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PROCESS FOR PREPARING DIALKYLBENZENE LUBRICANT COMPOSITION

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ABSTRACT OF THE DISCLOSURE

A process for preparing a di-n-alkylbenzene lubricant composition having improved pour point and low temperature viscosity properties is described. The process comprises disproportionation of mono-n-alkylbenzenes using a Friedel-Crafts catalyst (e.g., $AlCl_3$) in the presence of n-alkyl chlorides ($R=C_8$–C_{18}). Preferably, the mono-n-alkylbenzenes are pretreated with a Friedel-Crafts catalyst before disproportionation. The alkyl group of the monoalkylbenzenes and each of the alkyl groups of the dialkylbenzene contains from about 8 to about 18 carbon atoms. In order to concurrently produce a good yield and improved physical properties the reaction temperature is maintained in the range of 75 to 85° C.

RELATED APPLICATIONS

The following applications have the same assignee as the present application.

Ser. No. 529,284, filed Feb. 23, 1966, discloses and claims a process for preparing di-n-alkylbenzenes by the disproportionation of mono-n-alkylbenzenes using a Friedel-Crafts catalyst (preferably $AlCl_3$).

Ser. No. 725,908, filed May 1, 1968, discloses a lubricant composition comprising a mixture of dialkylbenzenes and monoalkylbenzenes.

BACKGROUND

Various petroleum fractions have been used as lubricants for many years. While the petroleum-derived lubricants have been satisfactory for most uses, there are fields of use, as for example, jet engine lubricants and arctic oils, wherein the requirements render the conventional petroleum-derived lubricants either unsatisfactory or of marginal utility. In an attempt to solve this problem synthetic lubricants (for example, diesters) have been developed having improved properties, particularly improved viscosity and pour point properties. Unfortunately, however, the synthetic lubricants of the prior art have been relatively expensive.

In an effort to provide lower-cost, high quality synthetic lubricants, work has been directed to synthetic hydrocarbons. For example, Pappas and Kant in U.S. 3,173,965 teach that dialkylbenzenes ($R=C_4$ to C_{21}) have properties which render them useful as lubricants. In addition, Becraft and Durr, in U.S. 3,288,716, teach that a bottoms fraction of the product resulting from the condensation of a substantially straight-chain paraffinic hydrocarbon, containing in the range of about 8 to about 18 carbon atoms, with an aromatic hydrocarbon, has properties which render it particularly useful as a lubricant.

I have discovered a process for preparing an improved di-n-alkylbenzene lubricant composition, wherein, briefly

stated, the process comprises disproportionation of mono-n-alkylbenzenes using a Friedel-Crafts catalyst (e.g., $AlCl_3$) in the presence of n-alkyl chlorides ($R=C_8$–C_{18}). Preferably, the mono-n-alkylbenzenes are pretreated with $AlCl_3$ prior to disproportionation. When it is desirable to concurrently produce a good yield and improved physical properties the disproportionation reaction temperature is maintained in the range of 75 to 85° C.

PRIOR ART

U.S. Pat. No. 2,688,643, to Raymond M. Dean et al., teaches a process for preparing an alkyl aromatic hydrocarbon which is useful as a pour point depressant. The process comprises alkylating an aromatic hydrocarbon with a haloalkane (C_8 to C_{30}) using a Friedel-Crafts catalyst. The catalyst may be in the form of a complex with a short-chain alkyl halide, e.g., methyl chloride.

Numerous patents (e.g., U.S. 2,753,384 to Arthur P. Lien et al.) teach the preparation of dialkylbenzenes ($R=C_4$ or less) by the disproportionation of monoalkylbenzenes using a Friedel-Crafts catalyst. In general the prior art on disproportionation teaches that the method cannot be used on higher alkylbenzenes (R is above a C_4) since cleavage and fragmentation of the alkyl chain occurs.

