DOI 10.1007/s10553-022-01444-x
Chemistry and Technology of Fuels and Oils, Vol. 58, No.5, November, 2022 (Russian Original No.5, September–October, 2022)

INNOVATIVE TECHNOLOGIES OF OIL AND GAS

DEPRESSANT AND DISPERSANT ADDITIVES FOR DIESEL FUEL. COMPONENTS, BRANDS, NEW TECHNOLOGIES AND DEVELOPMENTS

K. B. Rudyak, K. B. Polyanskii ✉, N. V. Vereshchagina, D. B. Zemtsov, D. M. Panov, T. M. Yumasheva

The market situation for depressant-dispersant additives for diesel fuel is discussed, the principal grades are listed, and methods for production of the depressant and dispersant components are presented. Information on a multipurpose depressant-dispersant additive designed at the Rosneft research and development RD Center, which improves the low-temperature, antiwear, and electrical behavior of diesel fuels is presented.

Keywords: depressant-dispersant additive, depressant, dispersant, diesel fuel.

The normal functioning of railways, freight, passenger and motor vehicles, and military and agricultural equipment is impossible today without the use of diesel fuel. The cold climate of Russia often makes tough demands on the low-temperature characteristics of diesel fuels.

The main low-temperature properties of diesel fuels include three indicators: cloud point, pour point, and limiting filterability temperature (LFT) [1-5].

There are several methods of improving the low-temperature characteristics of diesel fuels [6]:

– Lowering the final boiling point of the diesel fraction makes it possible to reduce the content of high-melting paraffins with normal structure in the fuel, but this significantly reduces the yield of the fuel;

– Dewaxing (carbamide, zeolite, microbiological, and catalytic) and isodewaxing on catalysts containing platinum group metals, which requires additional energy consumption and leads to losses of the diesel fraction;

– addition of depressant-dispersant additives to the fuel, which does not require large energy consumption, while the additives are introduced in quantities amounting to tenths or hundredths of a percent.

The additives are compositions that contain paraffin depressants and dispersants. The former improve the pumpability of the fuels at low temperatures, and the latter prevent separation of the fuels during storage at low temperatures [1, 2, 7, 8].

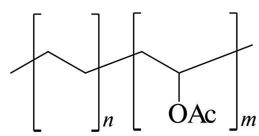
LLC «RN-RD CENTER», Moscow. *Corresponding author: K. B. Polyanskii ✉. E-mail: : PolyanskiyKB@rdc.rosneft.ru.* Translated from *Khimiya i Tekhnologiya Topliv i Masel*, No. 5, pp. 20–25 September–October, 2022.

Depressant Additives for Diesel Fuels

Depressant additives are substances that, when added to petroleum products in small amounts, lead to significant decrease in the pour point and improve the fluidity at low temperatures. While reducing the pour point, the depressants have practically no effect on the cloud point, do not prevent formation of the nuclei of alkane crystals, but prevent their growth. Here, instead of large ribbon-like crystals small needle-shaped and star-shaped crystals, which are less capable of forming a spatial lattice, are formed. The two most common mechanisms of action of the depressants involve cocrystallization of the paraffin and the depressant or adsorption of the depressant by the polar part on the crystal surface [2, 8, 9].

A large number of investigations in the search for depressant additives have led to practical use of the following: copolymers of ethylene and vinyl acetate, alkyl methacrylates with vinyl acetate, polyalkylmethacrylates, copolymers of maleic anhydride and various olefins, and copolymers of ethylene and propylene. It is known that polymeric and copolymeric depressant additives containing polar functional groups are more effective than other types of additives [1, 2].

Copolymers of Ethylene with Polar Monomers. A large proportion of the commercially produced depressants for diesel fuels are ethylene-vinyl acetate copolymers:



Such copolymers are characterized by statistical distribution of the monomeric units in the macromolecule, by various molecular masses (from 10^3 to 10^5), and by various ratios of the monomers, and as a result there is wide variation of both physicochemical and operational characteristics of the additive. Important features of the copolymer of ethylene with vinyl acetate are: the molecular mass, the composition of the copolymer, the molecular mass distribution, and the branching of the macromolecules. Investigations into the molecular-mass distribution of copolymers of ethylene with vinyl acetate have shown that as well as copolymers with the "normal" distribution there are copolymers that in addition to main substance contain a low-molecular fraction with an average mass of 500 and copolymers containing a high-molecular fraction with average mass of up to $1 \cdot 10^7$. The following characteristics of the copolymers are considered optimal: average molecular mass 2500-5000; content of vinyl acetate groups 30-40%; number of methyl side groups about 8.5 per 100 CH_2 groups [1, 2, 10].

