

# INFORMATION

## ADDITIVES USED IN LUBRICATING OILS FOR FOREIGN AVIATION GAS TURBINE ENGINES (REVIEW OF PATENTS)

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In a review article published previously,\* an analysis was made of the primary trends in the development of production of foreign synthetic oils for turbojet engines used in foreign countries. In particular, patent information was systematized relative to the compounds making up the base stocks for these oils. Along the same line, it is considered advisable to examine the question of the use of additives with these oils.

Currently used formulations include not only individual additives, but complexes consisting of up to seven or eight types of additives for different purposes. Moreover, oils for turbojet engines are likely to contain additives of new types that had not been used heretofore. As an example, we may cite an oil formulated with a trimethylolpropane sebacate base stock with eight different additives, specifically, two oxidation inhibitors, two corrosion inhibitors, a complex three-component antiwear additive, and a two-component dispersant [1]. Also characteristic is the use of two or three types of additive for the same purpose, these additives having a synergistic action (this usually applies to oxidation inhibitors).

### Oxidation Inhibitors†

Oils are usually protected against oxidation by the use of alkylated phenols such as 2,6-di-tert-butyl-4-methylphenol, which is known under the trade names of Ionol or Topanol 0. Since oils inhibited with Ionol are operable only up to temperatures of 150-175°C, the application of this additive is limited; it is usually combined with other oxidation inhibitors for better results. For example, a diester oil containing 1% Ionol and 0.5% phenothiazine gives good performance in an oxidation test in which the oil is bubbled with air at 178°C for 72 h in the presence of Fe, Cu, and Pb specimens [2].

A study of foreign patents for the past five years has shown that the principal antioxidant additives for turbojet oils are aryl- or alkylarylamines, in particular phenyl- $\alpha$ -naphthylamine (PANA) and bis(p,p'-octylphenyl)amine (OPA); these compounds are used in various combinations, either with each other or with other oxidation inhibitors. Examples of such use of PANA for the inhibition of synthetic oils are cited in Table 1 [3-16]. With regard to the OPA, its recent uses have rarely involved the additive alone [17, 18], but more often combinations of this material with other oxidation inhibitors to obtain a synergistic effect. It can be seen from the data of Table 2 that mixtures of alkylarylamines with organometallic compounds are extremely active oxidation inhibitors; these are used widely to formulate oils with a high level of oxidation resistance.

From the patent literature, cases are known in which the oxidation inhibitors belong to other classes of organic compounds, e.g., a synthetic mixture of phenothiazine (or alkylphenothiazines) and tributyltin sulfide [28, 29], thiazepines [30], polyesters of orthophosphoric acid [31], alkylthiazepines such as methylthiazepine [32], Na salts of tetrabutyl ester of ethylenediaminetetraacetic acid [33], phenothiazine in combination with alkylidihydrobenzothiazepine [34], copper trifluoroacetylacetonates [35], trihydroxydiphenylamine‡ [36], mixture of dipyridylamine and

\* See Khim. Tekhnol. Topl. Masel, No. 6, 58 (1973).

† Here and throughout article, all additive concentrations are given in % by weight - Translator.

‡ As in Russian original; should be trihydroxybiphenyl - Translator.

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TABLE 1. Oxidation Inhibitors Containing Phenyl- $\alpha$ -Naphthylamine (PANA)

