DIESEL FUEL THERMAL STABILITY AT 300°F

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ABSTRACT

Thermal stability is an important attribute of diesel fuel quality because of the fuel's design function as a heat transfer fluid.   A recent investigation led us to conclude that poor thermal stability, as measured by 300°F laboratory tests, was responsible for premature fuel filter plugging experienced by certain diesel fuel users.   The investigation focused on three sets of fuels: random samples of fuels from major suppliers of a particular California fungible fuel terminal, hand-blends of these, and "naturally-blended" terminal tank samples.   The results demonstrate that mingling fuels with reasonably good thermal stability can yield blends with poor thermal stability.   The degradation of thermal stability on blending is attributed to interactions between insolubles precursors in the fuel and added 2-ethylhexyl nitrate diesel ignition improver.

INTRODUCTION

Diesel fuel performs multiple functions in a diesel engine and the associated fuel system. In addition to its primary role as an energy source, the fuel also serves as the sole lubricant of critical moving parts and as a heat-transfer fluid.   Concerns that accompanied the introduction of low sulfur and low sulfur/low aromatics diesel fuels raised awareness of the fuel's critical lubrication function.   Awareness of the fuel's increasingly critical role as a heat-transfer fluid is substantially less.

It is well established[1] that diesel fuels can exhibit instability when stored for extended periods of time (storage stability), or when brought into contact with high temperature engine parts (thermal stability).   For the majority of diesel fuel users, storage stability was never very important because most fuel is consumed within a few weeks of manufacture; given the advent of hydrotreated low sulfur fuels, it is of even less concern today. Good/adequate thermal stability, on the other hand, is a necessary requirement for the effective functioning of diesel fuel as a heat-

transfer fluid. In modern heavy-duty diesel engines, only a portion of the fuel that is circulated to the fuel injectors is actually delivered to the combustion cylinders. The remainder is circulated back to the fuel tank, carrying heat with it. Good thermal stability may become even more important in the future. Diesel engine manufacturer representatives indicate that engines under development will expose the fuel to more severe operating environments, e.g., higher pressures and longer contact with high temperature surfaces. In the case of jet fuels, recognition of the importance of good thermal stability has resulted in establishment of thermal stability specifications.

A recent investigation of premature fuel filter plugging experienced by certain customers supplied with fungible Grade 2-D diesel fuel from a California terminal identified inadequate thermal stability as the likely cause. An initial phase of the investigation examined fuel samples from a particular trucking company. Subsequent phases focused on three sets of diesel fuels associated with the terminal: random samples of diesel fuel from the four major suppliers of the terminal, hand-blends of these, and "naturally-blended" terminal tank samples. Results of this investigation are the subject of this paper.

EXPERIMENTAL

Thermal stability was determined by the Octel/Du Pont F21 test method.[2,3] As prescribed, 50 mL samples of pre-filtered test fuel were aged in open tubes in a 300°F (149°C) oil bath for 1.5, 3.0, or 6.0 hours. After cooling, the fuel samples were filtered and the quantity of filterable insolubles estimated by measuring light reflection of the filter pads with a Photovolt Model 577 Digital Reflection Meter equipped with a Search Unit Y with green filter. High percent reflectance values indicate good thermal stability, i.e., low levels of dark insolubles formation.

2-Ethylhexyl nitrate diesel ignition improver (cetane number improver) content was determined by a proprietary gas chromatographic procedure, rather than by the established method (ASTM D 4046). Our experience is that the established method is not reliable. While the method appears to be able to readily determine the presence or absence of alkyl nitrate, the absolute amount determined is not always accurate, especially at low concentrations.

Determination of the temperature at which 2-ethylhexyl nitrate begins to decompose was carried out by pressure differential scanning calorimetry.

RESULTS AND DISCUSSION

Trucking Company Samples

The initial phase of the investigation involved examining/testing three diesel fuel samples acquired from a trucking company that was experiencing premature fuel filter plugging: a start-of-the-day yard tank sample and end-of-the-day samples of residual fuel in the saddle tanks of two trucks. The results reveal (Figure 1) that, while the physical/chemical properties of the three samples were substantially the same, the thermal stabilities were quite different. The yard tank sample exhibited poor thermal stability, while the end-of-the-day residual fuel samples exhibited good thermal stability. This suggests that the trucks' fuel recirculation/filter system upgraded the thermally unstable fuel by converting unstable species to insoluble material that was removed by the fuel filter. Over time, the collected material plugs the fuel filter prematurely.

Terminal Supplier Samples

The second phase of the investigation involved examining/testing four fuel samples acquired from the major suppliers of the subject terminal. Property measurements (Figure 2) indicate substantial differences that could impact thermal stability.

While all four fuels contained the <500 ppm sulfur required for California vehicular diesel fuel, the range extended from 7 to 434 ppm. The appreciable differences in nitrogen content undoubtedly reflect the nature of the crude oil from which the individual fuels were produced, as well as the level of 2-ethylhexyl nitrate added (if any). After discounting nitrogen contributed by the ignition improver, the inherent nitrogen content of the four fuels ranged from 1 to 164 ppm. [Since 2-ethylhexyl nitrate ($C_8H_{17}NO_3$) contains 8% nitrogen, adding 1000 ppm of the ignition improver to a fuel introduces 80 ppm of nitrogen.]

Fuels A and C contained <10% aromatics and thus qualify as true low aromatics diesel (LAD) fuels. Fuels B and D contained >10% aromatics and are undoubtedly alternative low aromatics diesel (ALAD) fuels produced to formulas that have been certified to yield emissions less than or equal to that of reference low aromatics diesel fuels.

Fuels B and D also contained 2-ethylhexyl nitrate. The positive discrepancy between the cetane number and cetane index of these fuels is consistent with the presence of the additive.