There are many additives of this type on the market. For example, there are some products of the Keroflux series from BASF and the BÉS410-D additive produced in Russia. This type of depressant also includes copolymers of ethylene with other polar copolymers, such as vinyl propionate, triple copolymers of the ethylene/vinyl acetate/polar comonomer (styrene, alkyl fumarates, alkyl maleates) type, and products produced by modification of ready-made copolymers.

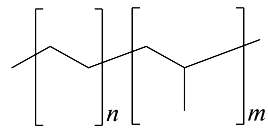
The consumption of additives based on copolymers of ethylene and vinyl acetate amounts to 0.01-0.1 wt.%. At the optimum concentration of depressant-dispersant additive in a diesel fuel the maximum pour point depression is up to 30°C, the LFT is up to 15°C, and depressants based on ethylene with vinyl acetate do not affect the cloud point of diesel fuel.

Additives based on copolymers of ethylene with vinyl acetate are obtained in two technological directions [1, 2, 11].

1. A periodic process, carried out in a solvent under harsh conditions: temperature up to 150°C and pressure 10–30 MPa in the presence of an initiator. Various hydrocarbons (cyclohexane, hexane, toluene, xylene, etc.) are used as solvent. Azobisisobutyronitrile, dilauryl peroxide, dibenzoyl peroxide, and other peroxy compounds are used as initiators. The molecular weight and the ratio of the monomeric units of the copolymer are determined by the pressure, the temperature, and the concentration of the reagents.

2. In the continuous process it is possible to produce a copolymer additive at high pressure in the presence of a molecular weight regulator. Technologically, the process is similar to the production of high-pressure polyethylene. Polymerization takes place at 200-250°C and 140-150 MPa. The conversion of the monomers is usually low (10-20%), and in addition the polymerization process is accompanied by significant release of heat. It is therefore very important to ensure dissipation of the heat. The instrumentation of the process is quite complicated: apart from the reactor itself equipment is required for mixing the reagents, creating the working pressure, cooling, and separating the polymer from the unreacted monomers.

Additives of Polyolefin Type. Low-molecular branched polyethylene and copolymers of ethylene and propylene have depressant characteristics [1, 2, 12, 13].

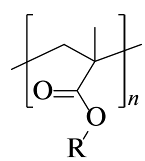


An example of such an additive is Keroflux 6100 and other BASF additives.

The consumption of additives based on ethylene copolymers is about 0.3% wt.%. The maximum depression of the pour point is up to 26–29°C.

As in the case of the copolymers of ethylene with vinyl acetate, the synthesis of additives of the polyethylene type requires high pressure and temperature to produce the initial copolymers of ethylene (up to 3000 atm and 200°C). In addition, the initial copolymers are subjected initially to ultrasonic treatment or to thermal oxidative degradation at a high temperature of about 200°C in the presence of catalysts (toxic manganese salts) [14].

Polyalkyl(meth)acrylate Copolymers. Polymers of higher alkyl(meth)acrylate copolymers can act as depressants for diesel fuels [1, 2, 7, 9, 15, 16, 17]:



Various monomers of the vinyl acetate, styrene, acrylonitrile, and other types can be included in the composition of the copolymer [18, 19]. Additives of this type are supplied by Evonik. Russian producers supply the depressant additives PMA-D and K-110 for oils.

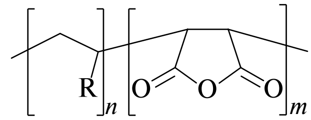
The consumption rate of the polymethacrylate depressant additives amounts to approximately 0.05-0.1 wt.%. The maximum depression of the pour point is 19-24°C and the LFT is 8-15°C. In some cases the use of methacrylate additives can lead to depression of the cloud point – to 10°C.

