STUDIES ON IMPROVING THE FLOW PROPERTIES AND WAXY DISTILLATE FUEL BY USING SOME POLYMERIC ADDITIVES

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ABSTRACT:

Esters of vinyl acetate -maleic anhydride copolymcrs were synthesized by reaction of vinyl acetate with malcic anhydride, then esterflying the product with dodecyl, hexadecyl, NAFOL1822 and -NAFOLI822C alcohol (l-SVAM).Thc resulting FSVAM is purified and characterized through infrared speelroscopy, average molecular weight (wl.average) and polydispersily index. Tf.cse additives were tested as How improvers/pour point depressant for distillate fuel oil.Thc prepared additives showed good performance in improving the How "properties of tested fuel oil.. Wax modification assessed through photoanalysis. The effect of additives type and concentration of wax crystallization behavior at low temperature $(0^{\circ}C)$ were evaluated. There is good correlation between wax modification and value of pour point of the additives.

Key words: Distillate fuel oil, flow improvements, pour point depressants, wax modification. flow additives.

INTRODUCTION:

When waxy crude oils and heavy fuels are stored in tanks, which are not healed, or insulated. the oil, which is in contact with the cold walls of the lank will cool down, and so may stiffen. This leads to difficulties, when the oil is pumped from the tanks (Time el al.,2003), (Khiclr and Mohamed, 2001), (Coutinho et al.,2000), and (El-Gamal et al.,1998). In the storage of crude oil considerable amounts of stiffened oil may remain in the tanks, which reduces the effective capacity of the tanks.This problem is even more important in the transport of waxy crude oils in unheatcd tankers, where the walls of the compartments arc partially formed by the ship wall, which is in direct contact with the cold sea water. The reduced liquefaction of waxy crude oil and heavy fuels at a relatively low temperature will also considerably hamper the transport of these oils through a pipeline. This problem has been well recognized in the past and various additives have been suggested for depressing the pour point \sqrt{t} oil. One function of such pour point depressants is used to change the nature of the crystals Hint precipitate from the oil, thereby reducing (he tendency of the wax crystals to interlock and set into a gel (Srivastava ct al., 2002), (Zuo et al., 2001). (Wang et al., 1999) and (Srivastava et al., 1995). Since adding chemical additives (such as pour depressants (PPDs), cold flow improvers or wax crystal

modifiers) is the most convenient and economic way. It has been found thai with the addition of die additives the shape of the wax crystal changes. Many postulated mechanisms have been predicted forward to explain this phenomenon and lo instruct the pour point depressant product design. Among the mechanism theories, adsorption, co- crystallization nuclcation and improved *waxvsolubility are widely accepted by mechanism researches (Zhang et al., 2004) and (Tang,et a!., 2Q01),The most extensively used flow *for* improvers waxy residual fuel oils are highly branched poly $-\alpha$ -olefin, poly n-alkylacrylate, alkyl esters of unsaturated carboxylic acid α clcfin copolymcrs (Liao and Zhao 1996), ethylene- vinyl fatty acid ester copolymers (Andre and Elizabete 2001), vinyl acetate α -olefin copolymers (Kejan, 1998), styrene- maleic anhydride copolymers (Abou Jil-Naga cf al.,1985) and long chain fatty acid amides (El- Gamal ct al., 1992),For evaluation of the improved opcrabilily of treated waxy distillate fuel determination of flow properties cloud point *(CP), pour* point *(PP)* and cold filler plugging point *(CFPP).* Photomicrographic anaylysis are the most widely adopted (Chen et al, 2003), (El-Sabagh et al., 2002) and (Megahed et al., 2001).

The work *hi* this paper deals with synthesis and evaluation of some types of csterfication of copolymers of vinyl acetate and maleic anhydride $(ESVAM)$ as pour point depressants for $\operatorname{distillator}$ fuel through the determination of flow properties (CP,PP,CFPP test) and pliotomicrographic analysis. The flow improvement activity is further discussed on the base of structure of additives and dislillute fuel composition.