In addition to U.S. 2,688,643, discussed above, a search of the prior art produced the following U.S. Pats.: 2,852,575; 3,173,965; 3,251,898; 3,281,483; 3,288,716; 3,342,886; 3,355,508; 3,392,206; 3,398,206; 1,658,176; 2,495,323; 3,031,513; 3,068,302. Since the above-listed patents are of no more pertinency than the references discussed herein it is not considered necessary that they be discussed.

To applicant's knowledge there is no prior art teaching the disproportionation of C_8–C_{18} mono-n-alkylbenzenes using a Friedel-Crafts catalyst in the presence of a C_8–C_{18} n-alkyl chloride. In addition, there is no prior art which teaches pretreatment of the mono-n-alkylbenzenes with a Friedel-Crafts catalyst prior to the disproportionation reaction. Furthermore, there is no prior art which teaches that a temperature range of 75–85° C. in the disproportionation reaction provides an optimum balance with regard to yield and physical properties.

BRIEF SUMMARY OF THE INVENTION

Broadly stated, the present invention relates to a process for preparing a di-n-alkylbenzene lubricant composition, having improved pour point and low temperature viscosity properties, said process comprising:

(a) Forming an admixture of mono-n-alkylbenzenes and n-alkylchlorides, the alkyl groups of which contain from about 8 to about 18, preferably from about 10 to about 14 carbon atoms;

(b) Contacting the admixture of step (a) with a Friedel-Crafts catalyst under reaction-promoting conditions, and

(c) Recovering from the reaction mass of step (b) a bottoms fraction consisting essentially of di-n-alkylbenzenes.

Preferably, the mono-n-alkylbenzenes are treated with a Friedel-Crafts catalyst prior to conducting the reaction. In addition, when it is desirable to concurrently produce a good yield and improved physical properties the disproportionation reaction temperature is maintained in the range of 75 to 85° C.

In another aspect, the present invention relates to a di-n-alkylbenzene lubricant composition prepared by the above-described processes.

DETAILED DESCRIPTION

Materials used

Suitable mono-n-alkylbenzenes are those containing from about 8 to about 18 carbon atoms in the alkyl groups. Preferably the alkyl groups contain from about 10 to about 14 carbon atoms. The term "n-alkylbenzenes" as used herein refers to benzene containing a substantially straight chain alkyl group, wherein at least 95 percent of the alkyl substituents are bonded to the benzene nucleus through a secondary carbon atom of the respective alkyl group.

In addition to pure mono-n-alkylbenzenes meeting the foregoing description my process can use mixtures of the described mono-n-alkylbenzenes and hydrocarbon compositions containing substantial amounts of mixtures of the described mono-n-alkylbenzenes.

A particularly suitable material for use in my process is a composition, containing a substantial amount of mono-n-alkylbenzenes conforming to the foregoing description, produced in accordance with the process of U.S. Pat. No. 3,316,294. Briefly, U.S. 3,316,294 relates to a process of preparing a detergent alkylate, wherein the process comprises the following steps, broadly stated:

(a) Separating a fraction of substantially straight-chain C_8–C_{18} hydrocarbons from a petroleum distillate substantially free of olefins and containing said straight-chain hydrocarbons together with non-straight chain hydrocarbons;

(b) Chlorinating said fraction to the extent whereby between about 10 and about 35 mole percent of the straight-chain hydrocarbons present are substantially only mono-chlorinated;

(c) Alkylating an aromatic compound, e.g., benzene, with the chlorination product of step (b) in the presence of an alkylation catalyst, and

(d) Recovering from the reaction mass, by distillation, a fraction consisting essentially of mono-n-alkylbenzenes.

N-alkylbenzenes of the type described in the foregoing are available under the trademarks "Nalkylene" 500 and "Nalkylene" 600 from Continental Oil Company. These materials have the following typical properties:

"NALKYLENE" 500

Test	Typical value	Test method
Boiling range, ° F	535–595	ASTM D-447.
Bromine No	0.05 max	ASTM D-1158.
Average molecular weight	231–241	Mass spec.
Color, Saybolt	+25	
Specific Gravity, 20/20	0.85–0.87	ASTM D-287.
Viscosity, Saybolt seconds	40–45 at 100° F	ASTM 88-44.