The technological scheme for production of the additives includes two stages: synthesis of the monomers (higher alkyl(meth) acrylates) and polymerization of the higher alkyl(meth)acrylates.

The initial alkyl(meth)acrylates can be obtained in several ways. The most widely used version is transesterification of methacrylic acid or methacrylonitrile. The initial components are methyl (meth)acrylate and C_{12}-C_{18} alcohols of natural or synthetic origin. The transesterification catalysts are various mineral acids, and the process is conducted at temperatures up to 120°C. After transesterification the product is purified from the acid catalyst and passed on to the next stage of polymerization.

Polymerization of the higher alkyl(meth)acrylates is carried out in an inert solvent (for example, industrial oil) at atmospheric pressure in the presence of radical polymerization initiators (various organic peroxides) and molecular weight regulators (alkylmercaptans). The reaction temperature is 100-150°C. Polymerization takes place with considerable release of heat, and dissipation of the heat is therefore extremely important [1, 20, 21].

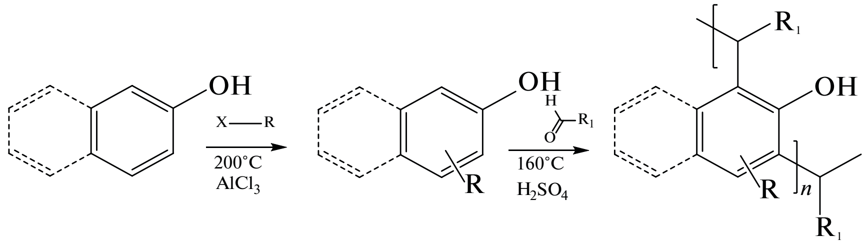
Copolymers of Maleic Anhydride with α-Olefins. Additives of this type can also be used as depressants not only in diesel fuels but also in oils and other petroleum products [22-24]:



The consumption rate of the depressant additives based on copolymers of maleic anhydride with α-olefins amounts to 0.05-0.1 wt.%. The highest pour point depression and LFT is 20°C. Such depressant additives have practically no effect on the cloud point of diesel fuel.

The distinguishing feature of such additives is the readily available and cheap raw material (olefin fractions, maleic anhydride) and the mild conditions of synthesis – atmospheric pressure, various polymerization initiators, synthesis temperature 80-185°C depending on the initiator of radical polymerization. It is possible to use ready-made polymers (such as polypropylene) and esterification of the obtained copolymers of maleic anhydride with various alcohols [23, 25, 26].

Depressants Based on Alkylphenols. The depressants are obtained according to the following scheme [27]:



The consumption of the depressants based on alkylphenols amounts to 0.05-0.2 wt.%.

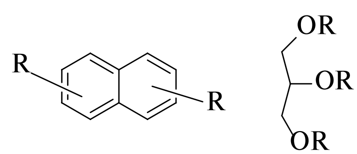
The technological scheme for the production of these additives includes two stages:

The first stage involves synthesis of the alkylphenols by a Friedel–Crafts reaction in which an olefin (for example an olefin containing an aromatic ring) or its halogenated or hydrohalogenated analog reacts with phenol in the presence of a catalyst (a Lewis acid, $AlCl_3$) at a temperature of about 200°C.

At the second stage the polyalkylphenols are produced by polycondensation of the alkylphenols with an aldehyde at 98-100°C followed by treatment with alkali.

The depressants based on alkylphenols have average molecular weights ranging from 1000 to 24000 Da. Such additives are being developed by the Lubrizol Corporation.

Chemical Substances of Nonpolymeric Type. Substances of this class include various types of nonpolymeric substances [1]:



For example, compounds such as alkylnaphthalenes, the esters of polyhydric alcohols with fatty acids, or the esters of polybasic acids with fatty alcohols have depressant properties [2, 28, 29]. In their molecules such depressants have long aliphatic radicals that secure reaction with the paraffins. It is known that heavy petrochemical residues, such as oxidized heavy pyrolysis resin, can also serve as the basis for the creation of depressant additives, but depression of the pour point in this case is small [30].

The consumption of depressants of nonpolymeric type amounts to 0.1-0.2 wt.%. The highest depression of the pour point amounts to 22-25°C, and the LFT is 12-18°C. In some cases the use of such additives can lead to lowering of the cloud point.