EXPERIMENTAL:

Materials used

Dodecyl alcohol, hexadecyl alcohol, vinyl acetate, maleic anhydride, two linear long-chain alcohol blends (NAFOL 1S22C and NAFOL 1322) were supplied by the CONDA Chemicals Co. with the typical analysis listed in Table (1). The other chemicals are of technical grade.

Tuel' compositions

A waxy fuel oil derived from the western desert crudes were used for evaluating the performance of the synthesized polymeric products. Their physicochcmicai characteristics arc given in Table (2). In addition, the n-paraffin content of the fuel oil tested was determined by urea adduction (Marquet ct al., 1986). Then subjected to gas liquid chromalographic (GLC) analysis (Ll-Gamal, Gad, Faramawi and Gobil 1992) for determination of average molecular weight (wt. average) and molecular distribution as shown in Table (3) and Figure (1).

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Synthesis of polymeric additives:

A 250 ml three $-$ neck flask with a stirring device, a reflux condenser and a capillary ventilated by nitrogen was fixed. The synthesized esters of vinyl acetate- maleic anhydride copolymers were synthesized by reaction vinyl accate (0,5 niol) with maleic anhydride (0.5 mol) in the presence of 2.5 gm of bcnzoyl peroxide and 200 gm. of xylone the mixtures were refluxed for four hours, with stirring in the temperature range 100-120°C under nitrogen flushing. Then remove the solvent by evaporating, finally white powder copolymer (intermediate product) was obtained. Then cstcrfication of copolymers by adding (1 mol) alcohol in the presence of 0.4 gm. P-Toluene sulphonic acid and 200 gm. xylene at 140° C for four hours with stirring continuously. At the same time, remove the water by -product continuously. After three hours from the reaction ,cool the product to 70-SO°C and wash it Iwo times by water. Finally a viscous liquid named esterified copolymer maleic anhydride (ESVAM) was obtained. A homologous series of alcohols with different carbon numbers are obtained : $C_{12}(RX-1)$. C_{16} (RX-2), C_{20} (RX-3), $C_{21.5}$ (RX-4). From IR spectroscopy data the proposed structure of the compound as:

Where R is $(CH_2)_{11}$ CH₃ = $(RX-1)$ or $(CH_2)_{15}$ CH₃ = $(RX-2)$ or NAFOL 1822 = $(RX-3)$ or $NAFOL$ $1822C = (RX-4)$.

Characterization of the prepared polymers:

The synthesized polymers were characterized in terms of average molecular weights (wt. average), and polydispersity index using gel permeation chromatography technique against polystyrene molecular weight standards. The measurements was carried out by a high performance liquid chromalography (I1PLC) apparatus (Waters Model 510) at the following conditions: Solvent: toluene HPLC grade. Column: ultrastyragel 500, 1000, 10000, 100000 Å. Temperature: 25°C.Flow speed: 18 cm³ min⁻¹.

Results are listed in Table (4).

The chemical structure of the prepared copolymers was further studied through infrared spectral analysis (FTJR Apparatus) that showed similar patterns. A representative example KX-1, RX-4 which showed the appearance of the characteristic bands at: $2955-2849$ cm⁻¹(CII stretch),

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1739cm⁻¹ (C=O stretching in aliphatic esters), 1465cm⁻¹ (CH₃ bending) and i 177 cm⁻¹ (C-C stretching) as demonstrated in Figure (2).

Evaluation tests:

Measurement of flow parameters PP₁CP and CFPP.

The prepared polymers were tested for their effectiveness as pour point depressants for the distillate fuel through pour point test according to the ASTM D- 97 procedure. The results are presented as pour point of the pure distillate fuel oil. The pour point reduction was calculated by: Pour point reduction $=$ pp_{pure} $-$ pp_{add}

Where, pp_{pure} is the pour point of fuel oil and pp_{add} is the pour point of the fuel oil containing ESVAM as additive. In addition, they were tested for improving the filterability of the fuel oil through cloud point *(CV)* lest according to the IP (239/82) procedure *ami* cold filler plugging point (CFPPJ lest according to the IP (309/83) procedure.

