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3,067,192

PROCESS FOR PREPARING ACYL POLYSACCHARIDE BORATES

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This invention relates to lubricating oil compositions and additives for improving the same, and more particularly, to acylated derivatives of polysaccharides having two adjacent cis hydroxyl groups and to borated acylated derivatives of polysaccharides having two adjacent cis hydroxyl groups and useful for improving the properties of lubricating oil compositions, and to oil compositions containing the same.

One of the most serious problems encountered in the operation of internal combustion engines is the deposits which form progressively and accumulate on the surfaces within the combustion zone, on the cylinder head, piston top, sparkplugs and the intake and exhaust valves. These deposits are made more stubborn by the tetraethyl lead present in most gasoline fuels, because this not only contributes to the deposit but it also converts it from an essentially carbonaceous deposit to one comprising appreciable quantities of lead and lead compounds mixed therewith, such as lead sulfate, and lead oxide. The carbonaceous deposits act as a cementing agent for the lead deposits, and the lead deposits are more difficult to remove than the carbon deposits. Thus, a deposit of this sort is more tenacious and troublesome than a purely carbonaceous deposit.

The nature of the lead-carbonaceous deposits is such that they are quite difficult to remove, once they have been built up. They are not attacked by the scavenging agents which are included in the fuel with the tetraethyl lead. Despite the fact that the amount of the deposits eventually levels off, after which there is no appreciable further increase, the presence of the built-up deposits interferes considerably with the operation of the engine, and it would be desirable both to prevent formation of deposits and to remove them after they have been formed. The disadvantageous effects of these deposits are well discussed in U.S. Patent No. 2,741,548 to Samuel M. Darling, Philip S. Fay and Lorraine S. Szabo.

It has been proposed to attack such deposits by incorporating in the liquid leaded motor fuel an organic boron compound which is soluble in the fuel. The boron compound is thought to modify the action of the fuel in the engine, and to react with the deposits so that the adverse effects due to the deposits are eliminated or markedly reduced.

It is known that the carbonaceous components of the deposits in the engine are built up not only from the gasoline but also from the oil, which enters the combustion system from the crankcase in various ways. While a smaller amount of oil enters the combustion zone than does gasoline, it is believed that the oil is responsible for a larger proportion of the deposits than is the gasoline. This oil is in the liquid phase when it enters the combustion zone of the engine, whereas the gasoline, of course, is in the vapor phase. However, it is essential that the boron compounds be soluble in the medium in which it is introduced into the engine. For use in lubricating oil, the solubility must be quite high, relative to that in gasoline, because more additive is needed in the lubricating oil to obtain an effect. Moreover, the stability of the boron compound against hydrolysis must be high, in view of the larger amounts of compound present, and in view of the fact that due to the breathing of an engine, moisture in the air is often

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condensed in the crankcase when the engine is cold so that water may accumulate in the crankcase. The hydrolysis product, if any, must be soluble in the oil as well, since insoluble boron deposits in the crankcase and lubricated parts of the engine might be harmful and certainly would be difficult to remove.

Moreover, the boron compounds incorporated in liquid-leaded motor fuels are volatilizable under the combustion zone conditions, and also exist in the vapor phase in the combustion zone. If such organic boron compounds were present in the oil, they would, under the combustion zone conditions, nonetheless be expected to volatilize. Compounds having a much higher boiling point are necessary for use in lubricating oils. Such compounds should also be stable in the presence of moisture, and they must of course be oil-soluble or -dispersible. Many of the boron compounds incorporated in the liquid-leaded motor fuels heretofore have not had the requisite solubility or requisite low volatility for incorporation in oils and because of this, it has not been practical to incorporate these compounds in oil.

It is known that boric acid will react with polymeric organic compounds having free hydroxyl groups in the molecule. Irany, Industrial and Engineering Chemistry 35, 1290 (1943) and British Patent No. 550,245 dated December 31, 1942 report that boric acid reacts readily with hydroxyl-containing polymers, such as cellulose esters and ethers and partially hydrolyzed polyvinyl esters and acetals and like compounds. The polymers are three dimensional and essentially infusible. As a result thereof, they are also oil-insoluble. Moreover, they are very water-sensitive, and are easily hydrolyzed to their original form by mere contact with water or an aqueous solution, whereby the ester-like bridges formed with the boric acid are thought to be hydrolyzed.

A literature search conducted by Wright Air Development Center (Wright Air Development Center Report 55-26 by W. L. Ruigh and C. E. Erickson, Research on Boron Polymers Literature Survey [March 1955]) indicates that all of the previously reported polymeric boric acid esters were sensitive to ready hydrolysis by water. However, it has been reported by Deuel, Neukom and Weber, Nature 161, 96-7 (1948), Macromol Chem. 3, 13-30 (1949), that polysaccharides having cis hydroxyl groups form essentially irreversible and infusible complexes which are quite similar to glasses or gels in their properties. The stability of such borates towards water appears to be due to the coplanar cis hydroxyl groups of the cyclic pyranosidal units of the polysaccharides. Polysaccharides which do not contain cis hydroxyl groups, such as cellulose, amylose, amylopectin or starch, all of which are made up of glucose units, do not form such irreversible borate complexes. However, the borate polymers which have been formed, whether water-sensitive or not, are infusible and oil-insoluble, and therefore not suitable for use as lubricating oil additives, for introducing boron into the oil or for any other purpose. The fact that the borated polymers are oil-insoluble is not surprising inasmuch as the starting materials usually are oil-insoluble too. This is true of cellulose esters and of polysaccharides having hydroxyl groups such as polymannoses and galactomannoses. If anything, boration increases the oil-insolubility because it introduces a three dimensional structure due to the formation of cross links; inasmuch as the boric acid has three reactive positions, each of which can associate with hydroxyl groups.