Depressants of nonpolymeric type based on esters are obtained by esterification of various acids and alcohols in the presence of catalysts (acids, bases, phase-transfer catalysts) at atmospheric pressure, at temperatures between 169 and 216°C, and with overall productivity from 6 to 36 h in two stages. The choice of initial alcohols and acids is restricted by their availability and cost.

All the types of depressants presented above can be divided into two structure types: nonpolar linear chains alternating with polar fragments (polymers of the ethylenevinylacetate type) and comb polymers in which the polymeric chain has polar fragments and long aliphatic tails that secure interaction with the crystals of paraffins (copolymers of higher methacrylates, maleic anhydride with α-olefins, etc.).

Dispersant Additives

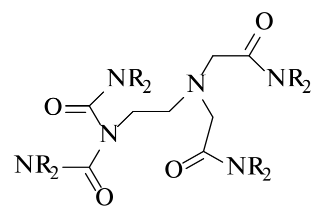
Depressant additives do not prevent fuel separation. Dispersant additives are used to prevent separation. They prevent the deposition of heavy paraffin hydrocarbons (wax), which leads to separation of the fuel into layers during cold storage on standing.

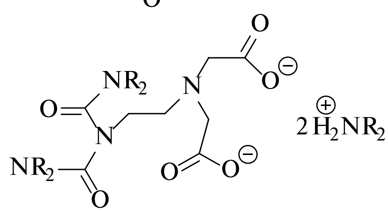
Mechanism of the Action of Dispersant Additives

The mechanism of the action of dispersants [8, 16] involves creation by the dispersant molecules of a charged layer on the surface of the paraffin crystals. This leads to repulsion of the crystals from each other and stops growth of the crystals. The molecule of the dispersant contains a long hydrocarbon radical that interacts with the molecules of the paraffins and a hydrophilic functional group. It is considered that the depressants in conjunction with the dispersants promote crystallization and the formation of polarized fine crystals. On account of electrostatic forces of repulsion the crystals (micelles) are furthermore dispersed and are distributed uniformly throughout the volume of the fuel.

Substances that have polar functional groups in their composition (amides [31], esters [32], and the imides of carboxylic acids [33, 34], quaternary ammonium salts and amides of the polyalkylenepolyamine type [35-37]) are added to diesel fuel as dispersants. Dispersants based on cresols obtained from alkylphenols with a long hydrocarbon chain of normal structure have been developed [38, 39].

Amide, Ester, and Quaternary Ammonium Salt Dispersants. The consumption rates of dispersants with amide, ester, and quaternary ammonium functional groups amount to 0.05-0.2 wt.%:

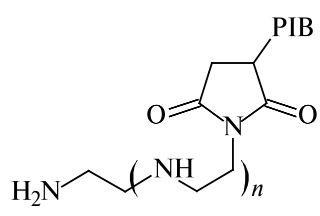




Synthesis of the amides of ethylenediaminetetraacetic acid and their derivatives takes place under harsh conditions: joint heating of the respective acids, amines, and alcohols in the melt at a temperature of about 190°C for 12-20 h [40-42].

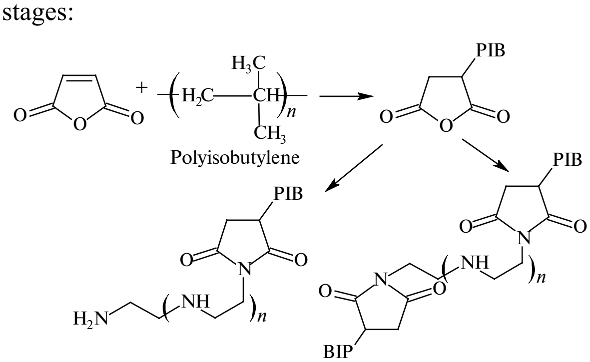
Dispersants of this type are developed and manufactured by BASF.

Dispersants Based on Polyisobutylene, Maleic Anhydride, and Polyethylenepolyamine with Succinimide Groups in the Composition. Dispersants with succinimide fragments in the composition are represented by the nitrogen-containing polymeric compound:



The consumption rates of the dispersants with succinimide groups amount to 0.05-0.2 wt.%.

