

## Alternating Copolymerized Derivative as a Pour Point Depressant for Gas Oil

Taisir Taha Ali Khidr

*Egyptian Petroleum Research institute (EPRI), 1 Ahmed El-Zomor St., Nasr City, 11727 Cairo, Egypt*

Received July 2, 2020; Accepted October 15, 2020

---

### Abstract

The efficiencies of copolymer maleic anhydride-styrene (MAST) were synthesized from maleic anhydride and Styrene based on molecular design. MAST further reacted with octadecyl alcohol/octadecylamine to generate two comb polymers called octadecanol-MAST (OMAST), octadecamide-MAST (NMAST). The effect of these polymers on the pour point and cold filter plugging point of gas oil investigated. Experimental results showed that besides the molecular weight, concentration of the polymers and the type of functional groups also had great influence on the pour point depressing performance. The photo analysis has showed that a wax modification caused by the effective pour point depressant on crystal growth.

**Keywords:** Additive; Copolymer; Pour point depressant; Gas oil; Photomicrography analysis.

---

## 1. Introduction

Wax precipitation from crude oils is a major problem faced by the petroleum industry during production, processing and transportation. When the temperature approaches the pour point, the oil may gel completely and causing the cold flow problems such as blockage of flow pipes or production lines [1-3]. In order to improve the low-temperature flowability of gas oils, polymer additives, such as vinyl acetate copolymer, acrylate copolymer, and their derivatives, have been widely used as so-called pour point depressants (PPDs) [4-6]. All PPDs are structured so that the part of the molecules is like the paraffin wax crystals, this part functions by providing the nucleation sites and co-crystallizing with the paraffin waxes, while the other part of the structure, dissimilar to the wax crystals, blocks the extensive growth of the wax matrices [7-8].

In general, inhibition of wax crystallization has been considered to occur in the presence of PPDs by nucleation, co-crystallization, or adsorption. Many theoretical and experimental studies have been put forward to explain the action mechanism of PPDs for the control of wax crystallization. PPD may also bind to larger crystals and prevent particle-particle interactions from forming aggregates, volume spanning networks, or deposits. This can be termed steric stabilization or adsorption. PPD additives do not work by changing the amount of wax that comes out of solution [9-10].

In this work, MAST copolymer between maleic anhydride -styrene and its esterification with octadecyl alcohol (OMAST) and amination with octadecyl amine (NMAVA) were prepared, characterized, and the performance of the cold flow improver was evaluated with gas oil.

## 2. Experimental

### 2.1. Material

Maleic anhydride was recrystallized from chloroform. Styrene was purified by shaking with dilute sodium hydroxide solution then with distilled water, dried over anhydrous sodium sulphate and distilled under vacuum. The initiator benzoyl peroxide (BP) was recrystallized from methanol. Octadecyl alcohol and octadecyl amine were supplied from Aldrich. Commercial additive Egyptian waxy gas oil (Com) was supplied from Alexandria Petroleum Company.

---

## 2.2. Fuel composition

The paraffinic gas oil derived from the waxy western desert crude oils with the physico-chemical characteristics given in Table 1 were used for evaluating the performance of the synthesized polymeric additives. The n-paraffin content of fuel composition is determined by urea adduction [11]. In addition, sample of the tested gas oil and their respective n-paraffin content are subjected to gas liquid chromatographic analyses (GLC) for determination of n-paraffin carbon number distribution and average carbon number for each gas oil sample.

Table 1. Physicochemical properties of the waxy Western Desert gas oil

Test	Method	Result
Density@15°C kg/L	ASTM D1298	0.8705
Cold Filter Plugging Point (CFPP), °C	ASTM D1500	9
Pour point(PP), °C	ASTM D97	18
Flash point °C (PMC)	ASTM D93	203
Kinematic viscosity@ 40°C cSt	IP 309/83	4.59
X-ray (sulfur) wt%	ASTM D4294	1.084
n-paraffins, wt%	GLC	62.27
Iso- paraffin, wt%	GLC	4.12
Total paraffins content, wt%	Urea adduct	66.39
Average carbon number (n)	GLC	28.56
Distillation	ASTM D86	°C
IBP		218
20%		232
30%		252
40%		263
50%		273
60%		283
70%		298
80%		305
FBP		302

## 2.3. Synthesis pour point depressants

### 2.3.1. Copolymerization of styrene and maleic anhydride

The maleic anhydride – styrene copolymer (MAST) was prepared by free-radical polymerization of equimolar proportion of styrene and maleic anhydride in acetone solution (2 M of monomer and 0.1% BP). The polymerization was conducted at 60°C for 4 h. The copolymer was precipitated in petroleum ether, filtered, washed with petroleum ether and dried at 60°C [12].