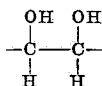
In accordance with the instant invention, acylated and borated derivatives of polysaccharides having two adjacent cis hydroxyl groups are provided which are oil-soluble and stable when dissolved in oil, and therefore are useful additives for adding boron to lubricating oils. In addition, and quite unexpectedly, the borated acyl-

ated polysaccharides of the invention have good water stability, and improve dispersancy of the oil, and the side chain-free polysaccharides also greatly improve the viscosity index of the oil.

The fact that the more linear compounds of the invention are capable of improving the viscosity index of the oil is surprising. Numerous polymeric cellulosic substances, such as cellulose esters, even though linear, are not very soluble in oil, and when dissolved have a negative effect on viscosity index. Moreover, the *cis* hydroxyl polysaccharides themselves before acylation and boration are oil-insoluble, and are not capable of improving the viscosity index.

Acylation of the *cis* hydroxyl polysaccharides converts them into compounds which are relatively oil-soluble and capable of improving viscosity index significantly. Boration of the acylated polysaccharide gives a further improvement in oil solubility and in ability to improve viscosity index, and converts the polysaccharide into a vehicle for boron in the oil.

Cis hydroxyl polysaccharides used in the invention contain in the polymer chain a plurality of *cis* diol units of the type:

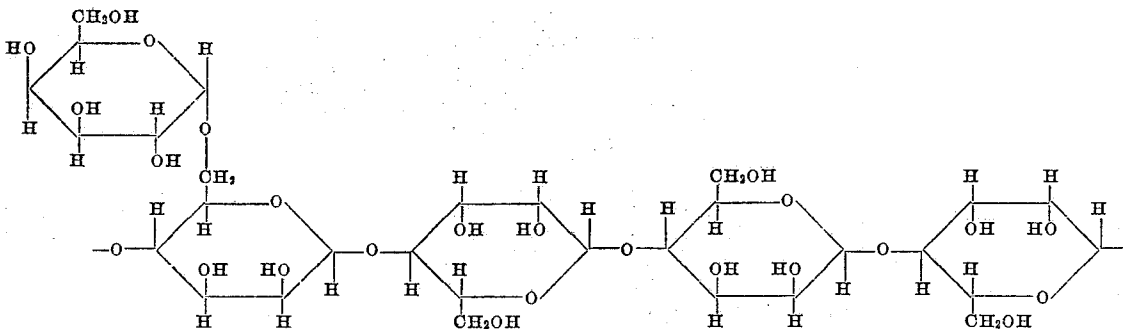


These units would usually be in the saccharide units making up the polymer chain.

The mannans are an outstanding group of complex *cis* hydroxyl polysaccharides which can be used in preparing the acylated borated polysaccharides of the invention. The polymannoses have two *cis* hydroxyl groups in the 1-, 2-position of each mannose unit in the polymannose chain and one OH group attached in the form of a CH_2OH group. Typical are vegetable ivory mannan A, vegetable ivory mannan B, yeast mannan, salep mannan and Konjuku mannan.

The galactomannans are polymannoses having single galactose units attached through 1,6-glycosidic linkages to the polymannose chain. Accordingly, the term "polymannose" is used herein to refer generically to both galactomannans and to mannans. The galactose side chains of the galactomannans probably are not distributed uniformly along the chain, but this makes no difference in this invention. Locust bean gum and guar gum are the principal sources of galactomannans, but they are also found in other vegetable mucilages and legume seeds such as alfalfa and clover seeds.

The structure of locust bean gum has been established to be as follows, and this also is illustrative of a typical polymannose chain, showing the two adjacent *cis* hydroxyl groups:



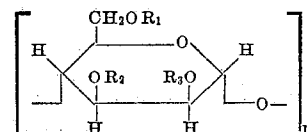
The hydroxyl groups attached to the saccharide units and the hydroxyl group attached to the CH_2OH group are chemically reactive, and can be acylated by reaction with the corresponding acyl chlorides. They can also be reacted with boric acid and borates.

It is important to note that in preparing the acylated borated polysaccharides of the invention, it is essential first to acylate the polysaccharide and then to borate it. If

the boration reaction is carried out first, even if it is sought to react the polysaccharide incompletely with only a small proportion of the reactive hydroxyl groups, the reaction product is a glass which is impervious to any further reactions. Accordingly, the polysaccharide first is acylated to introduce an average of about two acyl groups per saccharide unit, and the remaining hydroxyl groups then are borated. It will be understood, however, that although boration produces a more desirable lubricating oil additive, it is not essential if improvement in viscosity index of the oil is all that is desired. The acylated linear polysaccharides are capable of improving viscosity index, although of course they do not have the advantage of incorporating boron into the oil as well, nor do they improve the viscosity index as greatly per unit weight as do the borated acylated polysaccharides.