| Additive composition (and % by weight in oil)  | Base oil                                   | Test conditions and additive effectiveness   | Literature reference |
|--|--|--|----------------------|
| PANA (1-10%)   | Diester                                    | Oil meets thermal-oxidative stability requirements of U.S. specifications MIL-L-9236B and MIL-L-7808 and British DERD-2497.  | [3-5]                |
| Mixture of PANA (0.1-2%) + 0.001-2% trialkyl trithiophosphate (e.g., trilauryl trithiophosphate) or diaryl thiophosphonate (e.g., dicrosyl phenylthiophosphonate)  | Polyester                                  | Oil capable of operation up to 200°C. Thiophosphites and thiophosphonates give inhibiting effect only in combination with aromatic amines (PANA).  | [6]                  |
| PANA (1%) + 1% of mixture consisting of monocalcium salt of tributyl ester of ethylenediaminetetraacetic acid (4%) and monocalcium salt of tetrabutyl ester of same acid (96%)   | Ester of trimethylolpropane                | Time for absorption of 2500 ml of oxygen by oil with 1% PANA is 282 min, and after adding 1% mixed salts was 1124 min; oil capable of operation up to 230°C.   | [7]                  |
| Mixture of octyl- $\alpha$ -naphthylamine or PANA (1%) + OPA (3%)  | Diester                                    | Use of additive reduces amount of coke formed on aluminum panel (in 8 h at 316°C) from 82 to 8 mg.   | [8]                  |
| Mixture of N-benzyl-3,7-dioctylamine (1.7%) + OPA (3%)   | Ester                                      | Oil stable to oxidation up to 210°C.   | [9]                  |
| Mixture of 0.2-9.5% arylamine (e.g., diphenylamine, PANA, dinaphthylamine, phenylenediamine) and 1% alkali-metal salt of carboxylic acids or salt of acidic products from reaction of aminocarboxylic acids and alkylamines (naphthols or hydroxyanthroquinones) | Diester                                    | In oxidation by U.S. Fed. Std. 791a, Method 5308, viscosity of diester at 38°C increases from 14 to 229 cSt and acid number to 18.7 mg KOH/g; with additive (1% of each component), the respective values are reduced to 30 and 6.2. | [1, 10, 11, 12, 13]  |
| Mixture of PANA and OPA in various combinations, where content of each component varies from 1 to 5%   | Ester, diester, esters of neopentyl glycol | In oxidation of a diester oil containing 1% each PANA and OPA (bubbling oil with air at 5 liters/h for 72 h at 204°C), oil viscosity increases only 25%, and acid number by 5 mg KOH/g.  | [14]                 |
| Mixture of PANA (1%) + 2,2-dipyridylamine (0.5%) + salt of monochlorophosphonic acid and C <sub>18</sub> -C <sub>22</sub> primary amine (0.2%)   | Ester of pentaerythritol                   | Use of additive increases induction period for oil oxidation (Pratt and Whitney method) from 3 to 16 h.  | [15]                 |
| Mixture of PANA + OPA + pentaerythritol + bis(p-phenoxyphenyl)diphenyltin in various combinations  | Synthetic or petroleum                     | Oil oxidation-stable up to 230°C; effectiveness of combination of amines and tin phenolates is noted.  | [16]                 |
| Mixture of PANA (0.2%) + dilauryl selenide (0.5%)  | Alkylsilane                                | Oil stable against liquid-phase oxidation up to 230°C, and vapor-phase oxidation to 344°C.   | [16]                 |

TABLE 2. Oxidation Inhibitors Containing Bis(p,p'-octylphenyl)amine (OPA)

| Additive composition (and % by weight in oil)  | Base oil                    | Test conditions and additive effectiveness  | Literature reference |
|--|-----------------------------|---|----------------------|
| Mixture of OPA (4.4%) + copper phthalocyanine (0.001%)   | Ester of trimethylolpropane | With oil air-bubbled at 15 liters/h for 5 h at 237°C, oil viscosity increased by only 48.5%, and acid number by 2.4 mg KOH/g    | [19]                 |
| OPA (2%) + mixture of various chlorinated heterocyclic amines containing sulfur and nitrogen (1%)  | Diester                     | Oil oxidation-stable up to 220°C.   | [20]                 |
| Two-component additive from mixture of alkylated aromatic amines, e.g., OPA (1%) + organometallic oxidation inhibitor such as hydrated cobalt or manganese acetylacetonate (0.001-0.0015%) | "                           | Oil capable of operating up to 200-210°C; high-temperature component of additive is the organometallic compound.                | [21, 22]             |
| Mixture of various alkylated aromatic amines (e.g., 3% OPA and 1% octylphenyl-β-naphthylamine)   | "                           | In oxidation tests (90°C, 53 h), the oil acid number increased only by 1.5 mg KOH/g.  | [23]                 |
| Mixture of OPA (1-2%) + copper phthalocyanine or manganese or cobalt acetylacetonate (0.0001%)   | "                           | Oil capable of operation up to 200-210°C.   | [24]                 |
| Mixture of OPA (1.9%) + cobalt acetylacetonate dihydrate (0.001%)  | Ester                       | In test with air-bubbling for 5 h at 259°C, ester solidifies; with additive, the ester viscosity at 99°C increases only by 67%. | [25]                 |
| Mixture of OPA (1%) + decylphenylamine (1%)  | Diester                     | Oil capable of operation up to 220°C.   | [26]                 |
| Mixture of diphenylphosphoramidate (0.5%) + dioctylphenothiazine (0.7%) + OPA (1.4%)   | Ester of pentaerythritol    | Upon oxidation for 24 h at 232°C, oil viscosity increases by 55.7%, acid number by 2.8 mg KOH/g.                                | [27]                 |

alkylamine salt of chloromethylphosphonic acid [37], fluorinated arylphosphines [38], etc. The application of oxidation inhibitors will typically involve the use of two or three additives (synergistic action) and also organometallic compounds, which had not previously been used in oils for turbojet engines.