### 2.3.2. Esterification of the copolymer

The copolymer MAST was added to octadecyl alcohol, and reacted at 100-110°C for 8-12 h under vigorous stirring. Then the reaction product was added to excess volume of ethanol, finally the obtained product was dried in vacuum at 50°C and the unreacted octadecyl alcohol was removed.

### 2.3.3. Amidation of the copolymer

The copolymer MAST was completely amidated successively with n- octadecylamine in a molar ratio of 1:2, respectively, regarding complete amidation, it was conducted at 2 moles of amine per 1 mole of maleic anhydride. The reaction mixture was heated up to 140°C with vigorous stirring in the presence of xylene as a solvent and under nitrogen blanket while applying slight vacuum until the water of the reaction was collected in the trap azeotropically.

## 2.4. Characterization of additives

The structure of the prepared copolymer MASA, esterification with octadecyl alcohol and amidation with octadecyl amine was confirmed by using Infrared (IR) spectroscopic analysis. The infrared spectra were measured by using model Genesis series (USA) infrared spectrophotometer adopting KBr technique. The characterization of the prepared copolymers is illustrated in Table 2. The molecular weight was determined using gel permeation chromatography (GPC) includes Waters 515 HPLC pump, Waters temperature control module and 2410 refractive index detector from Waters company.

Table 2. Characterization of the synthesized copolymeric additives

Additive designation	Average side carbon length (Cav)	Mwt	Poly dispersity index
MAST	-	18 313	2.81
OMAST	18	24 522	2.72
NMAST	18	30 512	2.61

## 2.5. Evaluation tests

The investigated gas oil samples GO was doped with the prepared additive MAST, OMAST and NMAST at the prescribed concentration and temperature (90°C) to guarantee complete dissolution of both paraffinic and microcrystalline waxes, stirred for 5 min for homogenization then subjected to pour point PP and cold filter plugging point CFPP tests according to the ASTM/IP standard procedures without reheating. Pour points were measured by following the ASTM D97 method and cold filter plugging point were measured by following the ASTM D6371-17 method. After each time period, the PP and CFPP were determined so as to evaluate the stability of performance of the prepared additives both as wax dispersants and flow improvers.

## 2.6. Photo micrographic analysis

The photomicrographs showing wax crystallization behavior of the untreated and treated gas oil (GO) sample with the synthesized additives at 1000ppm has been recorded. An Olympus polarizing microscope model BHSP fitted with an automatic camera with a 35 mm format was used for photo micrographic analysis. The light source was a helium lamp. The temperature of the tested gas oil sample was controlled on the microscope slide by an attached cooling thermostat. All photos were taken at 0°C. The adopted magnification was 100X.

## 3. Results and discussion

### 3.1. Chemical structure and characterization of the prepared additives

The IR-spectra of MAST and an esterified OMAST and NMAST are showed the absorption peaks centered at 1770 and 1851  $\text{cm}^{-1}$  are the characteristic bands of MAST, which correspond to the absorption of CO of the anhydride groups in the five-membered ring. In the spectrum of OMAST, there are additional strong absorption bands at 2923 and 2854  $\text{cm}^{-1}$  assigned to  $\nu_s$  (CH<sub>3</sub>) and  $\nu_s$  (CH<sub>2</sub>) of the alkyl group of ester. It is seen that the intensity of the absorption bands due to the CO of the anhydride groups decreases after esterification, and the band position are shifted to lower wave number 1734 and 1710  $\text{cm}^{-1}$  due to ester and free acid formation [13].

For NMAST showed the peaks at 2926  $\text{cm}^{-1}$  and 2866  $\text{cm}^{-1}$  were assigned to the C-H stretching vibration of methyl and methylene groups, and the absorption peaks at 1736  $\text{cm}^{-1}$  and 1168  $\text{cm}^{-1}$  were attributed to C=O and C-O stretching vibration. The peaks belonging to MAST 1858  $\text{cm}^{-1}$  and 1789  $\text{cm}^{-1}$  disappeared. The characteristic band at 1568  $\text{cm}^{-1}$  was the absorption of C=C stretching vibration of the product introduced by reactant octadecylamine. The absorption peaks at 1062  $\text{cm}^{-1}$  and 1664  $\text{cm}^{-1}$  were attributed to the existence of amide. This spectrum showed that octadecylamine and MAST were completely reacted and polymerized to NMAST.

