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A SYSTEMATIC LOOK AT DESIGNING A FLOW IMPROVER ADDITIVE IN WAXY INDIAN DIESEL FUELS[#]

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ABSTRACT

With a view to probing into the various important factors that contribute to the success of a comb-type flow improver additive in commercial waxy Indian diesel fuels, several polymers of long-chain acrylates, vinyl alkanoates, and vinyl ethers have been synthesized and assessed as pour point depressants in well characterized diesel fuels. Matching of the polymethylene polymer pendant chain length with that of the *n*-alkanes of the diesel fuel and an optimum spacing of the long pendants achieved by insertion of smaller ones into the polymer backbone to improve the solubility parameter of the polymer have been recognized as important requirements in designing an efficient pour point depressant.

INTRODUCTION

The poor quality of diesel fuels the world over arising out of the increased use of waxy crude oils, particularly, in terms of their cold flow properties, can be traced mainly to the presence of large quantities of *n*-paraffins in them. It is, therefore, necessary to have a clear understanding of the behaviour of *n*-paraffins in diesel fuel under different temperature gradients.

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As the diesel fuel is sufficiently cooled, solidification occurs progressively over a range of *ca* 5-10°C. The basic structure of the wax crystals thus separating out is orthorhombic.[1] The principal components (>95%) of these waxes are *n*-alkanes in the carbon number range of *ca* C_{15}-C_{35} of a typical diesel fuel. Nucleation commences below the cloud point in a habit of thin flat rhombic plates whose dimensions in the plane of the plates could be in the region of 100-1000μ with a thickness of the order of 1-10μ. Ultimately, the edges get sandwiched resulting in the gel formation which occurs typically around 3°C below the pour point of the fuel.

One of the conventional additives used to overcome this problem was ethylene-vinyl acetate copolymer (EVA) of specific composition.[2] The additive partly destabilizes the fast growing faces of the wax crystals to produce more compact habits in which the crystals were usually needle-shaped and much reduced in size, *i.e.*, of the order of 10-100μ. To achieve a much smaller crystal size of, say, 1-2μ, an additive is required to be tailored to interact more specifically with the growing crystals. Such a new generation wax crystal growth inhibitor locks in to the optimum lattice sites in the growing crystal just as a drug binds to its biological host molecule. Further, in combination with other additives, our ultimate targets are to achieve: (i) thickening of the growing crystals after nucleation instead of lengthening (ii) depression of cloud point;[3] (iii) preventing the crystals from sticking together at all stages, and an (iv) antisettling effect, which keeps the separated crystals in suspension over long periods.[4] Attaining all these objectives would need a fresh look at designing effective flow improvers. In the present paper we have explored a few fundamental criteria for designing such comb-type polymeric additives. For this purpose, homopolymers of acrylates, vinyl alkanoates, and vinyl ethers derived from 1-alkanols and 1-alkanoic acids of even carbon number in the C_{12}-C_{18} range and several acrylate copolymers of *n*-octyl acrylate with long-chain acrylates have been synthesized, characterized, and their efficiency as pour point depressants assessed in commercial waxy Indian diesel uels through cloud point and pour point determinations of their toluene solutions.

MATERIALS

1-Alkanols and 1-alkanoic acids of even carbon number in the C_{12}-C_{18} range (97-98% purity) were from Fluka A.G. and used as such.

SYNTHESIS OF MONOMERS

n-Alkylacrylates : Long-chain acrylates of C_{12}-C_{18} 1-alkanols were prepared by their direct acid-catalyzed esterification with acrylic acid in the presence of *p*-toluenesulfonic acid.[5] After the normal work-up, the unconverted alcohol (5-10 wt%) present in the crude product was removed by passing through a freshly activated neutral alumina column. The products were obtained in yields of 75-85%.

n-Vinylalkanoates : Vinyl esters of C_{12}-C_{18} alkanoic acids were prepared by their vinylation with excess vinyl acetate in the presence of mercuric acetate and sulfuric acid as the catalyst following the procedure of Jordan and Swern.[6] The products were purified by distillation followed by passing through a neutral alumina column. The products were obtained in yields of *ca* 60%.

n-Alkyl vinyl ethers : *n*-Alkyl vinyl ethers were prepared by reaction of acetylene with C_{12}-C_{18} 1-alkanols in the presence of 5 wt% of potassium hydroxide in methanol at $180 \pm 2^{o}C$.[7] Pure alkyl vinyl ethers were obtained by distillation of the reaction mixture followed by percolation of the hexane solution of the product through freshly activated neutral alumina to remove any unconverted alcohol. The column was thoroughly washed with *n*-hexane to elute the desired vinyl ether, which was isolated by the solvent removal.