-Photomicrography

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Photomicrographs showing wax crystallization behavior of the untreated and treated fuel oil samples with polymeric additives at different concentrations have been recorded. An Olypmpus polarizing microscope model BHSP fitted with automatic camera with a 35 mn format was used for photomicrographic analysis. Tie light source was a helium lamp.Thc temperature of the tested gas oil samples was controlled on the microscope slide by an attached cooling thermostat at 0"C. All photos were taken at 100X magnification.

RESULTS AND DISCUSSION:

1-Influence of average molecular yveight of ESMVA copolymers on their effectiveness as flow improvers:

The four synthesized ESVAM (RX-1:R ==12, RX-2: R =16, RX-3:R =20 and RX-4:R =21.5) are assessed as flow improvers at 250 ppm concentration in fuel oil in terms of pour point depression. Their average molecular weights (vvt average) and polydispcrsity index arc determined by HPLC analysis in (Table 4). Data obtained showed that the prepared polymeric addilives have different molecular weights 19280-36760 and the optimum effectiveness is achieved at the range of 28000-34000 approximately (polymers RX-3 and RX-4) vinyl acetate : ..inaloic -.anhydride (2:1) in fuel oiL ll is also observed that the performance of polymers is improved with increasing the polydispcrsity index and the molar ratio of vinyl acetate (Va) maleie anhydride (M) is (2:1) more flowability than $(1:1)$ and $(3:1)$ respectively. Additive RX-4 with the highest polydispcrsity index (3.7) accomplished the optimum pour point depression with respect to other additives, whereas additive RX-I with lowest polydispersity index (1.55) achieved the least depression. This result is compatible with other authors (EI-GamaI, Gad,

Faramawi and Gobil 1992). Thus, it is concluded that average molecular weight and polydispersity index arc substantial parameters controlling the effectiveness of the used polymeric additives.

2-Depression effects on fuel oil by using ESVAM :

2.1 Investigation of PP depression effects:

The PP's of fuel oil are tested before and after using ESVAM (RX-1, RX-2, RX-3 and RX-4) with different concentrations 250,500,750,1000 and 2000 ppm (Table 5) ESVAM exhibited good PP depression effects on these fuel especially on sample RX-4 which showed better results (Where RX-4 dosage was 250,500ppm Δ pp = 21^oC). Synthesized additives are adsorptive and eutectic theories to explain the PP depression mechanism. The PPDs produced at home and abroad so far can only be explained by adsorptive theory. After using PPD and decreasing the temperature, the molecule of PPD adsorb on the surface of newly formed waxes and prevent the growth of the waxes, thus the PP of fuel is reduced. HSVAM's structure is different from the one above. It contains not only polar oxygen- containing groups, but also non polar groups $(-R)$. Its PP depression mechanism can be explained by both adsorptivc and eutectic theories. After using ESVAM and decreasing the temperature. Long chain aJkyls in liSVAM, which appear 'tree branch^{*} type crystallize with waxes together. Therefore the ESVAM \cdot s molecules exhibit a 'tree branch³ type. The waxes distribute in the "tree branches", and it is not easy for them to grow up. At the same time, the oxygen-containing groups can also take life role of preventing the growth of the waxes. In this way, the pp of fuel oil can be reduced. It is obvious that eutectic theory is superior to adsorptive theory. A synthetic path based on eutectic theory should be advanced and re fine that the should have better performance.

2.2 Tests of cloud point (CP):

Table (5) showed that none of denoted additives $(RX-1, Rx-2)$ has any effect on the CP of the fuel approximately. The CP of other samples $(RX-3, Rx-4)$ had more improvement on samples Δ CP_{250ppm} = 2^oC. This may indicate that this family of polymeric structures has no effect on the thermodynamic equilibrium of the fuel and thus do not influence paraffin solubility in (he fuel hydrocarbon system which represents the prime cause of CP depression.