### Antiwear Additives

In improving the antiwear and antiscuff properties of oils, the widespread use of organic phosphates (RO<sub>3</sub>)PO has been continued; R may be phenyl, cresyl, or C<sub>1</sub>-C<sub>10</sub> saturated alkyl radical. Such additives include tricresyl phosphate (TCP), which is used in amounts from 0.2 to 10% by weight [7, 11, 17, 18, 26, 39, 40], as well as mixtures of other neutral phosphorus-containing esters (e.g., a mixture of 2% TCP, 0.02% dibutyl ester of orthophosphoric acid, and 0.05% dibutyl ester of a phosphonous acid [1]) or mixtures of acid and neutral esters of a phosphorus-containing acid (e.g., dibutyl phosphite and dibutyl phosphate [41, 42]). Feasibility has been indicated for the use of a complex additive consisting of 2% TCP, 0.05% laurylammonium dibutyl phosphite, and 0.05% dicyclohexyl phosphate. Use can also be made of 0.17-0.2% of C<sub>18</sub>-C<sub>22</sub> alkyl-substituted amine salts of chloromethylphosphonic acid [8, 43], up to 5% salts of alkyl-substituted dithiophosphoric acid, e.g., zinc di(4-methyl-2-pentyl)dithiophosphate [44]; 0.01-5% neutral salts of thiocyanates (HSCN) with primary, secondary, and tertiary amines containing C<sub>4</sub>-C<sub>30</sub> radicals [45]; mixtures of an amine salt of an acid phosphate and ZnF<sub>2</sub> [46]; 10% of a mixture of o- and p-isomers of bis(amino-phenyl) disulfide [47].

In a number of patents, results are presented from tests of oils containing salts of dithiophosphoric acid, and also other compounds containing various metals, sulfur, and phosphorus. When phosphorus-containing additives are introduced into synthetic oils, the critical load for breakdown of the oil film is doubled (on the average), reaching 80-90 kg in four-ball tests at 200°C; if the additive contains phosphorus, sulfur, and metal at the same time, the load may reach 100-120 kg.

### Corrosion Inhibitors and Other Additives

In foreign practice, the use of corrosion inhibitors in oils for turbojet engines is aimed primarily at inhibition of corrosion effects on such metals as Cu and Pb. This emphasis is dictated by the fact that metals such as Al and Mg are more resistant to the action of high temperatures and the acidic products formed when oils are severely oxidized. In this connection, the majority of the corrosion inhibitors being patented are deactivators of lead or passivators of copper and other nonferrous metals or alloys.

The most frequently used materials for the passivation of Cu are compounds containing heterocyclic nitrogen, these compounds being used in amounts of 0.02 to 0.3% by weight. Triazoles are used widely [7, 18, 19, 42, 43, 48], in particular benzotriazoles [17, 18, 22, 24, 25] such as methylene-bis(benzotriazole) [43] and 3-amino-(4-tert-butylphenol-1,2,4-triazole) [43]. This last compound, being an effective deactivator, completely eliminates the corrosion of Mg, Al, Fe, and Cu specimens submerged in a polyester oil for 48 h at 218°C. Also used as passivators are imidazoles [7, 42, 49, 48] and pyrazoles [42].

For the protection of lead from lube oil corrosion, propyl gallate is usually added in amounts of 0.1-0.2% [7, 18, 40, 42]; other materials that have been used are a mixture of propyl gallate with 0.2% Acryloid HF-866 [23], quinizarin [7], up to 0.02% azelaic acid [8], up to 0.02% benzoguanamine, from 0.001 to 0.01% polyhydroxyanthroquinone [3], and dihydroxyanthroquinone [10].

Also added to synthetic lubricants for turbojet engines are antifoam agents, e.g., silicones [4] or dimethylpolysiloxanes [43] in amounts up to 0.005%; other additives may include materials to improve thermal stability of the oils (0.3% acridine, 0.1% phenothiazine, and quinizarin or alizarin) [2, 20]; another class includes additives to retard the process of hydrolysis of ester base oils, e.g., alkylphenols [7]. Additives may also be used to stabilize the aging process and prevent thickening of oils formulated with polysiloxane or polyaryl ether base stocks; such additives may be siloxaneferrocenes, such as 1,1-bis(5-phenylhexamethyltrisiloxane)ferrocene [49]. In connection with the trend toward higher operating temperatures of high-performance turbojet engines and the more severe oil oxidation, dispersant additives have begun to come into use in recent years. These may include polyacrylates and polymethacrylates [42], copolymers of N-vinylpyrrolidone and methacrylate (Acryloid HF-866) [7, 42], copolymers of N-vinylpyrrolidone and butyl lauryl stearyl methacrylate [20] (known under the designation Acryloid A), and certain other compounds.

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