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Features of Composite Additives Production Technology

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Annotation: The article analyzesmodern diesel fuels and requirements for them. Particular attention is paid to additives that improve the low-temperature characteristics of diesel fuels. The role of multifunctional composite additives has been studied. The mechanism of action of additives in diesel fuels has been studied. The features of the production technology of composite additives are revealed.

Keywords: Diesel fuel, additive, optimal method, petroleum products, low-temperature properties.

In recent years, there has been a steady increase in global demand for diesel fuel. The release of winter types of diesel fuel implies that the fuel meets the requirements of standards for such low-temperature properties as cloud point, pour point, and filterability limit temperature and sedimentation stability under storage conditions at temperatures below the cloud point.

The optimal way to improve the low-temperature properties of diesel fuels is the use of depressant-dispersant additives .Depressant additives promote the formation of small paraffin crystals and prevent the formation of a spatial framework when cooling diesel fuel, which makes it possible to reduce its filterability limit temperature and pour point.

However, they do not prevent crystal agglomeration during cold storage. Therefore, fuels with such additives during long-term cold storage are divided into two layers: the lower one, enriched with paraffin crystals, and the upper light one. Both layers retain mobility, but differ in composition and, consequently, thermophysical characteristics. This drawback is eliminated by introducing into the fuel, along with the depressant, another additive called a paraffin dispersant.

Diesel fuels are products that contain middle distillate fractions of oil, boiling in the range from 180 °C to 360 °C. Diesel fractions can be obtained by various industrial methods: simple distillation of oils and gas condensates, the process of catalytic cracking of fuel oils, vacuum gas oils and their mixtures, in the process of thermal cracking of fuel oils and visbreakingasphaltenes and half-tars, in the process of hydrorefining of fuel oils and reforming of gasoline, etc.

Commercial diesel fuels are produced by mixing straight-run and hydrotreated diesel fractions isolated from oil in a given range of boiling temperatures and in ratios that provide the necessary parameters of the commercial product.

Diesel fuels are characterized by the following main performance indicators:

cetane number, which determines high power and economic performance of the engine;

Fractional composition, which determines the completeness of combustion, smoke and toxicity of engine exhaust gases;

Viscosity and density ensuring normal fuel supply, atomization in the combustion chamber and operability of the filtration system;

Degree of cleanliness, characterizing the reliability of the operation of coarse and fine filters and the cylinder-piston group of the engine;

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Flash point, which determines the safety conditions for using fuel in diesel engines;

The presence of sulfur compounds, unsaturated hydrocarbons and metals, which characterize carbon formation, corrosion and wear;

Lubricity, which evaluates the wear of rubbing pairs of the fuel system operating in a diesel fuel environment;

Low-temperature properties that determine the functioning of the power system at negative ambient temperatures and fuel storage conditions.

The low-temperature properties of diesel fuels are characterized by such indicators as cloud point, filterability limit temperature and pour point.

It was believed that the cloud point characterizes the filterability of fuels at low temperatures, and the pour point characterizes their pumpability. However, experience in operating diesel engines in winter conditions and tests in road conditions have shown that these properties cannot unambiguously characterize the behavior of fuels at low temperatures.

Many years of searching for new indicators, more objective than cloud point and pour point, characterizing the low-temperature properties of diesel fuels, led to the establishment of the indicator “filterability limit temperature ”. The filterability limit temperature is the minimum temperature at which a given volume of fuel is pumped through a standard filter in a certain period of time.

Increasing requirements for the quality of diesel fuels leads to the use of a large number of additives and additives for diesel fuels.

Diesel fuels containing depressant additives are subject to additional requirements. The depressant should not worsen the filterability coefficient of diesel fuel. The additive package, which includes a depressant, should help keep small crystals of the solid phase in suspension and distribute them evenly throughout the entire volume of fuel.

For petroleum products that do not contain solid paraffin hydrocarbons, there are two types of solidification: thickening, associated with a significant increase in viscosity, and solidification of petroleum products in the form of amorphous glassy bodies. The most highly branched paraffin, as well as naphthenic and aromatic hydrocarbons with low crystallization temperatures, losing mobility at temperatures below 60 ° C, do not form crystals, but become amorphous and vitrified . With further cooling of the glassy mass, its fracture is observed.

It is known that crystal field forces can significantly change the conformation of molecules as a result of the formation of intermolecular hydrogen bonds. The most stable configuration of the n- alkane molecule is that which meets the condition of minimum free energy, achieved as a result of an energetically favorable combination of intra- and intermolecular hydrogen bonds.