2.3 Tests of cold filter plugging point (CFPP):

Table (6) shows determing results CFPP by using ESVAM.It had some filter aiding limited effects on sample RX-1 and RX-2 but the CFPP of other samples RX-3, RX-4 had much improvement Δ CFPP₂₅₀_{upm} = 5^oC. From both aspects of PP depression and filter aiding ability, the PP depression effect of ESVAM is excellent, and it is suitable for distillate fuel oil, ESVAM exhibited good CFPP depression but the reduction of CP is limited.

2.4. Photoanalysis:

Photoanalysis confirms the above flow tests that evaluate the cold flow properties of "unlrcaled/lrcalcd waxy distillate fuel oil through wax crystallization behavior. Photomicrographs illustrated in photo figures (3,4) show variant wax morphology changes according to the type and concentration of additive. Photofigure (3a) of untreated waxy distillate fuel oil shows large wax crystals. When the fuel oil treated with flow additives of various performance to determine the effect of concentration of each of the additives, RX-1 and RX-2.The wax modification or fuel oil was evaluated at 250, and 2000ppni by photoanalysis. Results shown *In* the pholofigurc (3b- 3c) explain that the wax crystal size becomes gradually from large crystal to a great number of small dots dispersed in the fuel oil. Decreasing the concentration of the flow improvers PPD's increasing small particle crystallites in the following order (fuel oil + 250 ppm RX-2 > fuel oil -i- 250 ppm RX~i).Photomicrographs illustrated in photo figure (4) show the action of either .active s RX-3 or RX-4 has led to signifcanl reduction of wax crystal size and formation of abundant number of fine dispersed crystals particularly by the action of RX-4 pholofigurc (4c). Concerning the correspondent How parameters measurements^ *is* revealed that with the increase of additive activity in terms of Δ pp and Δ CFPP, the induced wax modification is increased to a higher degree in the order $RX-4$ > $RX-3$ > $RX-2$ > $RX-1$ i.e.there is a good correlation between wax modification and measured flow parameters.

CONCLUSTION:

• Some of the prepared esters of C_{12} - C_{23} vinyl acetate-maleic anhydride copolymers with average molecular weight in the range of 19280-36760 were found to he effectiveas pour point depressants/ flow improvers for the investigated waxy distillate fuel oil.

• Both average molecular weight and the polydispcnsity index of additive drastically affect the ,.. ^performance of the pour point depressants / How improvers.

- NAFOL 1822C ester of C_{21.5} vinyl acetate-malcic anhydride copolymers RX-4 has excellent PP depression effects on the fuel oil used in this work, and certain CFPP reduction in part of them (Δ PP_{250ppm} = 2ⁿC , Δ CFPP_{250ppm} = 5^oC , Δ CP_{250ppm} = 2^oC). It is useful to improve low temperature fluidity of fuel oil.
- The PP depression mechanism of ESVAM can be explained by well known eutectic theory.
- Photomicrography is a simple, and fast analytical tooE that can reveal obviously the wax modification induced by flow improvers and wax dispcrsants according to their type and concentration in waxy fuel oil.
- The recorded wax crystallization behavior was correlated with the results of standard flow tests.

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REFERENCES:

Abou El-Naga, H.H., Wedad M. ElAzim, A. and Ahmed, M.M.J., Chemical Technology and Biotechnology, 35A, PP. 241-247 (1985).

Andre, I.C.M. and Elizabete, F.L.J, Petroleum Science and Technology , 19 (1&2) PP.197-204 (2001) .

Chen, J.; Zhang, J. and Zhang, F., Oil and Gas Journal, 101, (31) PP.60-64, August 11 (2003).

Continho, J.A.P., Cauphin, C.and Daridon, J.L., Fuel, 79, PP. 607 (2000).