"NALKYLENE" 600

Test	Typical value	Test method
Boiling range, ° F		ASTM D-477.
5%	580–590	
95%	600–615	
Bromine No	0.05 max	P.M. #921.
Average molecular weight	255–264	Mass spec.
Color, Saybolt	25 min	P.M. #20.
Specific gravity	0.85–0.87	ASTM D-287.
Viscosity, Saybolt seconds	40–46 at 100° F	ASTM 88-44.

Suitable n-alkyl chlorides are normal paraffins chlorinated to the extent that from about 10 and about 35 mole percent are substantially only monochlorinated. Particularly suitable n-alkyl chlorides are those prepared in accordance with U.S. 3,316,294, described hereinbefore. Preferred n-alkyl chlorides are those wherein the hydrocarbon portion has a molecular weight in the range of 154 to 164, in other words, the alkyl groups correspond to that of "Nalkylene" 500, described above.

A Friedel-Crafts catalyst is used in the disproportionation reaction. The term Friedel-Crafts catalyst is believed to be well understood in the art and refers in general to materials such as aluminum halides, boron trifluoride, boron trichloride, antimony chlorides, stannic chloride, zinc chloride and mercuric chloride. Of the Friedel-Crafts catalysts aluminum chloride is preferred. Ordinarily, when aluminum chloride is used as a disproportionation catalyst, a promoter such as water or hydrogen chloride is employed. It is of interest that no promoter per se is employed in the process of my invention.

PROCESS CONDITIONS

Disproportionation reaction

A suitable amount of n-alkyl chlorides for the disproportionation reaction is from about 0.1 to about 3 moles per mole of aluminum chloride (or other Friedel-Crafts catalyst). Preferably, on the same basis, the amount of n-alkyl chlorides is from about 0.5 to about 1.5 moles.

When aluminum chloride is used as the catalyst, a suitable amount is from about 0.50 to about 5 percent by weight based on the mono-n-alkylbenzenes (or pretreated mono-n-alkylbenzenes). Preferably, on the same basis, the amount of aluminum chloride is from about 1 to about 2 percent by weight.

Temperatures in the range of from about 50° C. to about 120° C. are suitable for conducting the disproportionation reaction. I have found that when it is desirable to obtain a good yield concurrently with improved pour point and low temperature viscosity properties it is preferable to use a temperature in the range of about 75 to about 85° C. More preferably the temperature is about 80° C. Temperatures below the preferred range result in a decrease in yield and an increase in the —40° F. viscosity, with the pour point staying substantially the same. Temperatures above the preferred range result in an increase in yield and a decrease in the —40° F. viscosity, but result in an increase (i.e., higher) in the pour point.

Reaction times in the range of from about 5 minutes to about 180 minutes are suitable in the disproportionation reaction. Knowing the other conditions of the process of my invention anyone skilled in this art, without undue experimentation, can readily determine the optimum reaction time.

Following the disproportionation reaction the reaction mass is treated to remove unconsumed catalyst and subjected to a distillation to recover the desired bottoms product. Since those skilled in this art are familiar with the steps of treating the crude alkylate it is unnecessary to discuss this procedure herein.

With regard to the distillation, a cut-point of about 197° C. at 5 mm. Hg is preferable in order to obtain a bottoms product having the desired properties.

PRETREATMENT

Pretreatment of the mono-n-alkylbenzenes provides an improvement in the —40° F. viscosity of the final product (di-n-alkylbenzenes). In addition, it provides a small increase (from 2 to 4 percent) of the yield of final product. In view of these improvements, the preferred aspect of the process of my Invention includes the additional step of pretreating the mono-n-alkylbenzenes.

In conducting the pretreatment, a suitable amount of aluminum chloride is from about 0.5 to about 1.5 percent by weight of the mono-n-alkylbenzenes. Preferably, on the same basis, the amount of aluminum chloride is about 1 percent.

