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3,159,608 COPOLYMERIZATION OF ETHYLENE AND

VINYL ACETATE Stephan Ilnyckyj, Sarnia, Ontario, Canada, assignor to Esso Research and Engineering Company, a corpora- ⁵ tion of Delaware

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The present invention relates to the manufacture of 10 pour depressants, particularly for use with middle distillates. The pour depressant of the present invention comprises copolymers of ethylene with up to about 50% by weight of an olefinically unsaturated aliphatic monomer containing from about 3 to 5 carbon atoms per 15 from about 60 to 99% as compared to parts by weight molecule. The copolymers of a particular average molecular weight are obtained by controlling the conditions of reaction. The preferred copolymer of the present invention is a particular copolymer of ethylene and vinyl acetate. Pour depressants of improved potency and at 20 a higher yield relative to amount of peroxide employed are secured by utilizing a benzene solvent containing a critical quantity of toluene.

The present application is a continuation-in-part of Serial No. 1,838, filed January 5, 1960, entitled "Process 25 for the Manufacture of Improved Pour Depressants for Middle Distillates," inventor: Stephan Ilnyckyj.

With the increase in the use of hydrocarbon fuels of all kinds, a serious problem has arisen in areas frequently subjected to low temperatures in the cold test charac- 30 teristics of fuels. Particularly, serious problems have been encountered with heating oils and diesel and jet fuels that have too high a pour point, resulting either in distributional or operating difficulties or both. For example, the distribution of heating oils by pumping or 35 syphoning is rendered difficult or impossible at temperatures around or below the pour point of the oil. Furthermore, the flow of the oil at such temperatures through the filters cannot be maintained, leading to the failure of the equipment to operate.

Also, the low temperature properties of petroleum distillate fuels boiling in the range between about 250° and about 750° F. have attracted increasing attention in recent years because of the growth of market for such fuels in subarctic areas and because of the development of turbo-jet aircraft capable of operating at altitudes where temperatures of -50° F. or lower may be encountered.

It is, therefore, an object of the present invention to set forth an improved process for the manufacture of very effective pour depressants for middle distillates and 50 lighter oils. In general, these oils boil in the range from about 250° to 750° F.

It is a still further object of the present invention to provide heating oils, diesel fuel oils, kerosines and jet fuels having low pour points. Aviation turbo-jet fuels in 55 which the polymers may be used normally boil between about 250° and about 550° F. and are used in both military and civilian aircraft. Such fuels are more fully defined by U.S. Military Specifications MIL-F-5624C, MIL-F-25554A, MIL-F-25558A, and amendments 60 thereto. Kerosines and heating oils will normally have boiling ranges between about 300° and about 750° F. and are more fully described in ASTM Specification D-396-48T and supplements thereto, where they are re2

ferred to as No. 1 and No. 2 fuel oils. Diesel fuels in which the polymers may be employed are described in detail in ASTM Specification D-975-53T and later versions of the same specification.

The process of the present invention produces copolymers of ethylene and up to about 50% by weight of an olefinically unsaturated aliphatic monomer containing from about 3 to 5 carbon atoms per molecule. In general, these compounds may comprise vinyl acetate, vinyl propionate, methyl methacrylate, allyl ethyl ether, divinyl ether, acrylonitrile, vinylacetonitrile and the like.

The preferred copolymers comprise ethylene-vinyl acetate copolymer. It is preferred that the parts by by weight of ethylene in the copolymer be in the range of vinyl acetate in the range from about 40 to about 1%. A very desirable ethylene vinyl acetate copolymer contains about 15 to 28% by weight of vinyl acetate as, for example, about 20 parts by weight of vinyl acetate.

The molecular weights of the ethylene-vinyl acetate copolymer are critical and should be in the range from about 1,000 to 3,000, preferably in the range from about 1,500 to 2,200. The molecular weights are determined by K. Rast's method (Ber. 55, 1051, 3727 (1922)).

The ethylene-vinyl acetate copolymer as described above is used in a concentration in the range from about .001 to 0.2% by weight, preferably in a concentration in the range from about .005 to .1% by weight.

In accordance with the present invention, the polymerization process is conducted in a benzene solvent having added thereto a critical quantity of toluene. The initiator comprises any peroxy compound, preferably ditertiary-butylperoxide. The temperature of the polymerization reaction is in the range from about 280° to 340° F. A very desirable temperature is about 300° F. The pressure is in the range from about 1000 pounds to 5000 pounds, preferably in the range from about 1200 to 3000 pounds. The amount of toluene present is in the range from 1% to 30% by volume, preferably in the range from about 5 to 20% by volume based upon the quantity of benzene present.