POLYMERIZATION OF ACRYLATES AND VINYL ESTERS

The homo- and copolymers of *n*-alkylacrylates and homopolymers of vinylalkanoates were prepared by free radical initiation, in each case, in benzene (monomer/solvent ratio 1:1 by weight) under nitrogen atmosphere at $70^{o}C$ for 7h in the presence of benzoyl peroxide (0.07 wt% of monomer). The polymers were precipitated by methanol and freed from any unconverted monomer by repeated precipitation with methanol. The products were dried at $45^{o}C$/3-5 mm Hg for several hours.

POLYMERIZATION OF VINYL ETHERS

Vinyl ethers were polymerized in *n*-heptane by cationic polymerization, at $20^{o}C$ using BF_3-H_3PO_4 complex as the initiator. After usual work-up, the polymers were precipitated by acetone.

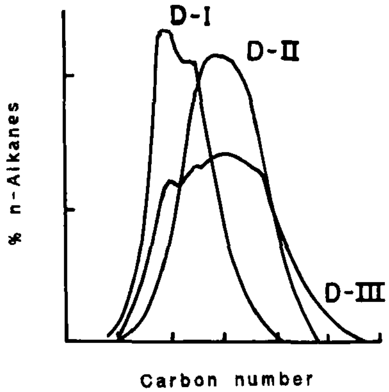

Fig: Carbon number distribution of n-alkanes in diesel fuels, DI-DIII.

TABLE 1
Properties of diesel fuels, DI-III

Property	D-I	D-II	D-III
Distillation (ASTM D86)			
IBP °C			
5% vol	142	113	147
50% vol	247	225	296
95% vol	262	339	307
n-Paraffins, wt%	23	22.6	17.7
Average Carbon No. of *n*-Alkanes	19.2	19.1	16.4
Density at 20oC	0.8409	0.8397	0.8271
RI, n^{20}_{D}	1.4801	1.4702	1.4615
Cloud Point, °C	20	17	3
Pour Point, °C	15	12	-3

CHARACTERIZATION OF POLYMERS

The number-average molecular weights were determined using a Knauer vapour pressure osmometer (VPO) at 60°C in toluene. Pour points (PP) and cloud points (CP) of 5% polymer solutions in toluene[9] were determined following the ASTM D-97 and D-2500 procedures respectively.

RESULTS AND DISCUSSION

n-Alkanes were isolated from three commercial Indian diesel fuels, D-I , D-II, and D-III, by urea adduction.[8] Their carbon number distribution, determined by GC, has been shown in the Figure. Other physical properties of the fuels have been given in Table 1.

All the homopolymers in Table 2 showed weak response as pour point depressants in D-I diesel at low doses, while A1 had no effect. With a view to introducing an n-octyl- "spacer" among the pendants of the poly (*n*-octadecyl acrylate) (A3), a series of copolymers (B1-B6) with varying mole ratios of *n*-octyl- and *n*-octadecyl acrylates were synthesized in accordance with the suggestion made by Knepper.[10] Similarly, *n*-octyl acrylate was copolymerized with C_{16}, C_{20}, and C_{22} acrylates in 1:1 mole ratio to obtain the respective copolymers (B7-B9). Their compositions were presumed to be nearly equal to the initial comonomer ratios due to the similar reactivity ratios of the monomers. Their number-average molecular weights along with the cloud and pour point data of their 5% solutions in toluene have been given in Table 3.