Temperature and time do not appear to be critical in the pretreatment step. Temperatures in the range of from about 40 to about 80° C. and times in the range of from about 15 to about 60 minutes are suitable.

The sludge which results from the pretreatment is separated from the hydrocarbons prior to conducting the disproportionation reaction.

USES FOR MY LUBRICANT COMPOSITION

The lubricant composition disclosed herein can be used per se in a variety of applications. It can be used to lubricate internal combustion and diesel engines under very low temperature operating conditions. In addition it can be used to lubricate turbojet aircraft engines. Still further, it is particularly useful in automatic transmissions.

While my lubricant composition may not meet all of the physical property requirements set forth in the various arctic oil and jet engine lubricant specifications, the composition is so close to meeting the requirements that only minor blending with other lubricants is required to meet the specification. For example, copending application Ser. No. 725,908, referred to in the foregoing discloses a lubricant composition comprising a mixture of dialkylbenzenes and monoalkylbenzenes. Addition of a small amount of monoalkylbenzenes enables the present dialkylbenzene composition to meet the required specifiiation. In order to illustrate how closely the lubricant composition of my invention comes to meeting the required arctic oil and jet engine lubricant specifications, these specifications are set forth below. Mil-L-10295A is an arctic oil specification, while Mil-L-23699A is a jet engine lubricant specification.

MIL-L-10295A—SPECIFICATIONS

Physical property	Requirement limits	
	Minimum	Maximum
Viscosity, kinematic, cs.:		
At 210° F	5.75	
At −40° F		8,500
Pour point, ° F		−65
Stable pour point, ° F		−65
Flash point, COC, ° F	290	

MIL-L-23699A—SPECIFICATIONS

Physical property	Requirement limits	
	Minimum	Maximum
Viscosity, kinematic, cs.:		
At 210° F	5.00	5.50
At 100° F	25.0	
At −40° F		13,000
Flash point, ° F. (COC)	450	
Pour point, ° F		−65
Evaporation loss, percent, 400° F. for 6.5 hours		10

In order to disclose the nature of the present invention still more clearly, the following illustrative examples will be given. It is to be understood that the invention is not to be limited to the specific conditions or details set forth in these examples except insofar as such limitations are specified in the appended claims.

EXAMPLE 1

This example illustrates the preferred conditions of my process, which include pretreatment of the mono-n-alkylbenzenes and an 80° C. temperature in the disproportionation reaction.

The mono-n-alkylbenzene used in this example was "Nalkylene" 600, described in the foregoing. The alkyl chlorides were intermediates resulting from the production of "Nalkylene" 500.

Duplicate runs were made.

PRETREATMENT

The mono-n-alkylbenzene was added to a creased reaction flask. While employing mechanical agitation the contents of the flask were heated to 40° C. whereupon the anhydrous $AlCl_3$ (one wt. percent) was added and the reaction continued for 30 minutes at 40–45° C. The reaction product was then gravity settled for 2 hours at ambient temperature. The crude alkylate phase was separated from the sludge phase by decantation and reserved for disproportionation; the sludge was discarded.

DISPROPORTIONATION

Materials

Pretreated alkylate—600 g.
Anhydrous $AlCl_3$—6.0 g. (0.045 mole)
Alkyl chlorides 4.6% Cl—39.3 g. (0.055 mole)

The pretreated alkylate was added to a creased reaction flask and, while mechanical agitation was used, heated to 65° C. The $AlCl_3$ and alkyl chlorides were then added to the reaction vessel and heating continued to 80° C. The reaction was maintained at 80° C. for one hour, after which the reaction mass was transferred to a separatory funnel where it was gravity settled for 1 hour at ambient temperature. The alkylate phase was separated from the sludge phase and washed as follows: 300 ml. water, 300 ml. 5% aqueous NaOH, then three 300 ml. to neutral point ("Hydroin" paper). The last gravity settle period was overnight. The washed alkylate was then distilled with the following fractions being obtained:

(a) benzene
(b) paraffin
(c) monoakylate
(d) Bottoms-di-n-alkylbenzenes (material boiling above 197° C. at 5 mm. Hg.)