The synthesis is realized in two stages:



At the first stage maleic anhydride reacts with polyisobutylene at 150-180°C, and the obtained polyisobutylenesuccinic anhydride is filtered from the resinous products while hot.

At the second stage the intermediate polyisobutylenesuccinic anhydride is treated with polyethylenepolyamine at 150-180°C with the formation of the final product.

Dispersant additives based on succinimides are produced in Russia [43-45]/

Depressant–Dispersant Additives

The development of depressant–dispersant additives in the industry began more than 30 years ago. From that time various depressant–dispersant additives have been developed predominantly on the basis of polymeric (polyethylenevinylacetate) components [46, 47].

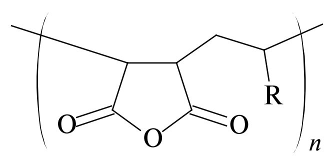
At the present time depressant–dispersant additives produced abroad predominate on the Russiam market. These are additives from firms such as: Clariant (the Dodiflow series), BASF (the Keroflux series), Innospec (the OFI series), Infineum (R410, R430, R490, R442M, and others), Lubrizol (ADX-3856), and others. Of the domestic additives the following products are well known: depressant VÉS 410D (JSC AZK and OS), dispersant Depran-DP (LLC NPF Depran), and also two depressant–dispersant additives Miksent-2020 **(**LLC Altai Center of Applied Chemistry**)** and Addi TOP (JSC Gazprom Neftekhim Salavat) [48].

It is known from scientific, technical and patent information that technologies for the production of depressant-dispersant additives are, as a rule, energy-consuming and require harsh reaction conditions and the use of expensive (and sometimes toxic) starting reagents.

Development of Depressant and Dispersant Additives at LLC «RN-RD CENTER»

A polyfunctional depressant-dispersant additive for diesel fuel has been developed at the LLC «RN-RD CENTER» [49-52].

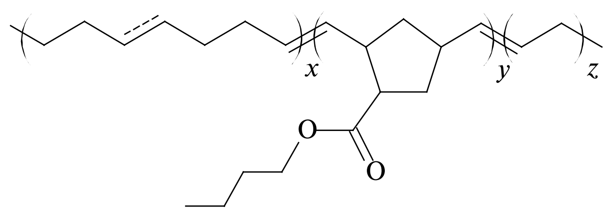
The general formula of the depressant component is:



where R = C_4–C_{32} *n*-alkyl.

It is produced by radical copolymerization of industrial fractions of linear α-olefins and maleic anhydride at 90-150°C.

The dispersant component has the general formula:



It is synthesized by metathesis depolymerization of synthetic divinyl rubber in the presence of carboxybutylnorbornene, industrial fractions of α-olefins, and a metal complex ruthenium catalyst developed at LLC «RN-RD CENTER» [53–55] at 70°C followed by hydrogenation.

The production of the additive does not require high pressure, high temperature, or complex apparatus. Distinctive features of the developed depressant-dispersant additive are its multifunctionality, which makes it possible to avoid the use of antiwear and antistatic additives at refineries, and also the flexibility of the technology in terms of creating a depressant component for various diesel fuels.

REFERENCES

1. R. A. Terteryan, *Depressant Additives to Petroleum, Fuels, and Oils* [in Russian], Khimiya, Moscow (1994), 237 pp.

2. S. G. Agaev, A. M. Glazunov, S. V. Gul'tyaev, et al., *Improvement of Low-Temperature Properties of Diesel Fuels: Monograph* [in Russian], Tyumen (2009), 145 pp.

3. GOST 5066–91, *Motor Fuels. Methods for Determining Cloud Point, Beginning of Crystallization, and Crystallization*.

4. GOST 20287–91, *Oil Products. Methods for Determining Pour Points and Pour Points* [in Russian]

5. GOST 22254–92. *Diesel Fuel. Method for Determining the Limiting Filterability Temperature on a Cold Filter* [in Russian].