There were substantial differences in the thermal stability of the four fuels, as determined by the 300°F (1.5-, 3.0-, and 6.0-hour) tests (Figure 3). Fuel A exhibited very good thermal

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stability regardless of the duration of the test; the opposite was true for Fuel B. Fuels C and D exhibited adequate thermal stability (>80% reflectance) in the 1.5-hour test, but substantially lower stabilities in the longer duration tests.

We believe that the observed differences in thermal stability reflect at least four factors:

- The relative abundance of nitrogen- and/or sulfur-containing insolubles precursors;
- The presence of thermally unstable 2-ethylhexyl nitrate to trigger the process of insolubles formation;
- The presence/absence of added chemical stabilizer to deter insolubles formation; and
- The solvency of the fuel.

The least stable fuel (Fuel B) contained a moderate level of inherent nitrogen (which suggests the presence of appreciable insolubles precursors) and the highest level of 2-ethylhexyl nitrate (which begins to decompose near 300°F). This combination is undoubtedly responsible for the observed poor thermal stability.

At the other extreme, the most stable fuel (Fuel A) contained essentially no nitrogen (or sulfur) and no 2-ethylhexyl nitrate; moreover, stability was further insured by the known presence of a chemical stabilizer additive. The intermediate thermal stability of Fuels C and D reflects the relative abundance of insolubles precursors and the absence/presence of 2-ethylhexyl nitrate.

Fuel solvency also plays a role in the expression of thermal instability. It is commonly accepted that the development of undesirable insolubles in aged fuels is a function of both the formation of complex, higher molecular weight species with limited fuel solubility and the capacity of the fuel to keep potential insolubles in solution.

Unlike the thermal stability tests, milder stability tests (ASTM D 2274 and D 4625, and 4-Week Peroxide[4]) designed to evaluate long-term storage stability do not reveal any serious deficiencies (Figure 4).

Interactive effects were explored by measuring the thermal stabilities of 1:1 blends of the fuels and comparing the results with the arithmetic average of the stabilities of the individual fuels (Figures 5A and 5B). The data reveal wide variations in thermal stability due to blend composition and test duration.

In a majority of cases, the observed thermal stability of the blend was significantly less than the arithmetic average of the stabilities of the individual fuels. The principle exception (Blend A:C) is the only blend that did not contain 2-ethylhexyl nitrate. Otherwise, the data suggest that the thermal stability of Fuel C was especially sensitive to the presence of 2-ethylhexyl nitrate. We speculate that the substantial decline in stability of Blends B:C and C:D reflects the effect of combining 2-ethylhexyl nitrate present in Fuels B and D with a high level of insolubles precursors present in Fuel C.

Our speculation was confirmed by examining the effect of the direct addition of 2-ethylhexyl nitrate on thermal stability (Figures 6A and 6B). Its addition to the reasonably thermally stable Fuel C caused a huge decline in thermal stability. Fuels B and D, both of which contained the additive to begin with, showed modest declines in thermal stability when more 2-ethylhexyl nitrate was added. The exceptional thermal stability of Fuel A was largely unaffected by added 2-ethylhexyl nitrate.

The level of 2-ethylhexyl nitrate used in foregoing tests (0.50 mass %) was chosen to examine the effect of what experience suggests is the highest practical use level. Other thermal stability tests using lower levels of added 2-ethylhexyl nitrate showed intermediate negative effects on fuel thermal stability. For example, reflectance values for Fuel C with 0, 0.15 and 0.50 mass % added 2-ethylhexyl nitrate were 83%, 23%, and 11%, respectively.

2-Ethylhexyl Nitrate Decomposition

It is commonly accepted that 2-ethylhexyl nitrate functions as a diesel ignition improver because it is unstable, i.e., it thermally decomposes at some moderately elevated temperature. Since 2-ethylhexyl nitrate lowered the thermal stability of most of the test fuels at 300°F, its thermal stability was examined by pressure differential scanning calorimetry. The results (Figure 7) indicate that 2-ethylhexyl nitrate begins to decompose at about 155°C (311°F), i.e., just above the 300°F stability test temperature. This result suggests that the stability test temperature and test duration together are just sufficient for 2-ethylhexyl nitrate to contribute to the observed fuel thermal instability in the 300°F test.

Terminal Tank and Pipeline Samples

The last phase of the investigation involved examining/testing 14 terminal tank samples and 27 incoming pipeline batch samples. The 300°F stability test data (Figures 8 and 9) show

that the stabilities of the tank samples were substantially lower than those of the batch samples. In the 1.5-hour test, all of the tank samples yielded reflectance values below 70%, while most of the batch samples yielded reflectance values above 70%. In the 3.0-hour test, the differences in thermal stabilities between the tank and batch samples were even more pronounced.

The differences in thermal stability between tank and batch samples are not explained by differences in key chemical properties, i.e., sulfur, nitrogen or aromatics content, or acid number. The tank samples, on average, contained lower levels of sulfur and nitrogen, higher levels of aromatics, and had lower acid numbers — property differences that would be expected to result in higher, not lower, thermal stabilities.

The differences in thermal stability between tank and batch samples are explained by differences in 2-ethylhexyl nitrate content. All of the tank samples contained 2-ethylhexyl nitrate (89 to 1470 ppm); only five batch samples contained 2-ethylhexyl nitrate (7 to 1210 ppm). Plots of thermal stability test reflectances versus 2-ethylhexyl nitrate concentrations (Figures 10 and 11) show a moderately strong correlation, especially for the 1.5-hour test values.

CONCLUSIONS

Based on the preceding results and discussion, we conclude that:

- Thermal stability of low sulfur diesel fuels, as determined by the 300°F test, can vary widely among producers;

- The presence of nitrogen- and/or sulfur-containing insolubles precursors and 2-ethylhexyl nitrate ignition improver are primary factors affecting thermal stability; and

- Individual fuels or fuel blends which contain both insolubles precursors and 2-ethylhexyl nitrate ignition improver exhibit especially poor thermal stability.