The bottoms fraction was then treated with 1.25 wt. percent Filtrol clay and filtered through Hyflo.

The data on each of the runs and on a composite of the runs are shown below.

	Run No.		
	A	B	Composite
Yield [1]	25.9	27.0	
Viscosity, cs. ° F.:			
100	32.85	30.99	31.80
210	5.44	5.24	5.36
−40	11,044	10,288	10,611
V.I.	112	111	113
Pour point, ° F	−70	−65	−70
Flash, C.O.C., ° F			470
Evaporation low, wt. percent (6.5 hours, 400° F.)			8.4

[1] Grams bottoms/grams mono-n-alkylbenzenes charged/100.

EXAMPLE 2

This example uses a series of runs to illustrate the effect of pretreatment and varying amounts of alkyl chlorides.

The mono-n-alkylbenzenes and alkyl chlorides were the same as in Example 1. The process conditions were the same as in Example 1, except for pretreatment and amount of alkyl chlorides. Where pretreatment was used, the conditions were the same as in Example 1.

EXAMPLE 3

This example is comparative and using a series of runs shows the effect of using water or HCl in the disproportionation reaction instead of alkyl chlorides. The example also shows the effect of varying temperatures in the disproportionation reaction.

The mono-n-alkylbenzenes were the same as in Example 1.

Other than discussed above or shown in the table, the conditions were the same as in Example 1.

The data for this series of runs are shown in the tables below.

DISPROPORTIONATION RUNS IN EXAMPLE 2

	Run No.						
	A	B	C	D	E	F	G
Pretreated	Yes	Yes	Yes	No	No	No	Yes
Disproportionation conditions:							
Alkylate g	600	600	600	600	600	600	600
Wt. percent $AlCl_3$ on alkylate	1.0	1.0	1.0	1.5	1.5	1.5	1.0
Mols $AlCl_3$	0.045	0.045	0.045	0.067	0.067	0.067	0.045
Alkylchlorides, g.[1]	9.3	19.7	78.6	19.7	39.3	78.6	None
Mols Cl charged [2,3]	0.012	0.026	0.10	0.026	0.051	0.10	None
Reaction time, hours	1	1	1	1	1	1	1
Reaction temperature, ° C	80	80	80	80	80	80	80
M Cl [3]/M $AlCl_3$	0.27	0.58	2.22	0.39	0.76	1.49	None
Crude alkylate, g	586.3	542.1	637.0	591.0	612.3	650.4	577.6
Distillation chg. g	576.8	532.6	623.2	584.9	606.5	628.5	563.7
Yield:							
Benzene fraction/alkylate chg. ×100	4.4	3.9	3.5	2.2	2.4	3.4	3.5
Paraffin fraction/alkylate chg. ×100	8.8	7.1	14.0	10.0	8.6	13.0	3.5
Monoalkylate fraction/alkylate chg. ×100	64.2	56.6	59.0	64.2	66.4	69.9	65.1
Btms. fraction/alkylate chg. ×100	23.4	22.2	27.8	20.3	22.7	21.7	22.6
Bottoms properties, viscosity, cs.:							
−40° F	11,345	11,425	11,272	13,422	13,286	13,052	13,485
100° F	34.71	33.81	32.99	34.84	34.28	33.94	33.94
210° F	5.52	5.46	5.41	5.60	5.52	5.49	5.49
V.I.	104	106	108	108	107	107	107
Pour point	−65	−65	−65	−65	−65	−70	−60

[1] Alkylchlorides 4.6 wt. percent Cl.
[2] G.; Cl, 35.46.
[3] Present as alkylchlorides.