In the reaction of the polymannoses with an acyl-containing compound, the hydroxyl of the CH_2OH group probably is the first to be esterified. Thereafter, one of the secondary hydroxyl radicals attached to the mannose unit is esterified. Usually, one of the hydroxyl radicals attached to the mannose unit is almost as readily esterified as the hydroxyl of the CH_2OH group, and therefore both of these may be esterified together at about the same rates.

The third hydroxyl group is more difficult to acylate, and therefore it is easy to protect this so as to preserve it for later boration. Therefore, in the final product, although from one to three of the hydroxyl groups of any given mannose unit can be acylated, it is probable that only two hydroxyl groups, those most readily esterified, actually are acylated on any given unit. Thus, it is possible to define the average mannose unit of the acylated or borated acylated polymannoses of the invention by the following general formula:



In the case of the acylated polymannoses, one of R_1 and R_2 is acyl, and one of R_2 and R_3 is acyl, and the remaining R is hydrogen.

In the case of the borated acylated polymannoses, one of R_1 and R_2 is acyl, and one of R_2 and R_3 is acyl, and the remaining R is a borate unit.

In both cases, n represents the number of such units, which can be the same or different, in the polymer chain; n has a value of from two to several thousand, usually not over 5,000. Preferably, n is from 15 to 500. The term "average" signifies the existence of units having from

one to three acyl groups and from one to three borate groups, averaging out to the ratio of two acyl groups per borate group per unit in the chain as a whole. Where only R_1 is acyl, R_2 and R_3 can be taken together in a single borate unit, as in (1) below.

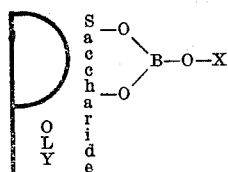
The acyl group can have from eight to eighteen carbon atoms and can be a straight or branched saturated or unsaturated aliphatic acyl radical. Preferably, it has

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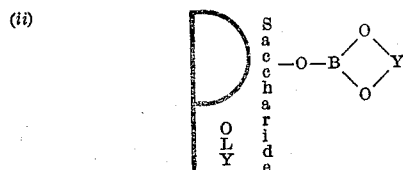
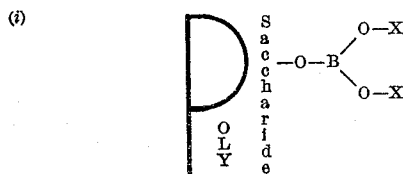
from twelve to fourteen carbon atoms. Such radicals are readily obtainable from the corresponding acyl chlorides of the corresponding aliphatic fatty acids. Acylation also can be effected by the corresponding acid anhydride, where these exist. Typical acyl radicals include acetyl, propionyl, butyryl, valeryl, stearoyl, caproyl, capryloyl, palmitoyl, myristoyl, oleoyl, linoleoyl, linolenoyl and lauroyl.

The borate unit in the acylated polysaccharides has from one to fifty-four carbon atoms, and probably has one of these general formulae:

- (1) Mono-acylated polysaccharides having two cis OH groups borated:



- (2) Mono-acylated polysaccharides having one OH group borated:

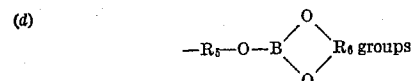


These structures have not been confirmed by experimental evidence, but they are strongly indicated by the data that is available, and are suggested to facilitate understanding of the invention.

P represents the polysaccharide polymer chain, to one or both hydroxyls of whose pair of cis hydroxyl groups the borate unit is attached, probably, or to the CH_2OH .

X is a monovalent radical selected from the group consisting of:

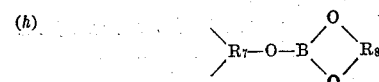
- (a) Aliphatic groups, such as alkyl and alkenyl
(b) Hydroxy aliphatic groups, such as hydroxyalkyl and hydroxyalkenyl



- (e) Hydrogen (in case of incomplete reaction)

Y is a bivalent radical selected from the group consisting of:

- (f) Aliphatic groups, such as alkylidene and alkenylidene
(g) Hydroxy aliphatic groups, such as hydroxyalkylidene and hydroxyalkenylidene



where R_7 and R_8 are aliphatic groups as in (f).

The aliphatic groups forming part of the borate unit have from one to eighteen carbon atoms and can be satu-

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rated or unsaturated. The highly branched aliphatic groups are preferred since they impart greater stability to hydrolysis, particularly in the case of the glycol units of the type of (c) and (d) above. Typical aliphatic groups include methyl, ethyl, propyl, butyl, amyl, tertiary butyl, isopropyl, secondary butyl, neopentyl, lauryl, decyl, myristyl and stearyl.