We believe that the data presented entirely support the contention that inadequate thermal stability is the primary cause of premature fuel filter plugging experienced by certain diesel fuel customers.

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(3) Henry, C.P., "The Du Pont F21 149°C (300°F) Accelerated Stability Test," *Distillate Fuel Stability and Cleanliness*, ASTM STP 751, L.L. Stavinoha and C.P. Henry, Eds., American Society for Testing and Materials, 1981, pp 22-33.

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Figure 1. Trucking Company Fuel Samples:
Selected Properties

	AA Yard Tank (Start Of Day)	AB W-25 Saddle Tank (End Of Day)	AC W-27 Saddle Tank (End Of Day)
Gravity, °API	35.0	34.9	34.9
Viscosity at 40°C, cSt	3.27	3.28	3.30
Total Sulfur, ppm	402	407	419
Total Nitrogen, ppm	267	266	268
Aromatics by SFC, Wt %	11.1	11.1	11.0
Acid No., mg KOH/g	0.10	0.12	0.12
Alkyl Nitrate, ppm*	24, 28	25	24
Cetane Index (D 4737)	47.9	48.0	48.3
Distillation (D 86), °F			
10 Vol %	437	437	439
50 Vol %	510	511	513
90 Vol %	628	630	634
Thermal Stability, 90 min. at 300°F, % Reflectance	63 (60.7, 65.9)	91 (90.6, 90.6)	92 (91.9, 92.3)

* Determined by proprietary gas chromatographic method.

Figure 2. Terminal Supplier Diesel Fuels:
Selected Properties

	A	B	C	D
Gravity, °API	36.7	38.7	36.4	38.3
Viscosity at 40°C, cSt	3.92	1.94	2.64	2.13
Total Sulfur, ppm	7	203	434	116
Total Nitrogen, ppm	1	265	164	150
Nitrogen, ppm (a)	1	106	164	25
Aromatics by SFC, Wt %	2.7	19.5	9.7	15.5
KF Water, ppm	54	55	80	75
Alkyl Nitrate, ppm (b)	<5	2000, 1980	<5	1570, 1550
Cetane Number	57.1	49.3	42.7	53.2
Cetane Index (D 4737)	56.8	44.7	46.2	45.7
D 86 Distillation, °F				
10 Vol %	455	381	404	387
50 Vol %	562	439	482	452
90 Vol %	622	591	608	593

a) Inherent nitrogen; alkyl nitrate ignition improver contribution discounted.

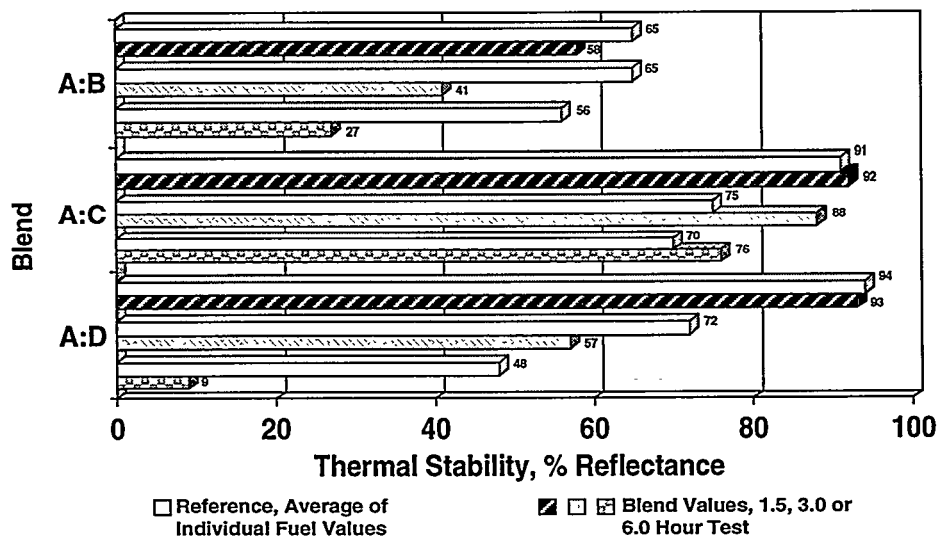b) Determined by proprietary chromatographic method.

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Figure 3. Terminal Supplier Diesel Fuels:
300°F Thermal Stability - Individual Fuels

Thermal Stability, % Reflectance

▨ 1.5 Hours ☐ 3.0 Hours ⊞ 6.0 Hours
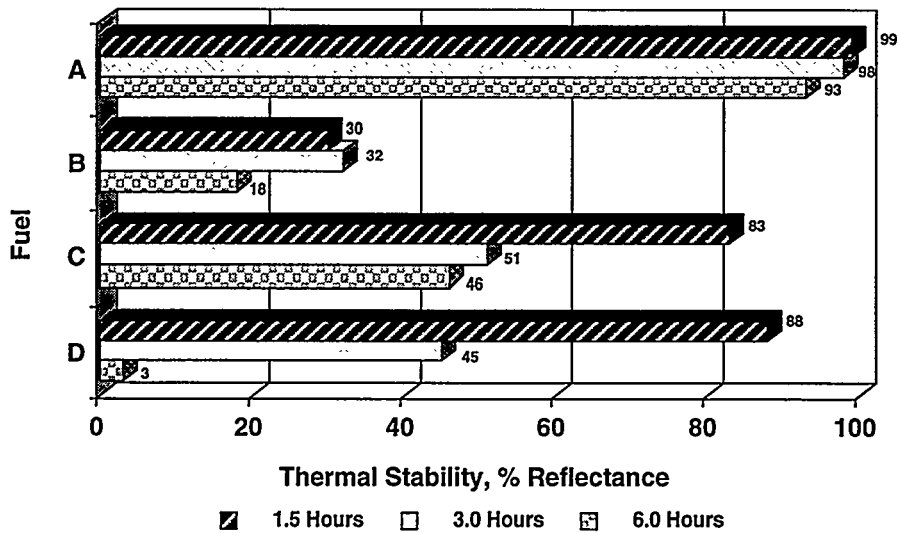
Figure 4. Terminal Supplier Diesel Fuels:
Stability Test Results