### 3.2. Gel chromatography

From the molecular weights (Mw) of three copolymers were all of the order of a hundred thousand, and their dispersancy indexes were in the range of 2.81-2.61. But the molecular weight of OMAST is smaller than that of NMAMA. Moreover, octadecyl alcohol and octadecylamine have almost the same relative molecular weight, indicating that the anhydride ring of NMAST can be opened and grafted [14].

### 3.3. Effect of molecular weight of additive on pour point of gas oil

Table 3 shows influence of the copolymer derivatives on the pour points. It can be observed that high molecular weight NMAST shows better efficiency for reduction of pour point of waxy gas oil. The crystal growth rate of the lower molecular weight OMAST is much slower than that of the higher molecular weight NMAST. As the crystal growth rate of higher molecular weight flow improver is faster, it cannot co-crystallize with reduced size of wax crystals. This is the reason why higher molecular weight wax inhibitor shows better efficiency for gas oil.

Table 3. Influence of the prepared additive at 1000ppm on PP and CFPP of gas oil

Sample	CFPP, °C	Δ CFPP, °C	PP, °C	Δ PP, °C
MAST	8	1	12	6
OMAST	7	2	9	9
NMAST	5	4	3	15

CFPP of untreated gas oil =9°C; PP of untreated gas oil =18°C

### 3.4. Effect of additive on pour point of gas oil

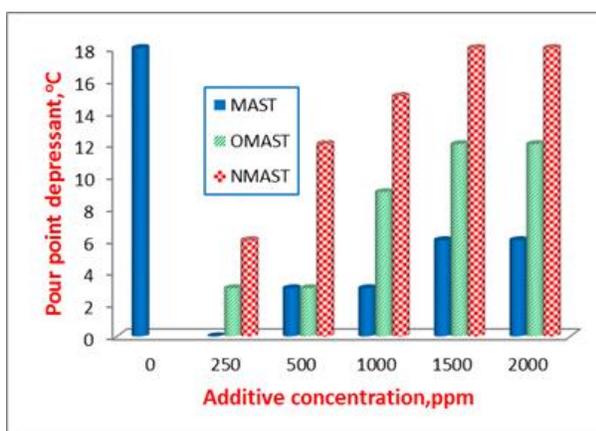


Figure1. Influence of additive on the pour point of gas oil

Figure 1 and Table 3 show the relationship between the concentration of copolymers and the pour point of gas oil. It can be seen that the pour point of gas oil decreased with increasing concentration of the copolymers. When the concentration of the copolymers was equal to or larger than 1000 ppm, the pour point temperature of gas oil changed very little. Therefore, the optimal concentration of polymers is 1000 ppm. The pour point of gas oil was decreased by only 3°C with MAST, whereas it was decreased by 9 and 15°C with OMAST and NMAST respectively, showing that the modified polymers OMAST and NMAST have significantly better pour point depressant properties.

### 3.5. Effect of additive on cold filter plugging point of gas oil

The cold flow performance of the additive was evaluated for gas oil at an additive concentration of 1000ppm. The results are listed in Table 3. It can be seen that the CFPP of the gas oil was lowered by 1°C with the polymer MAST, by 2°C with OMAST and by 4°C with NMAST.

Table 4. Influence of mixed commercial additive with OMAST/NMAST gas oil

Sample	CFPP, °C	Δ CFPP, °C	PP, °C	Δ PP, °C
Commercial	9	0	12	6
1mol. Com +1mol. OMAST	6	3	6	12
1mol. Com +1mol. NMAST	4	5	0	18

### 3.6. Pour point performance when copolymer OMAST/NMAST used together with commercial additive

The results are listed in Table 4, where the total additive concentration is 1000ppm and the ratio of OMAST/NMAST to commercial additive (com) is 1:1.

### 3.7. Effect of flow improver & pour point depressant type on wax crystal modification

Photomicrographs of wax crystals in the absence and presence of additives captured at 0°C are presented in Figure 2.