The hydroxyl aliphatic groups also have from one to eighteen carbon atoms. Exemplary are hydroxyethyl, hydroxymethyl, hydroxybutyl, hydroxyhexyl, and the hydroxy aliphatic groups derived from the following glycols (by the reaction of one of the hydroxyl groups of the glycol with boric acid): 2-methyl-pentanediol-2,4, 3,4-dimethyl-hexanediol-3,4, 3,4-diethyl-hexanediol-3,4, 2,2,4-trimethyl-pentanediol-1,3, 3,5-dimethyl-hexanediol-2,4, pentanediol-2,4, 2,2-diethyl-propanediol-1,3, 3-methyl-pentanediol-2,4, 2-ethyl-hexanediol-1,3, 3,4-dimethyl-pentanediol-2,4 and 2-ethyl-2-butyl-propanediol-1,3.

Such borate units are merely side chains like the galactose side chains attached to the polymer chain. This is the preferred type of structure. In the case of (c) and (d) there is however a possibility that cross links will form between parallel polysaccharide chains. This is not bad, provided cross links are few, constituting not over 20% of the borate units. When this type of polysaccharide is borated using boric acid, cross-linking between the polysaccharide chains occurs; the number of cross links is very large, and infusible, oil-insoluble products are formed. However, if the cross links are limited in number or nonexistent, the borated acylated polysaccharide obtained is oil-soluble.

The more linear the polysaccharide the better its properties as a viscosity index improver. The addition of galactosidal side groups or long chain borate side groups reduces linearity and reduces the ability to improve viscosity index. The formation of too many cross links results in a cage-type polymer which does not have the properties of a linear polymer, is less effective as a viscosity index improver, and in addition has reduced oil solubility. However, all the soluble borate additives have the ability of introducing boron into the oil in a form in which it is available to advantage in operation of the engine. All products produce increased dispersancy.

It is a surprising fact that the acylated borated polysaccharides in accordance with the invention are quite stable in lubricating oil but are not very stable in gasoline. To a certain extent these polymers are reactive with themselves. The borate side chains are capable of hydrolysis or other reactions. Apparently, in the presence of the oil the compounds are protected from these self reactions better than they are in gasoline, so that they remain more stable in lubricating oil.

The polysaccharides are acylated by reacting them with the corresponding fatty acid chloride in the presence of a formamide compound which swells the polysaccharide and facilitates the reaction. The reaction takes place at a temperature within the range from about 50° to about 150° C. and requires from twenty-four to thirty-six hours. External moisture should be excluded during the reaction and it is also desirable to dry the polysaccharide thoroughly before the reaction, preferably at 100° to 110° C. for twenty-four hours.

It is preferable to carry out the reaction in the presence of the tertiary amine in order to retain the halogen from the fatty acid chloride as the amine hydrochloride. An amount of the tertiary amine at least sufficient to accomplish this purpose is preferred. In addition to pyridine there can be employed aliphatic tertiary amines such as triethyl amine, tripropyl amine, tributyl amine and triamyl amine as well as other tertiary cyclic amines such as quinoline and N-methyl piperidine.

The polysaccharides are swelled by formamide compounds, including formamide and formamide derivatives having one or two alkyl groups of up to three carbon

atoms. Thus, the formamide compounds which can be employed are defined by the general formula HCONR_1R_2 , where R_1 and R_2 are selected from the group consisting of hydrogen and alkyl radicals having from one to three carbon atoms such as methyl, ethyl, propyl, and isopropyl, and can be the same or different. Exemplary are formamide, N,N'-dimethylformamide, N,N'-diethylformamide, N-ethylformamide, N-isopropylformamide and N-methylformamide. The amount of formamide likewise is not critical. Enough is used to swell the polymannan appreciably. Usually from two to three times the weight of polysaccharide will be adequate.

When reaction is complete, the mass is poured with vigorous stirring into a boiling solution of 2 moles of an alkaline-reacting salt such as potassium carbonate or sodium carbonate or bicarbonate in 2600 ml. of water and mascerated for fifteen to thirty minutes in order to leach out all unreacted acid chloride. The carbonate solution is then cooled to room temperature or below and the plastic mass filtered from the aqueous phase, washed thoroughly with water and dried overnight at 110 to 120° C. In most cases the desired diacylated polysaccharide is isolated from the plastic mass by means of extraction with four to eight liters of boiling chloroform or larger quantities of boiling benzene followed by filtration and subsequent evaporation.

The diacyl galactomannans are more soluble in chloroform than in benzene, while the diacyl mannan B's are only slightly soluble in chloroform and benzene, both of which readily dissolve the much lower molecular weight diacyl mannan A's. The purified diacyl galactomannans are clear or transparent to brownish translucent, tough plastics. The diacyl mannan B's are solid, insoluble materials.

The diacyl galactomannans generally are soluble in mineral oils when heated above 100° C. On cooling such hot solutions to room temperature, gels are formed which may settle out on standing to form a clear supernatant phase. The diacyl mannan A's are more soluble in mineral oils, and the diacyl mannan B's are less soluble. The following is a specific example of the preparation of a diacyl galactomannan from locust bean gum:

Example A

One mole of powdered polymannan obtained from locust bean gum (molecular weight approximately 31,000) dried at 100 to 110° C. for twenty-four hours, 1.5 moles of lauroyl chloride, 1.5 moles of pyridine and about 4.7 moles of N,N'-dimethylformamide were heated on a steam bath with stirring for twenty-four hours, taking precautions to exclude external moisture. At the end of the reaction time the mass was poured with vigorous stirring into a boiling solution of 2 moles potassium carbonate in 2600 cc. distilled water and mascerated for thirty minutes in order to leach out all unreacted fatty acid chloride. The solution was cooled to room temperature and filtered. The material on the filter paper was washed thoroughly with water and then dried overnight at 120° C. The desired polysaccharide was then isolated from the reaction mass by extraction with 8 liters of boiling chloroform followed by filtration and evaporation. Analysis showed that approximately 2 moles of the lauroyl chloride had reacted per mole of saccharide unit in the mannan polymer.