	Thermal Stability Tests, 300°F, % Reflectance			Storage Stability Tests		
				ASTM D 2274	ASTM D 4625	4-Wk at 65°C
Fuel	1.5 Hr	3.0 Hr	6.0 Hr	Residue, mg/100 mL	Residue, mg/100 mL	Peroxide, ppm
A	99	98	93	0.11	0.25	<1
B	30	32	18	0.19	1.19	<1
C	83	51	46	0.30	0.62	<1
D	88	45	3	0.28	0.36	<1

Figure 5A. Terminal Supplier Diesel Fuels:
300°F Thermal Stability - 1:1 Fuel Blends

Thermal Stability, % Reflectance

☐ Reference, Average of
Individual Fuel Values

▨ ☐ ⊞ Blend Values, 1.5, 3.0 or
6.0 Hour Test

Figure 5B. Terminal Supplier Diesel Fuels:
300°F Thermal Stability - 1:1 Fuel Blends

Thermal Stability, % Reflectance

☐ Reference, Average of
Individual Fuel Values

▨ ☒ ⊞ Blend Values, 1.5, 3.0 or
6.0 Hour Test
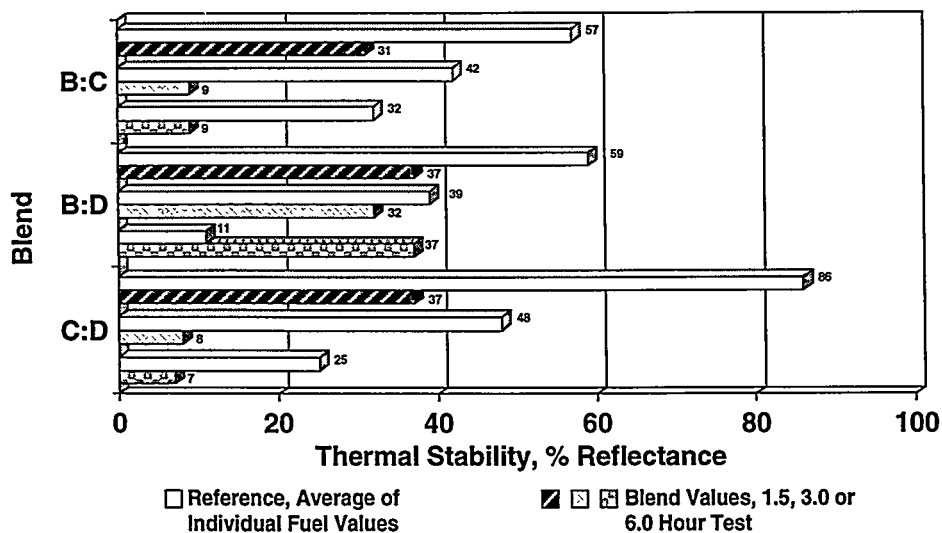
Figure 6A. Terminal Supplier Diesel Fuels:
300°F Thermal Stability, Effect of Added 2-Ethylhexyl Nitrate

Thermal Stability, % Reflectance

Fuel

□ "As Received" Fuel   ▨ □ ⊞ 0.5 Mass % 2-Ethylhexyl Nitrate Added, 1.5, 3.0 or 6.0 Hour Test
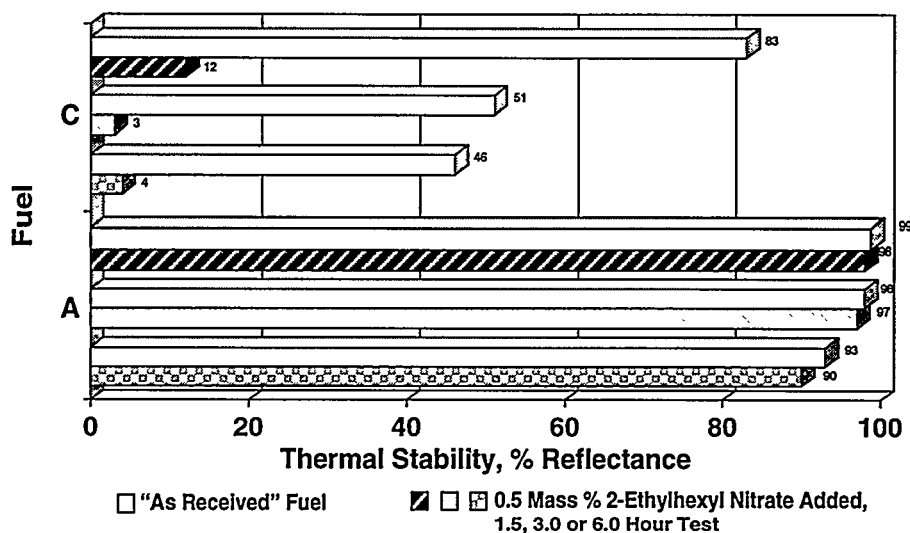
Figurer 6B. Terminal Supplier Diesel Fuels:
300°F Thermal Stability, Effect of Added 2-Ethylhexyl Nitrate