The autoclave or similar equipment containing the solvent, initiator and vinyl acetate is purged with nitrogen, then with ethylene before charging with a sufficient amount of ethylene to yield the desired pressure when heated to the reaction temperature. During the polymerization, additional ethylene is added to maintain the pressure at the desired level. Polymerization is considered complete when the pressure drops less than 50 p.s.i.g. per hour. The product is stripped free of solvent and unreacted vinyl acetate under vacuum.

A number of operations were carried out wherein copolymers were produced under different pressures and other varying conditions. These copolymers were then tested as pour depressants in a blend of virgin gas oil and a catalytically cracked gas oil having an ASTM pour of $+20^{\circ}$ F. The virgin gas oil boiled in the range from about 350° to 700° F., and the cracked gas oil boiled in the range from about 350° to 650° F. As pointed out heretofore, the critical factors with respect to producing desirable polymers are the molecular weights and the concentration of the vinyl acetate in the polymer. The results of these tests are shown in the following Table I. [Conditions: Temperature 300° F., total time 3½ hours. Vinyl acetate 300 mls. over 3 hours, di-t-butyl peroxide 30 mls. over 3¼ hours.]

Operation	A	в	с	D
Conditions:				
Pressure, p.s.i.g	900	1,200	1,200	1,200
Benzene, mls	1,800	1,800	1,710	1,440
Toluene, mls Product:	nil	nil	90	360
Yield, g	731	970	870	753
Copolymer, g./Peroxide, g Yield and Efficiency, Increase,	30.7	40.8	36.6	31.6
Percent	0	36.0	19.4	3.0
Vinyl Acetate, wt. percent	30.4	23.7	24.0	26.4
Molecular Weight 1	1,800	3,170	2,780	1,800
Viscosity at 100° F., cs. ² Pour Depression, ⁸ ° F.:	318	995	345	102
With 0.015 wt. percent	55	25	50	65
With 0.025 wt. percent	75	55	65	>85

¹ By cryoscopy in phenanthrene.
² 50/50 copolymer/kerosene solution.
³ In Reference Oil, ASTM Pour +25° F.

From the above it is apparent that in Operation A with a pressure at 900 pounds, a very satisfactory pour depressant was secured. This depressant had a molecular

weight of about 1800 and a satisfactory viscosity of 318. On the other hand, in Operation B, the yield was 25 greatly increased. However, the product had a molecular weight of about 3170 and a viscosity which is not at all satisfactory. Furthermore, the potency of the product was not satisfactory.

In Operation C and D conducted at 1200 pounds, in the 30 presence of relatively minor quantities of toluene, the yields were appreciably increased and the viscosities excellent. Furthermore, the potency of the resulting prod-ucts were very great. The increased yield obtained in Operation C indicates that there is an optimum concen- 35 tration of toluene in benzene for any given conditions.

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This optimum concentration is determined by pressure and desired composition of copolymer.

What is claimed is:

1. Process for the manufacture of a pour depressant 5 comprising a copolymer of ethylene and vinyl acetate which comprises introducing ethylene into a reaction zone containing a peroxy compound and a benzene solvent to which has been added from about 1-30% by volume of toluene, thereafter raising the temperature of said re-10 action zone to a temperature in the range from 280° to 340° F. and to a pressure in the range from 1000 to 5000 pounds per sq. in., thereafter adding to said reaction zone vinyl acetate and sufficient ethylene to maintain the pressure in said range, carrying out said reaction at a tem-15 perature in the range from 280° to 340° F. for a period of from 2 to 16 hours under conditions wherein the concentration of the vinyl acetate in the benzene solution varies from about 0.2 to 10.0%, whereby a polymer having a molecular weight in the range from about 1000 to 20 3000 is secured, wherein the concentration of the vinyl

acetate in the product will vary from about 15 to 28% by weight.

2. Process as defined by claim 1 wherein the amount of toluene present is in the range from about 5 to 20% by volume as compared to the benzene present.

3. The process as defined by claim 1 wherein said peroxy compound is di-tertiary-butyl-peroxide.

References Cited in the file of this patent UNITED STATES PATENTS

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OTHER REFERENCES

Mellan: Industrial Solvents, page 272, Reinhold (1950).