By the same procedure, the other acylated polysaccharides listed in Table I also were prepared.

The acylated mannan compound is ready for use as a lubricating oil additive to improve the viscosity index of a lubricating oil. However, it is preferable to borate it, so as to better oil solubility and obtain the advantages of boron in the oil.

The introduction of a borate unit into the acylated polysaccharide can be effected by conventional procedures, and borating reagents. Boric acid and boric anhydride are the usual borating reagents in these pro-

cedures; boric acid is preferred, and is referred to in the ensuing discussion for convenience, but it will be understood that the anhydride is its equivalent. Suitable methods are given in U.S. Patent No. 2,741,548 referred to above. The reaction mixture must include a component other than the polysaccharide and the borating agent having at least one reactive hydroxyl group, which will have the function of holding the number of cross links formed by boric acid or boric anhydride at a minimum.

Boration of the acylated polysaccharide with boric acid or anhydride alone produces a glassy or plastic material which is insoluble in oil. For example, boration of the dilauroyl locust bean gum of Example A with boric acid in benzene alone under reflux at the boiling point of benzene followed by cooling of the benzene at 100° C. produced a glassy or plastic material insoluble in lubricating oil even at 150° C. Similarly, boration of dilauroyl mannan A and dilauroyl vegetable ivory nut mannans (predominantly mannan A with some mannan B and a small percentage of cellulose) with boric acid produced a product not dispersible with the lubricating oil and not completely stable.

If the boration is effected in the presence of an alcohol, oil solubility is maintained through the limitation of cross linking which favors the formation of non-cross-linked side chains of the type enumerated above in connection with the general formula of the borate unit.

The alcohol which is employed as a third component can be a monohydric or dihydric aliphatic alcohol. A monohydric alcohol will give a borate unit of the type of (1) or (2)(i) above. The dihydric alcohol is preferably a glycol in which the hydroxyl groups are α or β to each other. Glycols will give a borate unit of the type of (1), (2)(i) or (2)(ii) above, depending upon the relative proportions of boric acid and the glycol.

The alcohol will, of course, have a sufficient number of carbon atoms and a structure corresponding to the aliphatic and hydroxy aliphatic groups mentioned above in discussing the formula of the borate unit. A mixture of alcohols will give complex additives with desirable properties.

It accordingly follows that in the borate reaction mixture there will be from 1 to 2 moles of boric acid per mole of saccharide unit of the polysaccharide, and from 1 to 1.5 moles of alcohol per mole of boric acid. There would usually be employed a slight excess of the alcohol, to ensure that a minimum of cross links are formed involving boric acid, or if formed are broken in the course of further reaction, to react with the alcohol remaining.

In addition to the polysaccharide and borating agents, it is desirable to include in the reaction mixture a solvent for all of the components. This most conveniently is the lubricating oil used as a base for the final lubricating oil composition. Thus, the product of the boron reaction is the lubricating composition which is desired, and the concentration of the additive therein can be readily adjusted as desired by dilution with more lubricating oil.

If the boration of the acylated polysaccharide is carried out in the presence of a solvent other than lubricating oil, the solvent is removed and the composition of the invention then is prepared simply by mixing the polysaccharide additive with the oil at room temperature or above. These additives are soluble in the oil at room temperature, although in most instances solution is expedited by heating the oil with stirring. No supplemental solvents are required.

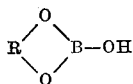
The following example is illustrative:

Example B

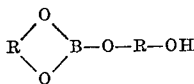
One mole of 2-ethyl-hexanediol-1,3, 1.4 moles of the dilauroyl galactomannan of Example A and 2 moles of boric acid were heated in 15 liters of lubricating oil of conventionally refined neutral stock, 70 SSU at 100° F., with stirring at 130 to 140° C. for 0.5 hour. The reaction mixture was filtered while hot through fine porosity filter paper.

The alcohol also can be tied to the boric acid in the form of an organic borate. The monohydric alcohols can be used in the form of, for example, the corresponding trialkyl borates, for instance, triethyl borate, tributyl borate and trihexyl borate. The glycols can be used in the form of the corresponding glycol borates, e.g.,

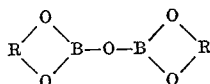
(a) Monoglycol monoborates of the form:



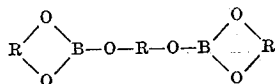
(b) Diglycol monoborates of the form:



(c) Diglycol diborates of the form:



(d) Triglycol diborates of the form:



where the R's are aliphatic radicals as defined in the borate unit general formulae above, and can be different in the same compound.

The organic borates react with the hydroxyl groups of the polymannose chain by a form of ester exchange, in which one of the —B—O—R— linkages is ruptured, and the boron becomes attached to the mannan chain through the oxygen of one of the hydroxyl groups.