El-Gamal I.M.; Gad, E.A.14.; Faramawi, S. and Gobeil, S. J. Chem. Tech. Biotechnol., 55, PP.123 $-130(1992)$.

Habuib, O.M.O. Bulletin of Faculty of Science, M.A.and El-Gamal, $M.I.$; Radom, Mansoura, University, 19 (1) (1992).

El-Gamal, I.M., khidr, T.T.and Ghuiba, F. M., Fuel, 77 PP.375-385 (1998).

El-Sabagh, A.M.; Khidr,T.T. and Atta, A.M.,Petroleum Science and Technology 20, (7&8) PP.693-711 (2002).

Kejan, L., Shiyou Lianzhi Yu Huagong, (China) 29 (1) PP.28-30 (1998).

Khidr, T.T.and Mohamed, M.S. Petroleum Science and Technology (19 (15 & 6) PP.547 -560 $(2001).$

Liao, K.T. and Zhao, J. Petroleum Scinence and Technology , 17, (1&2) PP.51-56 (1996).

Marquet, J.R.; Dellow, G.B. and Freitas, E.R., Anal. Chem., 40, PP. 1933 (1968).

Megahed, M.G. and El-Gamal I.M., Modelling, Measurement and Control, 62 (3&4) PP.31-41 $(2001).$

Srivastava, S.P.; Tandon, R.S.; Verma, P.S.; Pandey, D.C. and Goyal, S.K., Fuel, 74 (6) PP. 928-931 $(1995).$

Srivastava, S.P.; Butz ,T.; Tiwari,G.B.; Oschmann ,H.J. and Rahimian,I. Petroleum Science and Technology, 20 (3&4) PP.291-304 (2002).

Tang;N.P.; Phong,N.T.P.;Long,B.Q.K, Thuc-P.D. and Son, T.C.,SPE International Symposium on Oilfield Chemistry , PP.383-394 (2001).

Thue, P.D.; Bich, H.V.; Son, T.C.; Hoe, I.D. and Vggovsky, V.P., Journal of Canadian Petroleum Technology, 24 (6) PP.15-18, June (2003).

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Wang, S.L.; Flamberg, A., and Kikabhai, T., Hydrocarbon Processing, PP.59-62 Feb.(1999).

Zhang, J.; Wu, C.; Li, W.; Wang, Y.and Cao, H. Fuel, 83 (3) PP.315-326 (2004).

Zuo, J.Y. Zhang, D.D. and Ng, H.J., Chem. Engny. Sci., 56, PP.6941 (2001).

Long chain alcohol blend							
	NAFOL.	1822C	NAFOL	1822			
Alcohol composition (wt.%)	C_{16-OH}	$0.\mathbf{i}$	C_{16-011}	0.1			
	$C_{18 \times 00}$	5.0	C_{18} - O_{11}	44.5			
	C_{20} - $_{\text{OII}}$	16.5	C_{20-OH}	10.3			
	$C_{22, \text{OH}}$	77.G	C_{22} on	44.8			
المتعارض والموالي	$C_{24,GHz}$	0.8	$C_{24 \text{ cm}}$	0.3			
Average carbon number (calculated)		C_{av} = 21.5		$C_{av} = 20$			
Density (y/cm^3) approx.		at 80° C = 0.802		at 80° C = 0.810			
Solidification point $(^{\circ}C)$ approx.		64		57			
Flash point $(^{\circ}C)$ approx.		204		202			
Ester No. (mg KOH/g)		0.14		0.02			
Acid No. (mg KOH/g)		0.05		0.01			
fodine No. (mg I/100 mg)		0.31		0.24			
Water $(Wt, %)$	0.04		0.03				

Table 1: Typical Analysis of Linear Long Chain Alcohol Blends (NAFOL)

Table 2: Characteristics of Fuel Oil.

