the nature of the oil, the degree of detergency required and the potency of the polymer. The actual amount can readily be determined by the Phorone Number mentioned above or by other methods known to the art. Such an effective proportion is referred to herein as a detergent proportion. Generally for concentrates for later blending, products having between 10% and 90% of polymer are useful. For lubricating compositions themselves it is preferred to use less than 30% by weight and preferably between .5% and 20% calculated on the polymer content.

Although the polymeric additives of this invention are primarily intended for use in lubricating oils, they may be used with other oils. For example, a fuel oil containing an appropriate proportion of the additives of this invention shows less tendency to deopsit carbonaceous material on filters and lines similarly with a diesel fuel. Generally, however, it is preferred to add the polymers to lubricating oils which may be animal, vegetable or particularly mineral oils.

What we claim is:

1. An oil-soluble copolymer prepared by copolymerizing a mixture of a compound having up to 24 carbon atoms and selected from the group consisting of monoolefinic unsaturated carboxylic acids and esters of monoolefinic unsaturated carboxylic acids, with an anil which is the reaction product of an aromatic amine and an aldehyde, said anil making up from 1 to 30 weight percent of said mixture.

2. Product as defined by claim 1 wherein said anil is present in said mixture in amounts of from 10 to 15 weight percent.

3. Product as defined by claim 1 wherein said anil comprises benzalaniline.

4. Product as defined by claim 1 wherein said unsaturated compound comprises an ester of methacrylic acid.

5. An oil-soluble reaction product obtained by copolymerizing a mixture of from 85 to 90 weight percent of lauryl methacrylate and from 10 to 15 weight percent of benzalaniline in the presence of a small proportion of lauryl alcohol.

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