Thermal Stability, % Reflectance

Fuel

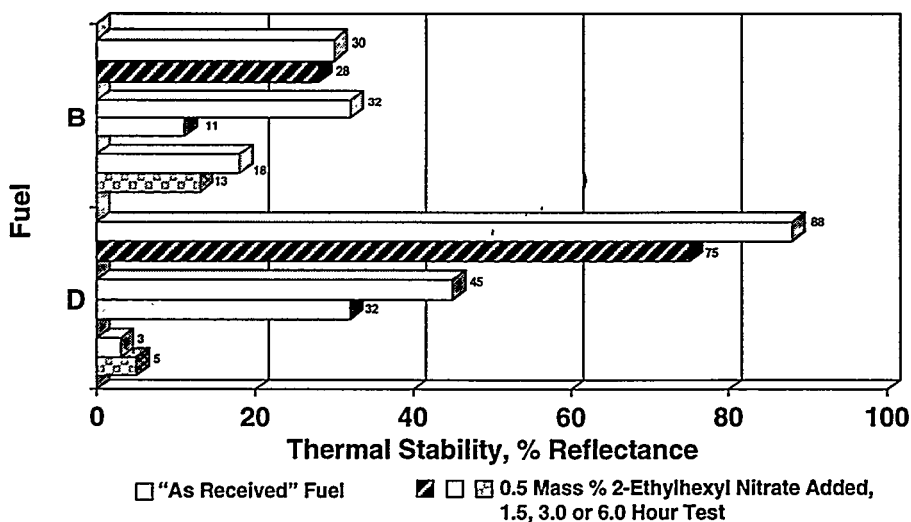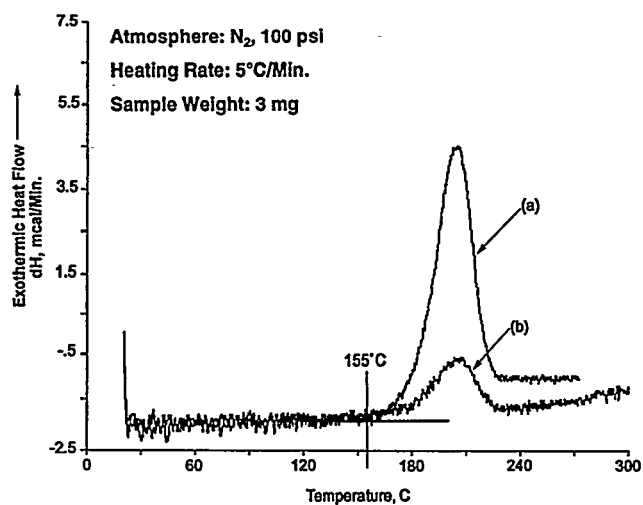□ "As Received" Fuel   ▨ □ ⊞ 0.5 Mass % 2-Ethylhexyl Nitrate Added, 1.5, 3.0 or 6.0 Hour Test

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Figure 7. Pressure Differential Scanning Calormetry
Neat 2-Ethylhexyl Nitrate (a) and 20% Solution in Diesel Fuel (b)