Taking this into account, the legislation of industrialized countries pays increased attention to the environmental safety of diesel engines and supports the desire to reduce harmful emissions from exhaust gases. The solution to this problem is the production of environmentally friendly fuels, modern engines and catalytic exhaust gas aftertreatment systems used to reduce harmful emissions into the atmosphere.

The trend towards reducing sulfur content can be seen in diesel fuel specifications in all countries. Sulfur compounds cause the emission of aggressive and toxic sulfur dioxide. Reducing the sulfur content of fuel leads to an overall reduction in emissions of sulfur oxides, which cause respiratory irritation and the formation of acid rain, as well as corrosion of metals and destruction of catalytic converters. At the same time, there is also a decrease in the amount of particulate matter in the exhaust gases and deposits in the fuel system.

It is known that the low-temperature properties of diesel fuel depend not so much on the amount of n-paraffin hydrocarbons, but on their distribution over molecular weights. For all classes of hydrocarbons, the following pattern is true: with an increase in molecular weight, and, consequently, the boiling point, the melting point of hydrocarbons increases. However, the structure of the hydrocarbon has a very strong influence on the melting point.

Hydrocarbons of the same molecular weight, but different structures, can have melting points within a wide range. Paraffinic hydrocarbons with a long, unbranched chain of carbon atoms have the highest melting points. Aromatic and naphthenic hydrocarbons melt at low temperatures (except benzene, p-xylene), however, these hydrocarbons, but with a long unbranched side chain, melt at higher temperatures.

As a paraffinic hydrocarbon chain or paraffinic side chain attached to aromatic or naphthenic rings branches, the melting point of the hydrocarbons decreases.

Studies have shown that when diesel fuels are cooled, high-melting paraffin hydrocarbons of normal structure are precipitated first.

The simplest and most common method in our country for producing low-solidification diesel fuels is to lighten their fractional composition in direct oil distillation plants. It is closely related to jet fuel resources. The resulting diesel fuels are characterized by good low-temperature properties. However, taking into account that the need for jet fuel is satisfied by increasing its selection from the potential content in oil, it becomes obvious that the production of winter diesel fuels by lightening the fractional composition is extremely limited. As a rule, the bulk of winter diesel fuel varieties are obtained by reducing the end boiling point to 300-320 ° C , arctic ones to 280 ° C, versus 360 ° C for summer fuel.

However, the addition of kerosene is ineffective, especially in relation to cloud point temperature and filterability limit temperature , which is explained by the low solubility of high-melting n-paraffin hydrocarbons contained in summer diesel fuel. As for the pour point, when kerosene is added, a decrease in this indicator is observed.

However , under operating conditions, the pour point is not significant, since it does not correlate with the temperature of fuel use and can only characterize the behavior of the fuel in the tank.

The disadvantage of this method is a change in the quality of the fuel: a decrease in viscosity, cetane number, and deterioration in its lubricity. Mixing with kerosene is also limited by the flash point of diesel fuel.

Urea dewaxing is based on the ability of urea to form a solid complex with normal paraffin hydrocarbons. As the molecular weight of normal paraffin hydrocarbons increases, their ability to form a complex compound with urea increases and the temperature at which it forms decreases.

Experience in operating urea plants dewaxing showed that complete removal of high molecular weight hydrocarbons is not achieved, it is not possible to meet the necessary requirements for cloud point, therefore, installations of urea dewaxing dismantled.

The inclusion of the hydrocracking process in the technological scheme of an oil refinery makes it possible to widely transform the chemical composition of the feedstock, significantly increase the degree of its use and, consequently, increase the yield of target products and their quality. A significant role in the hydrocracking process belongs to the reactions of splitting and isomerization of paraffin hydrocarbons .

Diesel fuels produced by hydrocracking are characterized by a low content of sulfur compounds and good low-temperature properties.

Polymers have long been widely used as depressant additives for fuels and oils. In recent years, the most widespread additives in our country and abroad are copolymers of ethylene with vinyl acetate, produced at high pressure, and copolymers of acrylic and methacrylic acid esters.

Composite additives usually consist of two or more polymers, and sometimes polymer compounds are used in combination with low molecular weight substances.

The leading place among the entire range of depressant additives produced in the world, which is occupied by polymers, is due, first of all, to the relative simplicity of the technological design of the process of their production, the availability of raw materials used in their production, as well as the high depressant effect that manifests itself when introducing polymers of a certain structures in fuels and lubricants.