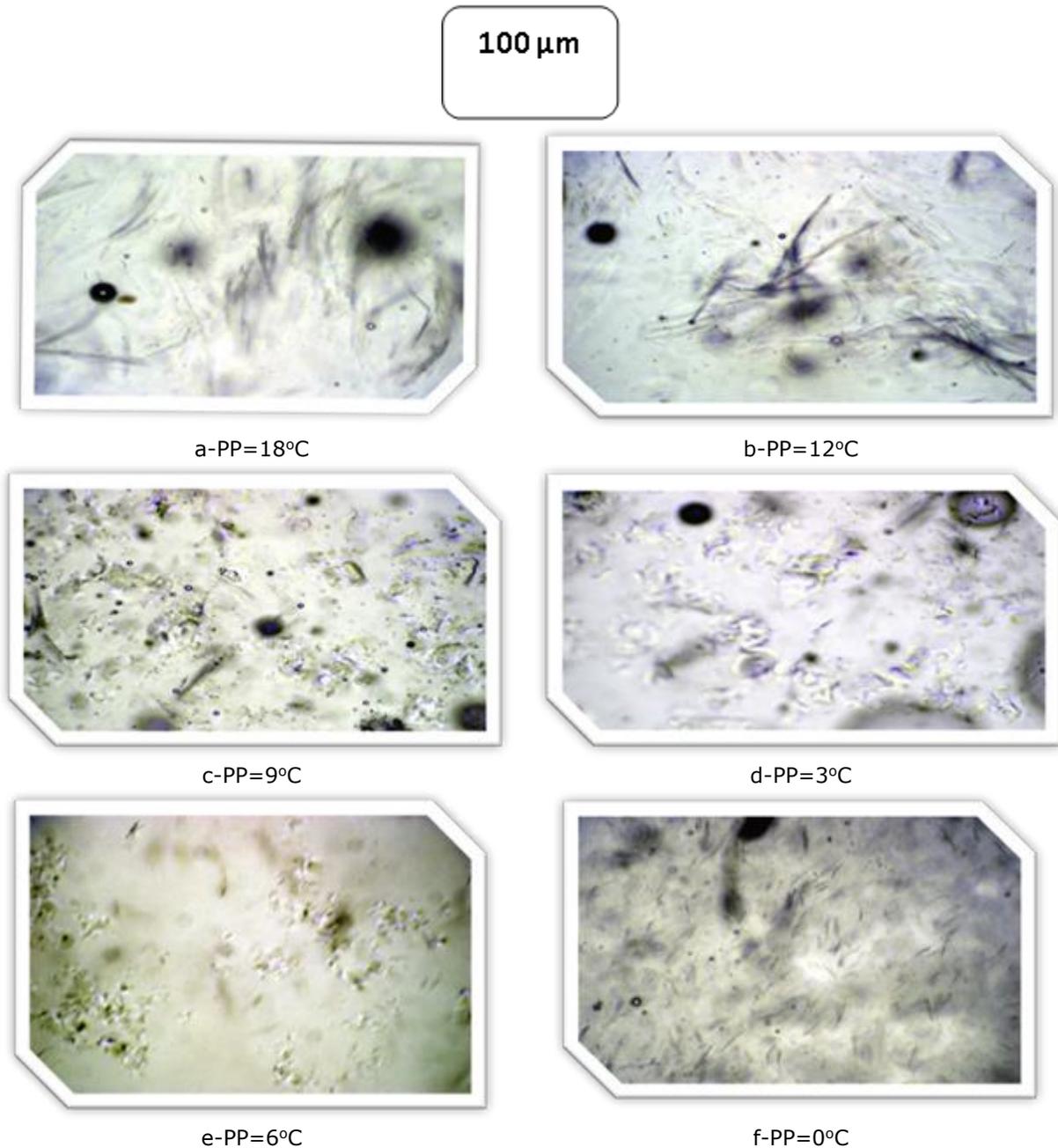


Figure 2. Photomicrographs of (a: GO untreated) and (b: GO+MAST), (c: GO + OMAST), (d: GO+NMAST), (e: GO+Com+OMAST) and (f: GO+Com+NMAST) at 1000 ppm

Figure 2a shows that wax crystals formed from virgin gas oil are needle-shaped, which have a large crystal–liquid oil surface area and high surface energy. As the temperature decreases, wax crystals will easily interlock with each other to form gel structures; hence, the low-temperature fluidity of gas oil will be greatly deteriorated. However, the photographs of the three samples (MAST, OMAST and NMAST) with gas oil are shown in Figure 2(b-d). The snow-like picture of MAST indicated the crystallization of paraffin. The pictures of OMAST and NMAST were of small-and-uniformly-distributed particles, showing the dispersancy of paraffin crystals had been improved greatly. It suggested that the paraffin grew up in a certain direction when MAST was added to gas oil. However, when OMAST or NMAST was added to gas oil, the paraffin crystals became to be small-and-uniformly distributed particles due to different attachment points, thus preventing paraffin from further crystallization and reducing the pour point of gas oil. This effect was more pronounced in case of NMAST with commercial additive (com) in Figure 2f where less wax crystals and their agglomerates appeared. These results assure the findings of pour point and cold filter plugging point measurements, where they indicated that the polymeric PPDs hinder growth and agglomeration of the wax crystals, thereby reducing the dissipated energy and improving the flowability of oil.