Figure 8. Terminal Tank Diesel Fuel Samples:
300°F Thermal Stability - 1.5 Hour and 3.0 Hour Tests
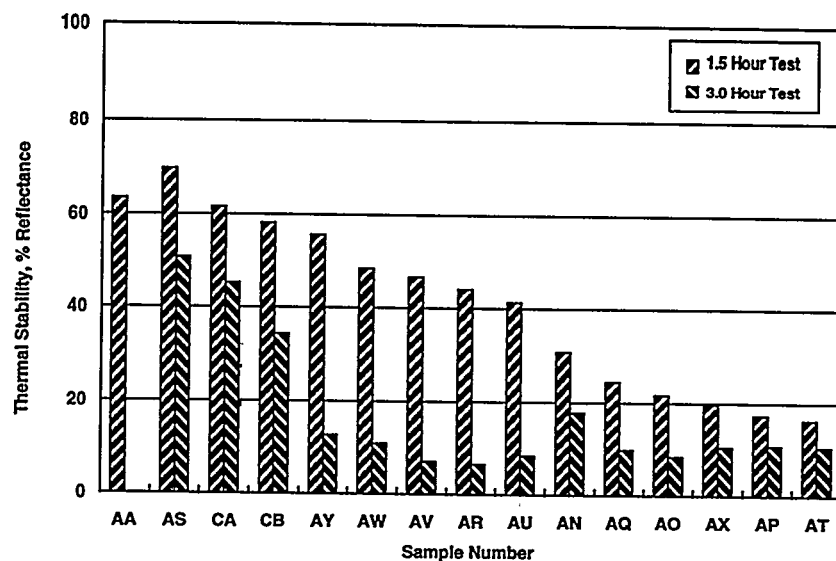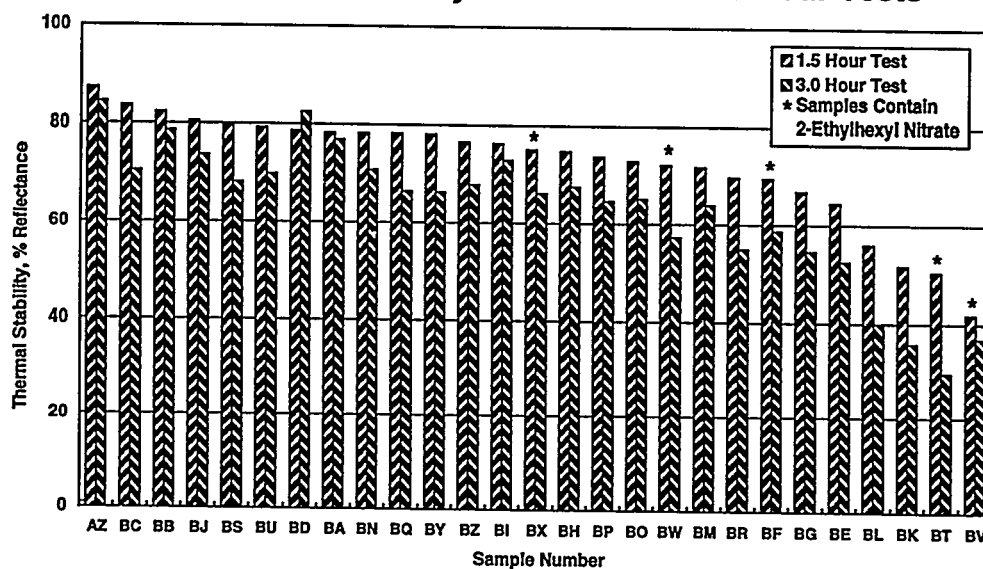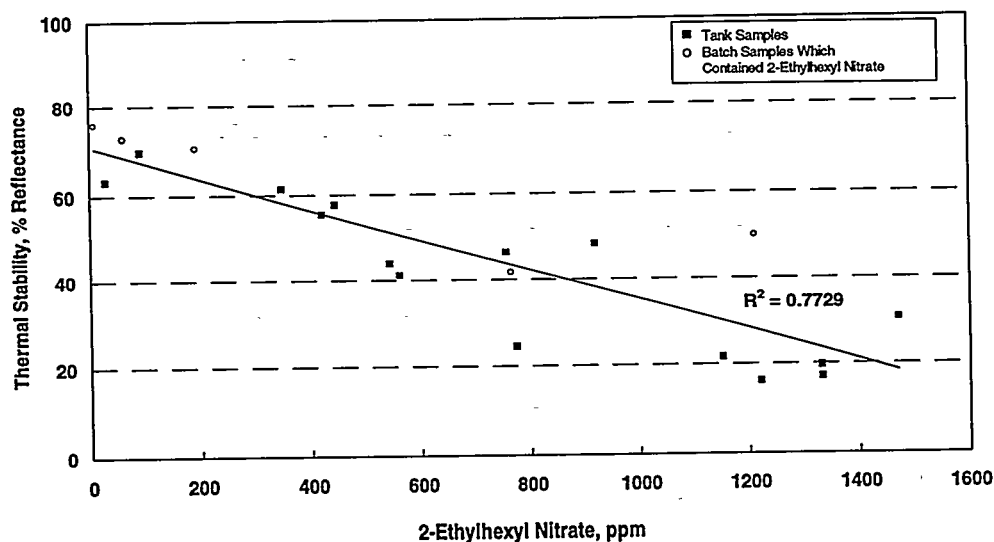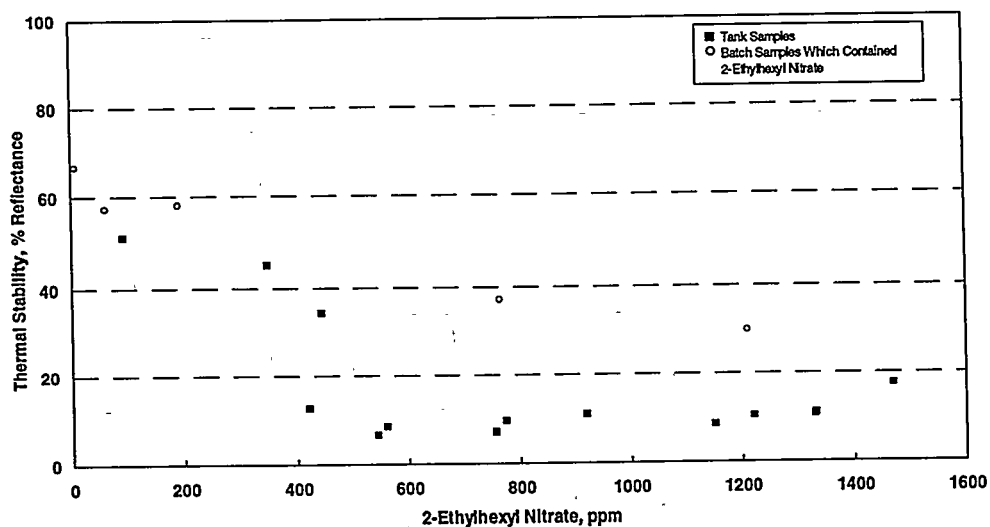

Figure 9. Pipeline Batch Diesel Fuel Samples:
300°F Thermal Stability - 1.5 Hour and 3.0 Hour Tests

Figure 10. Terminal Diesel Fuel (Tank and Selected Batch Samples)
300°F Thermal Stability (1.5 Hour) Versus 2-Ethylhexyl Nitrate

Figure 11. Terminal Diesel Fuel (Tank and Selected Batch Samples)
300°F Thermal Stability (3.0 Hour) Versus 2-Ethylhexyl Nitrate

THERMO-CHEMICAL AND THERMO-OXIDATIVE STABILITY OF DIESEL FUELS CONTAINING COMPONENTS OF LIGHT CATALYTIC GAS OIL

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The influence of Light Catalytic Gas Oil on the tendency to total insolubles formation of conventional Diesel Fuels with higher sulfur content (up to 0.2 %) is investigated. They are of special interest for a long term storage and exploitation for military purposes. The experiments are carried out under different conditions: diffusion, diffusion-kinetic and kinetic. Special attention is paid to the suppressing of total insolubles formation by commercial stability additives. It is shown that metal surfaces substantially affect the fuel stability. The addition of Light Catalytic Gas Oil deteriorates the tendency to total insolubles formation of Diesel Fuels. Several criteria are selected for prognostication of the storage terms of Diesel Fuels on the basis of the existing standards in Russia and U.S.A.