Since the above compounds are not generally available, it usually will be easier to use a mixture of boric acid or anhydride and the corresponding glycol or monohydric alcohol.

The borate compounds of the invention can be used with any petroleum hydrocarbon oil of lubricating viscosity. The SAE viscosities for lubricating oils range from No. 10 to No. 70. The neutral oils and refined oils, such as the acid-treated and solvent-extracted oils, are equally useful in the compositions of the invention. The oils may be blended from suitable bright stocks and finished neutral or refined oils of light and heavy viscosities. It is impossible here to give a complete description of the various methods used in the preparation of lubricating oils, but reference is made to the text by Georgi entitled *Motor Oils and Engine Lubrication*, published by Reinhold Publishing Corporation, New York (1950), chapter V, wherein the various types of lubri-

improve engine performance, an amount would be used to give such improvement. Proportions of the boron-containing additives in the lubricating oil composition conveniently are based on the amount of boron in the compound as a percent of the total oil composition, since it is the boron that is the active component in removing deposits. At least 0.05% is the minimum. Use of amounts in excess of 0.5% usually cannot be justified economically, from the standpoint of engine performance improvement.

However, it will be appreciated that the polysaccharide additives of the invention can have a function in addition to that of furnishing boron to the oil. The more linear polysaccharides, for example, the polymannoses which do not have galactose side chains, such as the mannans derived from the vegetable ivory, are capable of greatly improving viscosity index. All of the polysaccharides improve dispersancy of the oil. Therefore, amounts well in excess of 0.5% may be justified on the basis of viscosity index improvement or dispersancy improvement, even though such amounts may not be justified from the standpoint of improvement in engine performance due to boron content.

The following examples of lubricating oil compositions containing polysaccharide additives represent in the opinion of the inventor the best embodiments of his invention:

Examples 1 to 4

By the procedure of Examples A and B there were prepared a number of lubricating oil compositions containing a borated acylated polysaccharide in solution in sufficient amount to furnish about 0.1% boron by weight of the oil. The lubricating oil compositions thus obtained were tested for dispersancy and viscosity index, and analyzed for boron content. The dispersancy test is a measure of the ability of an oil to hold carbon black dispersed. The oil (generally containing the additive to be evaluated) is made up as a 5% solution in benzene and 100 ml. of this solution is placed in a glass stoppered graduate. Carbon black in increments of 0.2 g. is added to the solution and after the addition of each increment is shaken for fifteen seconds and then permitted to stand for five minutes in front of a light and the contents observed for a "break point." This point is seen as a thin upper layer of transparent liquid containing no carbon black particles. The largest amount of carbon black which does not produce a break point is recorded as the result of the test. The test has been calibrated against various additive concentrations of dispersant additives in oil and is a measure of the dispersant or detergent properties of the oil. The following data was taken:

TABLE I

Example No.	Percent 2-ethyl hexane-diol-1,3	Percent H ₃ BO ₃	Polysaccharide percent to furnish a total of 0.1% boron in oil	Approx. percent boron in compound	Carbon black dispersancy (g.)	Viscosity index of oil
Control	None	None	None—base oil alone	None	0.2	103
1	1.27	0.59	5.9% dilauroyl mannan B ¹ mono-2-ethyl hexane-1,3-borate.	0.106	6.5	129
2	1.24	0.58	5.7% dilauroyl mannan A ² mono-2-ethyl hexane-1,3-borate.	0.101	8.5	112.5
3	1.30	0.62	6.4% dilauroyl whole vegetable ivory (mixture of 70% A and 18% B) mono-2-ethyl hexane-1,3-borate.	0.108	6.0	115
4	1.28	0.59	5.9% dilauroyl locust bean gum ³ mono-2-ethyl hexane-1,3-borate.	0.107	7.0	<100

¹ Molecular weight about 100,000, polymannose having n (Formula, p.9) equals about 250.

² Molecular weight about 10,000–14,000, polymannose having n (Formula, p. 9) equals about 23–29.

³ Molecular weight about 310,000, polygalactomannose having n (Formula, p. 9) equals about 380.

cating oils are discussed fully. Any of the oils mentioned therein can be employed in the compositions of the invention.

Inasmuch as the function of the polysaccharide additives of the invention is to furnish boron to the oil to

The increase in carbon black dispersancy is remarkable, of the order of 3000 to 4000%.

The viscosity index of the lubricating oil used in this work was exceptionally good. Yet, an additional improvement in viscosity index was obtainable using the

more linear borated acylated polymannans derived from vegetable ivory. This shows how effective they are as viscosity index improvers. The galactomannans, exemplified by locust bean gum and guar gum, are less effective viscosity index improvers, due no doubt to the inhibiting effect of the galactose side chains.

A much more effective viscosity index improvement is obtainable with an initially low or only moderately good viscosity index oil base, such as, for example, pale paraffin oil, having a viscosity of 74.1 SSU at 100° F.