According to the latest requirements for depressant additives, they must not only reduce ^ but also ensure sedimentation stability of diesel fuels at low temperatures, that is, keep small crystals of the solid phase in suspension and facilitate their uniform distribution throughout the entire volume of fuel, in other words, act as n-paraffin dispersants . This need is due to the fact that when storing diesel fuels with the additive at low temperatures, it may delaminate and accumulate crystals of the solid phase (paraffins) in the lower part of the containers.

Thus, in fact, today we can talk about the emergence of a new class of additives for diesel fuels, which are called “depressant-dispersant additives”.

In addition to the previously listed properties, depressant-dispersant additives should not worsen such an indicator of diesel fuels as filterability coefficient , which is defined as the ratio of the time of filtering through a special paper filter at atmospheric pressure of the tenth portion of filtered fuel to the first and determines the operational properties of diesel fuels.

The mechanism of action of depressants in diesel fuels has been of interest to scientists for a long time. On this matter, there were different points of view and theories explaining the loss of mobility of petroleum products with decreasing temperature. The micellar theory considers a hydrocarbon mixture as a strongly associated liquid, in which micelles are formed due to the association of molecules, and the formation of micelles is possible at a temperature significantly higher than the hydrocarbon mixture.

The solvation theory provides for the interaction of n- alkane crystals with the surrounding hydrocarbon medium: when the temperature decreases, a solvation shell is formed around the emerging n- alkane crystals due to the orientation of the molecules of the liquid phase, which immobilizes part of the dispersion medium, as a result of which the system loses its mobility.

The crystallization theory proceeds from the fact that the solidification of petroleum products, including diesel fuels, is caused by the formation of a crystalline phase: when the temperature decreases, solid crystals of n- alkanes are released , which, attracting each other, form a spatial network (framework) connecting the liquid phase.

Depressant additives should be added to the fuel before the crystallization of paraffins begins, therefore, before adding the additive, the fuel should be heated to 40-50°C. It is impossible to introduce additives into frozen fuel, since in this case it is not effective. Using a depressant is more profitable and safer than diluting diesel fuels with kerosene, since it does not increase wear on parts of high-pressure fuel pumps. Recently, depressants have been used in combination with wax dispersants to prevent segregation of diesel fuels at low temperatures.

Additives intended for middle distillate and residual fuels take second place after detergent additives in the number of security documents issued. However, as mentioned above, their share in the total volume of patenting is gradually decreasing, although it still remains high.

Even within the same chemical class and among additives of the same functional purpose, in recent years preference has been given to compositions. This is understandable, since it is much easier to achieve improvement in various indicators simultaneously by combining compounds that, due to their individual characteristics, exhibit maximum activity in influencing a particular indicator. Combinations of these compounds, of course, are possible only in cases where, firstly, they mix well with each other and, naturally, with diesel fuels and, secondly, a mixture (composition) prepared from them, in which the components are included in specially selected optimal ratios, when introduced into diesel fuels it has synergism. It is the phenomenon of synergy, when the effectiveness of a composite additive when introduced into diesel fuels significantly exceeds the effectiveness of each of its components, and is not the sum of the efficiencies of each component separately, and is the difference between composite additives and the so-called additive package. The requirements for the additive package are limited to the fact that the components included in the package are mutually soluble and dissolve in diesel fuels and did not suppress each other's actions. It is typical for additive packages to obtain effects that are the sum of the effects of the components that make up the package.

When developing multifunctional additives, it must be remembered that, for example, cetane-increasing additives often significantly worsen the lubricity of diesel fuels, increasing the wear scar diameter. This can also be explained by the increased oxidizing ability of cetane-boosting additives. Oxidation products, entering the friction zone, interact with the metal and increase its wear. As a result, the concentration of anti-wear additives in the package must be increased.

The method for producing composite additives usually involves the process of mixing chemical compounds or additives in a selected solvent for a certain (optimal) time at an optimal temperature. Next, the mixture is kept until the starting substances are completely transferred into solution.

The ratio of components in the mixture should be optimal. Optimal conditions are considered (time, temperature, ratio of initial components, nature of individual components and solvent) under which the resulting additive exhibits maximum efficiency in achieving the required values of diesel fuel quality indicators. Typically, composite additives are obtained as a ready-made concentrate in a selected solvent.

Currently, there is no single chemical compound containing various functional groups responsible for the multifunctional nature of the action of this compound as an additive for diesel fuels . In this regard, it is relevant to develop composite additives or select components to create additive packages designed to improve the quality of diesel fuel, which, in turn, will lead to reliable and long-term operation of equipment operating on these fuels.

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