Test	Method	Value
Specific gravity 60/60°F	IP 160/87	0.8290
Kinematic viscosity mm^2S^3 at 40 $°C$ cSt \rightarrow	1P 71/80	4.41
Elash point, "C	IP 34/85 (87)	136
API gravity	D 287-92	30
Cloud point (cp), ^o C	JP 219/82	24
Pour point (pp),"C	JP 15/67 (86)	18
Total sulphur (wt%)	IP 266/87	0.373
Total paraffins content	Urea adduct	19.03
n-paraffins (wt%)	GLC	18.01
lso-paraffins (wt%)	GLC	1.02
Cold filter plugging point (CFPP), °C	1P 309/83	$12 \,$
Distillation ^e C	ASTM 1>-86	
[]		230
10%		250
20%		258
30%		275
40%		286
50%		299
60%		310
40%		335
80%		360
FBP		400

Table 3: Carbon Number Distribution of n-Paraffin Fraction Separated from the Fuel Oil.

Table 4: Characterization of the Prepared Copolymers and Their Performance as Pour Point Depression for Fuel Oil at 250ppm Concentration.

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Va:M= The molar ratio of vinyl acetate (Va) to Maleic anhydride (M).

 $Cn =$ Carbon number of alcohol.

Av M_{wt} = Average molecular weight.

PDI=Polydispersity index.

 ΔPP = Pour point depression.

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Additives*		0.0 ppm	250ppm	500ppm	750ppm	1000ppm	2000ppm
	$\overline{\text{CP}}$	24	24	24	24	24	24
	$\triangle CP$	0	0	0	0	0	0
$RX - 1$	P	18	12	12	15	15	18
	ΔPP	0	6	6	3	3	$\boldsymbol{0}$
	CP	24	23	23	24	24	24
	\triangle CP	Ω			0	0	θ
$RX - 2$	PP	18	6	9	9	12	12
	$\triangle PP$	0	12	9	9	6	6
	CP	24	23	23	23	24	24
	Δ CP	0				0	0
$RX - 3$	ΡP	18	O	0		6	6
	ΔPP	θ	18	18	15	$12 \,$	$\overline{2}$
	CP	24	22	22	22	23	24
	$\triangle CP$	0	2	2			0
$RX - 4$	PР	18	-3	-3	0		
	ΔPP	0	21	21	18	18	15

Table 5: Effect of Concentration of Esters of Vinyl Acetate - Maleic Anhydride Copolymer on Cloud Point and Pour Point of Fuel Oil

 $CP = Cloud$ point

 $\Delta CP =$ Change in cloud point depression

 $PP =$ Pour point

 $APP = Change$ in pour point depression

* The molar ratio of vinyl acctate to maleic anhydride (2 : 1).

 $CFPP \approx Cold$ filter plugging point.

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 $ACFPP = Change in cold filter pingging point depression$

* The motar ratio of vinyl acctate to malcie anhydride $(2 : 1)$.

Figure 1. Carbon Number Distribution of n - Paraffin Content in Fuel Oil

b¹) RX-4 additive.

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a- Fuel oil Untreated, PP =18 $^{\circ}$ C, CBPP = 12 $^{\circ}$ C

d-Fuel oil + 250 ppm RX-2, PP = 6 °C , CFPP = 9 °C = e Fuel oil + 2000ppm RX-2, PP = -12°C, CFPP = 11 °C

Photofigure 3 . Photomicrographs of Fuel Oil Treated and Fuel oil with Different Concentration from RX-1 and RX-2 Additives.

b-Fuel off + 2000 ppm RX-3, PP= 6 °C, CFPP = 11 °C

c- Fuel oil + 250 ppm RX-4, PP = $\mathbb{E}^{n} \widetilde{C}$,
CFPP = $7\,^{\circ}\mathrm{C}$

d- Fuel oil + 2000 ppm RN-4, PP = 3 $^{\circ}$ C, CFPF = 10 $^{\circ}$ C

Photoligure 4: Photomicrographs of Fuel Oil with Different Concentration

from RX-3and RX-4Additives.

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