Examples 5 to 13

A group of dilauroyl mannan A borates were prepared using different glycol and alkyl borates. The polysaccharides were prepared according to Examples A and B, as set forth above, using plate paraffin oil as the base oil (API gravity at 60° F. 31-4, viscosity 74.1 SSU at 100° F., 36.6 SSU at 210° F.). The viscosity index of the lubricating oil composition obtained was then determined as well as the stability of the additive to moist air. The following data was taken:

TABLE III

Example No.	Weight of dilauroyl mannan A, g.	Weight of alkyl or glycol borate	Weight of oil, g.	Before moist air treatment		After moist air treatment		
				Viscosity index	Initial percent boron	Visc. index	Weight of recovered H ₃ BO ₃ , g.	Remaining percent boron
Control	None	None		59	None			
5	6.2	1.4 g. tris(2-ethylhexane-1,3)-diborate	92.4	96	0.109	96	.0119	0.107
6	6.2	2.5 g. triethylborate	91.3	103	0.227	99	.2639	0.181
7	6.2	6.82 g. tris(2-ethylhexyl) borate	87.0	99	0.253	94	.3078	0.199
8	6.2	1.83 g. tris(cyclohexyl) borate	92.0	94	0.119	97	.0199	0.116
9	6.2	1.36 g. tributylborate	92.4	98	0.106	100	.1675	0.077
10	6.2	2.31 g. 2-octanol plus 0.37 g. H ₃ BO ₃	91.3	91	0.107	93	.0535	0.098
11	6.2	1.05 g. hexylene glycol-1,6 plus 0.37 g. H ₃ BO ₃	92.4	95	0.107	90	Nil	0.10
12	6.2	0.55 g. ethylene glycol plus 0.37 g. H ₃ BO ₃	92.4	94	0.107	94	.0289	0.102
13	6.2	0.67 g. propylene glycol-1,3 plus 0.37 g. H ₃ BO ₃	92.8	92	0.107	88	.1232	0.085

¹ Base oil alone.

The initial viscosity index of the base oil was 59. Thus, each of the borated acylated mannan A compounds of the invention increased the viscosity index by at least 50%. The viscosity index was practically unaffected by moist air, practically no boric acid was formed, and boron content was only slightly diminished, showing the great stability to moisture maintained by these compounds.

Examples 14 to 18

A group of acylated borated locust bean gum mannan compounds were prepared as set forth in Examples A and B above, using dilauroyl galactomannans from locust bean gum with various glycol and alkyl borates. The lubricating oil compositions thus obtained were tested for viscosity index before and after moist air treatment to determine stability. The following data was taken:

TABLE IV

Example No.	Weight of dilauroyl galactomannans (locust bean gum), g.	Weight of Alkyl or Glycol Borate	Weight of oil, g.	Before moist air treatment		After moist air treatment		
				Viscosity index	Initial percent boron	Visc. index	Weight of recovered H ₃ BO ₃ , g.	Remaining percent boron
Control	None	None		59	None			
14	6	2.55 g. triethyl borate	94	91	0.22	28	0.0668	0.21
15	6	3.9 g. tributyl borate	94	88	0.22	85	0.1017	0.20
16	6	2.3 g. tris(2-ethylhexyl) borate	94	97.5	0.11	60	0.0273	0.10
17	6	1.8 g. tris(cyclohexyl) borate	94	80	0.115	78	0.0194	0.112
18	6	1.3 g. 2-ethylhexanediol-1,3 plus 0.36 g. H ₃ BO ₃	94		0.10	100		

The viscosity index of the pale paraffin oil was 59. These additives were capable of increasing the viscosity index by at least 1/3, and this increase was maintained in the case of Examples 15, 17 and 18. This shows the increase in water stability with increase in size and extent of branching of the borate side chain. The smaller ethyl borate had a much lesser stability to moist air.

When the above oils were used in the crankcase of an internal combustion engine operating for a period of over seventy-two hours on nonboron-containing gasoline and the engine was then dismantled, the deposits in the combustion chamber were found to contain boron with the attendant advantages of the same in the deposit as discussed earlier.

The compositions were subjected to the Falex E.P. test, run by the standard procedure, where the load on the bearing was increased automatically and the pressure reported was that registered at failure. The wear tests were run on the same equipment using a constant pressure on the bearing.

The data showed that the oil of the invention containing the boron compound tolerated higher pressure and produced less wear than either the corresponding blend without boron or the base oil alone.

It is apparent from the data in the preceding examples that the more linear acylated borated polysaccharides are capable of greatly improving the viscosity index of the oils in which they are incorporated. The acylated

borated polysaccharides containing galactosidal side chains do not have as great an effect on viscosity index. Where the lubricating oil has an initially good viscosity index, they may actually decrease it. However, if the oil has a poor viscosity index to start with, as in the case of pale paraffin oil, they may improve the viscosity index considerably.

All of the acylated borated polysaccharides of the invention, whether or not they contain side chains, are capable of improving the dispersancy of the oil, and they also furnish boron to the oil of a form in which it is advantageous in improving engine deposits.