Of all the polymers studied, the two homopolymers, A2 and A3 had the lowest number-average molecular weights. The solubility in toluene, of the copolymers, indicated by CP and PP (nucleation and gel points under temperature gradient), varied with their composition. It is clear from the Table 4 that B4 was fairly efficient in all the three diesel fuels while B7, was most effective in D-III *only* and B1 to B3 fared better in D-I and D-II *only* as PP depressants. A comparison of these results with the *n*-paraffin characteristics of all the three diesels indicated that B7 a copolymer of C_{16} acrylate matches well with the average carbon number of the *n*-alkanes of D-III, *i.e.*, 16. Similarly, B1-B3 contained more of C_{18} acrylate and *n*-alkanes of D-I and D-II had an average carbon number of 19. Again B6

TABLE 2

Evaluation of certain long-chain homopolymers as pour point depressants in DI diesel

Sample Designation	Polymer	$\bar{M}$n	Concentration (ppm)	Pour point Depression,^{0}C
A1	Poly (*n*-octyl acrylate)	7121	up to 2000	nil
A2	Poly(*n*-hexadecyl acrylate)	3200	775	12
			1650	15
			2780-3000	18
			3960	21
A3	Poly(*n*-octadecyl acrylate)	3400	750	9
			1365	12
			2400	18
			3265	21
			4000	27
A4	Poly(vinyl *n*-hexadecanoate)	12,100	383-1880	9
A5	Poly(vinyl *n*-octadecanoate)	12,100	103-170	9
			300-550	12
			780-2200	15
A6	Poly(*n*-hexadecyl vinyl ether)	9786	800-1300	6
A7	Poly(*n*-octadecyl vinyl ether)	12,056	500-3000	6

TABLE 3

Cloud and pour point data on 5 wt% solutions of long-chain acrylate copolymers in toluene

Sample Designation	Polymer	$\bar{M}$n	Cloud Point ^{0}C	Pour Point ^{0}C
	Poly(acrylate)			
A1	*n*- C_8	7121	3	-
A2	*n*- C_{16}	3200	-	-
A3	*n*- C_{18}	3400	6	3
	Monomer mole ratio			
	C_{18} : C_8			
B1	4 : 1	6900	6	-3
B2	3 : 1	6912	6	-3
B3	2 : 1	6814	6	-9
B4	1 : 1	6504	9	-12
B5	1 : 2	6814	3	-
B6	1 : 3	7012	3	-
	C_{16} : C_8			
B7	1 : 1	8261	-	-
	C_{20} : C_8			
B8	1 : 1	8091	9	-12
	C_{22} : C_8			
B9	1 : 1	9812	9	3

TABLE 4
Effect of various polymers at 500 ppm dosage on the pour points of diesel fuels DI-III

Polymer	D-I	D-II Δ POUR IN oC	D-III
B1	9	6	3
B2	12	9	3
B3	12	9	3
B4	9	12	9
B5	3	15	12
B6	3	6	15
B7	3	3	18
B8	6	9	6
B9	6	3	3
A1	0	0	0
A3	6	3	0

contained less of C_{18} acrylate and had similar effect as B7 in D-III. An average of these two extreme specificities of these copolymers was achieved by B4, having *n*-octyl- and *n*-octadecyl acrylates in a 1:1 mole ratio.

These facts point towards the importance of the requirement of the polymethylene segment chain length of the polymer matching the average carbon number of the *n*-alkanes of the diesel fuel for proper additive effectiveness along with the optimum utility of a "spacer". At higher dosage A3 was found to be a very efficient PP depressant in D-I diesel as given in Table 2, but failed in D-II and D-III (Table 4). The optimum utility of the "spacer" was clearly demonstrated in the fact that B4 proved a more versatile PP depressant compared to other copolymers.

In more specific terms introduction of *n*-octyl acrylate into the poly(*n*-octadecyl acrylate) had increased its solubility parameter. A comparison of the temperature range of occurrence of nucleation to the gel formation of different polymers reveals that A3 had a very narrow range of 6°C to 3°C whereas B4 had the widest range of 9°C to -12°C. This clearly points out to the effectiveness of *n*-octylacrylate in increasing the solubility of the polymer and strengthens the concept of "spacer" for a proper additive designing.

The effect of the functionality of the pendant linking the backbone of comb-type polymers on additive efficiency has been shown in Table 2. All the products were tested in D-I diesel under different concentrations. Polyacrylates and polyalkanoates were nearly equally effective with polyethers limping behind.

CONCLUSION

The natural pour point of a diesel fuel was the consequence of an integrated effect of the amount, carbon number distribution, and average carbon number of *n*-paraffin contained therein. For proper design of an efficient comb-type cold flow improver in waxy diesel fuels, optimum polymethylene pendant spacing and matching chain length of the pendant with the average chain length of the *n*-alkanes of the wax have been recognized as important factors. Poly(vinyl ethers) were found to be less efficient as pour point depressants compared to the polyacrylates and poly(vinyl alkanoates) having pendants of the same chain length.

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