#### 4. Conclusions

Synthesis copolymer maleic anhydride with styrene (MAST), then react this copolymer with octadecyl alcohol/octadecylamide to produce OMAST and NMAST respectively. Their structures were characterized by IR and GPC. The effects of chemical structures on the pour point and cold filter of plugging point behavior in gas oil were investigated.

The pour point depressing properties and mechanisms of polymers were studied and the results show that, besides the molecular weight and concentration of copolymers and the type of functional groups also have obvious influence on the depressing ability. Higher molecular weight of additive showed better efficiency as a flow improver and wax crystal modification

When the dosage of improver OMAST, NMAST were 1000ppm, the CFPP of gas oil was lowered by 2 and 4°C and the PP was lowered by 9 and 15°C respectively. At the same total improver concentration, the CFPP was lowered by 3 and 5°C when the improver OMAST, NMAST were used together with commercial additive and the PP were lowered by 12 and 18°C respectively. Thus, it can be concluded that the synergetic effect of the compound improver is excellent.

#### References

- [1] Khidr TT. Preparation and Evaluation of n- Alkyl Methacrylate - Vinyl Acetate – Methacrylic Acid Terpolymers as Pour Point Depressant for Fuel Oil. *Petroleum and Coal*, 2019; 61(2): 277-284.
- [2] Khidr TT, Doheim MM, and El-Shamy OAA. Effect of ethoxylate on pour point depressant of fuel oil. *Energy sources, Part A: recovery, Utilization and environmental effect*, 2015; 37: 1697-1703.
- [3] Al-Sabagh AM, Sabaa MW, Saad GR, Khidr TT, and Khalil TM. Synthesis of polymeric additives based on itaconic acid and their evaluation as pour point depressants for lube oil in relation to rheological flow properties. *Egyptian J. Pet.*, 2012; 21:19–30.
- [4] EL-Shamy OAA. Khidr TT, and Badr E. Studies the Effect of Hydrazide Derivatives as Flow Improvers for Waxy Crude Oil. *Petroleum and Coal*, 2019; 61(3): 533-539.
- [5] Khidr TT. Preparation of terpolymer additives and used their as pour point depressant for crude oil. *Petroleum and Coal*, 2017; 59 (4): 420-428.
- [6] Khidr TT, and Omar AMA. Anionic/nonionic mixture of surfactants for pour point depression of gas oil. *Egyptian J. Pet.*, 2003; 13: 21–26.
- [7] Ahmed SM, Khidr TT, and Ismail DA. Effect of gemini surfactant additives on pour point depressant of crude oil. *Journal of Dispersion Science and Technology* 2018; 39(8): 1160-1164.
- [8] Al-Sabagh AH, El-Hamouly SH, Khidr TT, El-Ghazawy A, and Higazy SA. Synthesis of phthalimide and succinimide copolymers and their evaluation as flow improvers for an Egyptian waxy crude oil. *Egyptian J. Pet.*, 2013; 22:381–393.
- [9] Pilgrim A. Wax formation in oil pipelines: A critical review. *Int. J. Multiphase Flow*, 2011; 37: 671–694.

- [10] Marie E, Chevalier Y, Eydoux F, Germanaud L, and Flores P. Control of n-alkanes crystallization by ethylene–vinyl acetate copolymers. *J. Colloid Interface Sci.*, 2005; 290: 406–418.
- [11] Marquat JR, Dellow GB, and Freitas ER. Determination of Normal Paraffins in Petroleum Heavy Distillate by Urea Adduction and Gas Chromatography. *Anal. Chem.*, 1968; 40: 1633–1637.
- [12] Al-Sabagh AM, Noor El-Din MR, Morsi RE, Elsabee MZ. Demulsification efficiency of some novel styrene maleic anhydride copolymers monoesters. *J. Appl. Polym. Sci.*, 2008; 108: 2301–2311.
- [13] Chen G, Zhang Y, and Zhou X. Synthesis of styrene-maleic anhydride copolymer esters and their surface enriched properties when blending with polyethylene. *Appl. Surf. Sci.*, 2006; 253(3): 1107–1110.
- [14] Kostanyan A, and Voshkin A. Analysis of cyclic liquid chromatography. *Theoretical Foundations of Chemical Engineering*, 2011; 45(1): 67-72.

---

*To whom correspondence should be addressed: professor Taisir Taha Ali Khidr, Egyptian Petroleum Research institute (EPRI), 1 Ahmed El-Zomor St., Nasr City, 11727 Cairo, Egypt, E-mail: [kkidrr@yahoo.com](mailto:kkidrr@yahoo.com)*