I claim:

1. Dilauroyl polymannoside 2-ethylhexane-1,3 borate.
2. Dilauroyl polygalactomannoside 2-ethylhexane-1,3 borate.

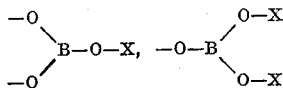
3. Dilauroyl polymannoside ethyl borate.
4. Dilauroyl polygalactomannoside ethyl borate.
5. An oil-dispersible acyl polysaccharide borate having an average per saccharide unit of two aliphatic acyl radicals and borate radicals, the polysaccharide being derived from a cis-hydroxy polysaccharide, the cis-hydroxyl groups of which are substituted with radicals

13

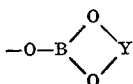
selected from the group consisting of said aliphatic acyl radicals and borate radicals, the aliphatic acyl radicals having the general formula



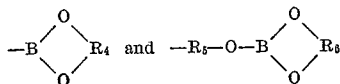
in which R is an aliphatic hydrocarbon radical having from seven to seventeen carbon atoms, and the borate radicals selected from the group consisting of:



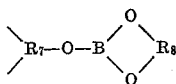
and



the free valences of the borate radical being attached to the polysaccharide nucleus, wherein X is selected from the group consisting of hydrogen, aliphatic hydrocarbon groups having from one to eighteen carbon atoms, hydroxy aliphatic hydrocarbon groups having from one to eighteen carbon atoms,



wherein R₄, R₅ and R₆ are aliphatic hydrocarbon groups having from one to eighteen carbon atoms, and Y is selected from the group consisting of aliphatic hydrocarbon groups having from one to eighteen carbon atoms, hydroxy aliphatic hydrocarbon groups having from one to eighteen carbon atoms, and



wherein R₇ and R₈ are each aliphatic hydrocarbon groups having one from one to eighteen carbon atoms.

6. An oil-dispersible acyl polysaccharide borate in accordance with claim 5, in which the polysaccharide is a polymannoside.

7. An oil-dispersible acyl polysaccharide borate in accordance with claims 6 in which the polymannoside is vegetable ivory.

8. An oil-dispersible acyl polysaccharide borate in accordance with claim 6, in which the polymannoside is vegetable ivory mannan A.

9. An oil-dispersible acyl polysaccharide borate in accordance with claim 6 in which the polymannoside is vegetable ivory mannan B.

10. An oil-dispersible acyl polysaccharide borate in accordance with claim 5 in which the polysaccharide is a polygalactomannoside.

11. An oil-dispersible polysaccharide borate in accordance with claim 10 in which the polygalactomannoside is locust bean gum polygalactomannoside.

12. An oil-dispersible polysaccharide borate in accordance with claim 10 in which the polygalactomannoside is guar gum polygalactomannoside.

13. A process for preparing oil-dispersible acyl polysaccharide borates which comprises reacting a polysaccharide having two adjacent cis-hydroxyl groups per saccharide unit with an aliphatic acyl chloride having the general formula:

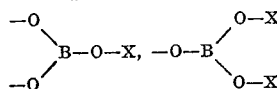


wherein R represents an aliphatic hydrocarbon group

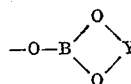
14

having from seven to about seventeen carbon atoms, in the presence of a tertiary amine base capable of forming an amine hydrochloride with hydrogen chloride liberated from the acyl chloride, and a formamide compound

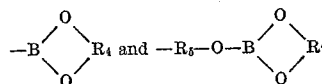
5 having from one to seven carbon atoms, at a temperature within the range from about 50 to 150° C. for a time sufficient to introduce an average of 2 acyl radicals per saccharide unit, and then reacting the acyl polysaccharide with a borating reagent including a borate unit selected from the group consisting of:



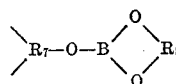
15 and



20 the free valences of the borate radical being attached to the polysaccharide nucleus after such reaction, wherein X is selected from the group consisting of hydrogen, aliphatic hydrocarbon groups having from one to eighteen carbon atoms, hydroxy aliphatic hydrocarbon groups having from one to eighteen carbon atoms,



30 wherein R₄, R₅ and R₆ are aliphatic hydrocarbon groups having from one to eighteen carbon atoms, and Y is selected from the group consisting of aliphatic hydrocarbon groups having from one to eighteen carbon atoms, hydroxy aliphatic hydrocarbon groups having from one to eighteen carbon atoms, and



40 wherein R₇ and R₈ are each aliphatic hydrocarbon groups having from one to eighteen carbon atoms.

14. A process in accordance with claim 13 in which the borating reagent is an aliphatic hydrocarbon borate, the aliphatic hydrocarbon group having from about one to about eighteen carbon atoms.

15. A process in accordance with claim 13 in which the borating reagent is a mixture of boric acid and an aliphatic hydrocarbon alcohol having from one to eighteen carbon atoms.

16. A process in accordance with claim 13 in which the tertiary amine is pyridine and the formamide compound is N',N'-dimethylformamide.

References Cited in the file of this patent

UNITED STATES PATENTS

1,959,590	Lorand	May 22, 1934
2,223,948	Bremer	Dec. 3, 1940
2,224,011	Bremer	Dec. 3, 1940
2,589,226	Carson	Mar. 18, 1952
2,795,547	Harle et al.	June 11, 1957
2,795,548	Thomas et al.	June 11, 1957

OTHER REFERENCES

Deuel et al.:	Nature, vol. 48, pages 96-7 (1948).
Deuel et al.:	Makromol Chem., vol. 3, pages 13 to 30 (1949).