INTRODUCTION

During the entire lifetime of the fuel, when it is first produced in the refinery, until the moment when it is consumed by the engine, the problem of fuel instability always exsists[1]. The storage stability or the length of time the fuel can be stored is of great concern to the diesel fuels users[2]. The study of the literature data shows that the catalytic cracking fraction 468 - 623 K (Light Catalytic Gas Oil) is widely used as a component of automotive diesel fuels. This fraction has a significantly higher content of arenes, alkenes and heterocyclic compounds than the straight middle distillate fractions. The latter fact determines the unsatisfactory chemical stability of the

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fuels containing light catalytic gas oil (LCG). However, it has never been clearly demonstrated, why a proportion of the reaction products formed in fuels, becomes insoluble. One of the methods for monitoring of thermally induced insoluble reaction products is light scattering[7,8]. The problem of the chemical stability of motor diesel fuels, containing components of catalytic cracking, wisbracking, thermal cracking is solved by the usage of additives - stabilizing, antioxidative, dispersing, metal deactivators, multifunctional, etc.[5,6]. The usage of these additives is recommended also in the cases of preliminary hydrogenization or alkaline treatment of the unstable fraction. The analysis of the literature data shows that the effect of the metal surface on the processes of destabilization and sludge formation[2-7] should be taken into account.

The purpose of the present paper is to study the kinetics of total insolubles formation in diesel fuels containing 6 vol. % LCG and to evaluate its effect on the thermal and thermo-chemical stability of the fuel. In addition a prediction of the storage terms of these fuels, based on a method developed by us in our previous papers, has been made.

EXPERIMENTAL PART.

The basic physico-chemical characteristics of the studied diesel fuels are given in Table 1. They are a combination of light diesel fraction (LDF, cut 453-513 K), hydrogenizate (HG, cut 513 - 633 K), denormalizate (DN, cut 473 573 K), heavy diesel fraction (HDF), diesel fraction from hydro-purification - catalytic cracking (DFHP) and LCG.

Our studies on the formation of total insolubles were carried out according to the method described in Ref. 9. The kinetics of total insolubles formation was followed by nephelometric measurements confirmed by gravimetry[9,10]. Thus we excluded the possibility for mixing of light scattering and the fluorescence, due to the presence of compounds with condensed nuclei, in the diesel fuels[9] .The gravimetrical measurements were carried out after the samples subjected to accelerated aging were filtered through Schott -filter 4G, under vacuum, according to Ref.[11]. The content of hydroperoxides and acids in the samples was determined according to Ref. 12.

The storage terms for samples A (basic diesel fuel sample) and B (diesel fuel sample + 6 vol. % LCG)(Table 1) were predicted using the method given in Ref. 10. The IR spectra had been measured on Bruker IFS 113 V with KBr cells and $CHCl_3$ solvent with 1% max. concentration, at ambient temperature .

RESULTS AND DISCUSSION

As it has been shown the most important parameter determining the chemical stability of diesel fuels is their stability towards formation of total insolubles [1, 2, 3, 11]. Stringent demands involving this parameter under the conditions of accelerated aging at 368 K, are stipulated in the USA and Russian standards[3, 11]. The process of accelerated aging according to them is not carried out in the kinetic region and this fact is discussed in our previous works [9, 10]. The experiments showing the kinetics of solid phase formation in the kinetic region shows that the process proceeds without induction period in the temperature range - 398 - 423 K (elevated temperatures). In Figure 1 are shown the kinetic curves at 413 K for sample B (basic diesel fuel + 6 % LCG), sample A (basic diesel fuel) and for pure LCG. The results for samples A and B correlate with the data of the gravimetric analysis.

The results of the accelerated aging of samples A and B according to the modified by us ASTM-2274-80 are given in Table 2. The details of the modification are described in Ref. 9. The initial samples with indexes (o) and the samples after the accelerated aging with indexes (τ) do not contain hydroperoxides. As we have shown before[9, 10], for other diesel fuels, no hydroperoxides are formed after accelerated aging tests. Here is confirmed our supposition that this is due to the presence of sulfur-containing compounds in the studied samples (see Table 1). We measured the IR spectra of the samples after the accelerated aging in order to determine the presence of carbonyl compounds in them. No such compounds were detected within the limits of the sensitivity of the method - 0,04 vol. %. The content of organic acids in the initial samples (see Table 2) is relatively low, but after oxidation at 368 K the acid number rises 4 - 5 times. In the pure fraction LCG this effect is strongest. All the studied samples and also those containing commercially available additives I, III and DTBP (2,6- di- tert-butyl-4-methyl phenol), do not satisfy the stringent requirements stipulated in American[11], and Russian standards[3]. The best result obtained by us at 368 K, regarding the amount of total insolubles (see Table 2), is for B sample blended with additive II. The value of total insolubles 3,68 mgr./100 ml. is below the requirements ASTM[2], which is 5,00 mgr./100 ml. The increase of the concentration of additive III four times does not improve the obtained results. The lowest stability towards the process of total insolubles formation is observed in LCG, under the experimental conditions in Table 2. As a whole the stability of the samples A and B is at an order of magnitude lower than that of the diesel fuels containing 20 % LDF and 80 % HG or 20 % LDF and 80 % DN(see also Refs 9,

10).Thus the data of Table 2 confirm undoubtedly the negative influence of LCG on the thermo-oxidative stability of the diesel fuel.

In order to predict the time when these samples will reach the boundary values of the standards (1,5 mg\100 ml[11] and 5 mg\100 ml[3]) at 284 K, the average year temperature in Bulgaria, we followed the kinetics of total insolubles formation at 5 different elevated temperatures (383, 393, 403, 413, 424 K). The method which includes nephelometric measurements is described in details in Ref. 9. The type of kinetic curves in Figure 1 gives us the possibility to determine the reaction rate, the activation energy and the pre-exponential factor of the reactions causing the formation of total insolubles. One of the reason for using of these kinetic data at low temperature is the fact that the rate of formation of total insolubles in an inert atmosphere is very small[9]. Our experiments at elevated temperatures were carried out with vigorous stirring in order to minimize the difference between the solubility of oxygen at elevated temperatures and at 284 K[13] .

We intended to make a quantitative evaluation of the results based on the prediction at elevated temperatures and the standard methods recommended for determination of the storage stability. It is known from the literature [14, 15] that the overall rate of any chemical oxidation process can be represented by the following equation :

$$W_1 = W_{1o}.e^{-E_1/RT} \qquad 1)$$

where: W_1 is the total rate of oxidation; W_{1o} is the preexponential factor; E_1 is the activation energy of the reaction and T is the temperature in Kelvin.