EXAMPLE 3

	Run No.					
	A	B	C	D	E	F
Disproportionation conditions:						
Temp., ° C	110	80	50	100	80	50
Time, hrs	1	2	2	1	2	2
Promotion	HCl	HCl	HCl	H_2O	H_2O	H_2O
Wt. percent $AlCl_3$	1.0	2.0	2.0	1.5	1.5	2.0
Properties of bottoms:						
Viscosity, cs., −40° F	12,297	10,000	10,376	12,035	13,038	13,052
V.I.	113	116	118	101	111	110
Pour point, ° F	−60	−55	−60	−60	−65	−70
Yield, percent	29.2	32.1	19.7	29.1	20.5	11.8

While particular embodiments of the invention have been described, it will be understood, of course, that the invention is not limited thereto, since many modifications may be made; and it is, therefore, contemplated to cover by the appended claims any such modifications as fall within the true spirit and scope of the invention.

The invention having thus been described, what is claimed and desired to be secured by Letters Patent is:

1. A process for preparing a di-an-alkylbenzene lubricant composition, each of the alkyl groups of said di-n-alkylbenzene containing from about 8 to about 18 carbon atoms, said composition having improved pour point and viscosity properties, said process consisting essentially of:

(a) forming an admixture of mono-n-alkylbenzenes and n-alkylchlorides, the alkyl groups of said mono-n-alkylbenzenes and said n-alkylchlorides containing from about 8 to about 18 carbon atoms,
(b) contacting the admixture of step (a) with from about 0.5 to about 5 weight percent, based on said mono-n-alkylbenzenes, of a Friedel-Crafts catalyst under reaction-promoting conditions,
(c) recovering from the reaction mass of step (b) a bottoms fraction consisting essentially of di-n-alkylbenzenes,

said process being characterized further in that said n-alkyl-chlorides of step (a) are present in an amount in the range of from about 0.1 to about 3 moles per mole of said Friedel-Crafts catalyst in step (b).

2. The process of claim **1** wherein said Friedel-Crafts catalyst is aluminum chloride.

3. The process of claim **2** wherein said mono-n-alkylbenzenes are pretreated with aluminum chloride.

4. A process for preparing a di-n-alkylbenzene lubricant composition, each of the alkyl groups of said di-n-alkylbenzenes containing from about 10 to about 14 carbon atoms, said lubricant composition having a pour point of at least −65° F., said process consisting essentially of:

(a) forming an admixture of mono-n-alkylbenzenes and n-alkylchlorides, the alkyl groups of said mono-n-alkylbenzenes and said n-alkylchlorides containing from about 10 to about 14 carbon atoms,
(b) contacting the admixture of step (a) with from about 0.5 to about 5 weight percent $AlCl_3$, based on said mono-n-alkylbenzenes, at a temperature of from about 50° C. to about 120° C. for a time in the range of from about 5 to about 180 minutes,
(c) recovering from the reaction mass of step (b) a bottoms fraction consisting essentially of di-n-alkylbenzenes,

said process being characterized further in that said n-alkylchlorides of step (a) are present in an amount in the range of from about 0.1 to about 3 moles per mole of aluminum chloride catalyst in step (b).

5. The process of claim **4** wherein the monoalkylbenzenes are pretreated with from about 0.5 to about 1.5 weight percent $AlCl_3$ at a temperature in the range of about 40 to about 80° C. and for a time of from about 15 to about 60 minutes.

6. The process of claim **4** wherein the amount of $AlCl_3$ is from about 1 to about 2 weight percent.

7. The process of claim 6 wherein said n-alkyl-chlorides of step (a) are present in an amount in the range of from about 0.5 to about 1.5 moles per mole of aluminum chloride catalyst in step (b).

8. The process of claim 7 wherein the reaction temperature is from about 75 to about 85° C.

9. The process of claim 8 wherein the monoalkylbenzenes are pretreated with from about 0.5 to about 1.5 weight percent $AlCl_3$ at a temperature in the range of about 40 to about 80° C. and a time of from about 15 minutes to about 60 minutes.

10. The process of claim 9 wherein the bottoms fraction is obtained by distilling the reaction mass using a cut-point of 197° C. at 5 mm. Hg.

References Cited

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