6. A. V. Kameshkov, A. A. Gaile, *Izvestiya SPbGTI(TU)*, No. 29(55), 49-60 (2015).

7. A. M. Danilov. *Application of Additives in Automotive Fuels. Handbook* [in Russian], Khimiya, Moscow (2000), 232 pp.

8. T. N. Mitusova, E. V. Polina, M. V. Kalinina, *Modern Diesel Fuels and their Additives* [in Russian], Tekhnika, Moscow (2002), 64 pp.

9. V. A. Lyubimenko, *Trudy RGU Nefti i gaza imeni I. M. Gubkina*, No. 3 (276) 88-96 (2014).

10. J. W. Qian, G. H. Zhou, W. Y. Yang, et al., *Journal of Applied Polymer Science*, **83**, 815-821 (2002).

11. A. M. Danilov, *Khimiya i Tekhnologiya Topliv i Masel*, No. 6, 41-50 (2011).

12. N. S. Ahmed, A. M. Nassar, R. M. Nasser et al., *Journal of Dispersion Science and Technology*, **33**, 668-675 (2012).

13. RF Pat. 231444.

14. RF Pat. 2337944.

15. RF Pat. 2119528.

16. A. M. Al-Sabagh, F. Abdel_Hai, A. M. M. Abd El Rhman, et al., *Life Science Journal*, **11**, 731-737 (2014).

17. H. P. Soni, D. P. Bharambe, A. Nagar, *Indian Journal of Chemical Technology*, **12**, 55-61 (2005).

18. A. M. Al-Sabagh, S. H. El-Hamouly, T. T. Khidr, et al., *Egyptian Journal of Petroleum*, **22**, 381-393 (2013).

19. Chinese Pat. 104710560.

20. R. A. Soldi, A. R. S. Oliveira, R. V. Barbosa, et al., *European Polymer Journal*, **43**, 3671-3678 (2007).

21. US Pat. 20150344801.

22. R. A. El-Ghazawy, A. M. Atta, K. I. Kabel, *Journal of Petroleum Science and Engineering*, **122**, 411-419 (2014).

23. US Pat. US4240916.

24. Rasha A. El-Ghazawya, Ayman M. Atta, Khalid I. Kabel, *Journal of Petroleum Science and Engineering*, **122**, 411-419 (2014).

25. US Pat. 2007/0161519.

26. US Pat. 4652611.

27. RF Pat. 2016047.

28. N. El Mehbad, *Journal of Power and Energy Engineering*, **1**, 90-94 (2013).

29. Chinese Pat. 104529767).

30. RF Pat. 2548359.

31. Chinese Pat. 104403706.

32. US Pat. 954572.

33. US Pat. 5725610.

34. US Pat. 0037512.

35. US Pat. 6071993.

36. US Pat. 6786940.

37. US Pat. 5071445.

38. N. P. Andryukhova, M. V. Ermolaev, V. A. Kovalev, et al., *Mir Nefteproduktov*, **1**, 16-18 (2010).

39. RF Pat. 2016047.

40. US Pat. 6071993.

41. US Pat. 6786940.

42. US Pat. 5071445.

43. E. A. Burov, *Investigation of the Effectiveness of Additives in Diesel Fuels with Various Hydrocarbon Compositions* [in Russian], N. M. Gubkin Russian State University of Oil and Gas, Moscow (2015), 152 pp.

44. RF Pat. 2330875.

45. RF Pat. 2561279.
46. D. F. Grishin, *Neftekhimiya*, No. 5, 489-502 (2017).
47. A. M. Danilov, *Neftekhimiya*, **60**, No. 2, 163-171 (2020).
48. A. A. Shevchenko, R. I. Kuz'mina, V. T. Liventsev, in: *Modern Problems of Theoretical and Experimental Chemistry: Interuniversity Collection of Scientific Papers of the XIII All-Russian Conference of Young Scientists with International Participation*, Saratov, October 1-10, 2018. Saratovskii Istochnik, Saratov (2018), pp. 245-249.
49. D. B. Zemtsov, K. B. Polyanskii, D. M. Panov, *Neftepererabotka i Neftekhimiya*, No. 2, 31-34 (2020).
50. RF Pat. 2647858.
51. RF Pat. 2684412.
52. RF Pat. 2715896.
53. RF Pat. 2375379.
54. RF Pat. 2393171.
55. RF Pat. 2462308.