The reaction in the kinetic region (equation 1) to a certain extend will proceed for a time τ_1, while the chemical oxidation process in the diffusion region will proceed with different rate according to the following equation :

$$W_2 = W_{2o}.e^{-E_2/RT} \qquad 2)$$

where the abbreviations used are the same as in equation (1).

The time for the proceeding of the reaction to the same extend (in the diffusion region) will be τ_2. Obviously, by the way the times are defined the following inequality will be valid $\tau_1 < \tau_2$, because the process is a heterophase one. The expression (3) is valid for the activation energies for the both processes :

$$E_2 = E_1 + E_D \qquad 3)$$

where E are the respective activation energies of the processes in equations (1) and (2), and E_D is the activation energy of diffusion. From equation (3) it follows that:

$$W_2 = W_{2o} \cdot e^{-(E_1 + E_D)/RT} \qquad 4)$$

It should be pointed out that in W_2 and E_2 is not included the coefficient - γ accounting for the dissolved oxygen according to the Henry's law since it is known that γ is not temperature dependent[11] (up to 433 K). Thus we obtain the following expression for the rates ratio:

$$W_1/W_2 = W_{1o}/W_{2o} \cdot e^{-[E_1 -(-E_1 - E_D)]/RT} = W_{1o}/W_{2o} \cdot e^{E_D/RT} \qquad 5)$$

If we accept that $W_{1o}/W_{2o} = k_{d_o}$ and $W_1/W_2 = k_d$, we get the following final expression:

$$k_d = k_{d_o} \cdot e^{-E/RT} \qquad 6)$$

Using equation (6) we can calculate the correlation coefficient k_d at different temperatures. For checking the validity of our data at elevated temperatures (Table 3) we used the data for the total insolubles formation obtained by us at 316,3 K according to the method developed by UOP, where the experiments are carried our without bubbling of air, stirring and in dark bottles. It has been shown in the literature[16] that the correlation of the data obtained by it with the real terms are 90 %. We calculated the data with the help of the following equation:

$$k_d = g^{316,3 \text{ (calculated)}} / g^{316,3 \text{ (experimental)}} \qquad 7)$$

The value we obtained for k_d by equation (7) is 18,1. This coefficient may be used to correct the data for prognostication of the proceeding of the process of total insolubles formation at ambient temperature[11]. The dependence in equation (6) we have used to calculate the activation energy of the process of formation of total insolubles. Since the process of total insolubles formation verus time (Fig. 1) is a linear one and this dependence is observed in all the experiments carried out by us in the temperature range 383 - 423 K, we can use the method of correlation coefficients for predicting this process at ambient temperature. The amount of total insolubles we have determined at the 16-th our (mg/100ml) expresses the Arrhenius behavior. The dependence of ln g at the 16th hour versus 1/T allows the extrapolation of these data by computation down to 284 K. The latter is the average temperature for storing fuels in Bulgaria. The computing was made according to equation (8) with the help of a computer program "Prognoz".

$$\ln g_r = \ln g_o - E/RT \qquad 8)$$

where: g_τ is the amount of total insolubles determined gravimetrically; ln g_0 is the preexponential factor; E is the energy of activation of this process; R is the universal gas constant and T is the temperature in Kelvin.

Equation (8) gives us the possibility to determine the time of the storage in real terms calculating when the fuel will reach the necessary parameters according to the values given in the standard methods [3, 11].

The molecular mass of the total insolubles showed that 70 % of them have the same molecular mass and this fact allows to use the Arrhenius dependence in mg/100 ml., directly.

The results obtained after the computation of the results according to equation (8) are given in Table 3. The storage terms are given in the respective two columns in Table 3 by comparing the value of g in mgr./100 ml with the boundary values in the standards of Russia and USA.

In Table 3 are given also the activation energy of the process of total insolubles formation (E); the preexponential constant in equation 1 (ln g_τ); the prognosticated by equation 8 amount of total insolubles at temperature 368 K. The observed by us a linear dependence of the process of formation of total insolubles (see Fig 1) is giving us a basis to consider that the time for reaching of g_{284K} will be proportional to g_{368K}. The relatively low activation energy for sample B (with 6 % LCG) in the kinetic region could be explained by the increased solubility of oxygen in the diesel fuel sample containing LCG. The latter is rich in nonsaturated and aromatic hydrocarbons. As a whole the activation energies determined for sample B are about by 40 %

lower than those found for straight diesel fuels[10]. This is due both to the increased solubility of oxygen and to the higher reactivity of the system as a whole.

It should be noted that the determined storage terms have a deal of reserve obtained by the experimental conditions of the aging which carried out in the kinetic region. In real conditions the fuels are not often in this region. This is proved simply by comparing the values for the predicted total insolubles formation at 368 K in Table 3 and the measured values in Table 2 for the respective samples.

In our previous studies we have shown that the metal surface is deteriorating the thermal stability of diesel fuels [9, 10]. It has been shown that soluble copper is most reactive to catalyze the fuel oxidation[24]. In order to take into account the influence of the metal surface on the storage terms we have chosen in our experiments steel which serves as a material for reservoirs.

Obviously, in this case the fuel oxidation proceeds as a homogeneous - heterogeneous process and a significant role plays the metal surftace type. We accept that a linear dependence is observed between the metal surface and the process of total insolubles formation rate. This supposition is based on the studies of Bulgarian authors, who have shown that there exists a linear dependence between the rate of the oxidation process and the surface of the of the metals and metal oxides [18, 12].

On the last two rows of Table 3 are given the results of accelerated aging in the presence of steel surface. The same type of steel is chosen used for production of steel tanks where diesel fuels is held. The surface/volume ratio used in our prediction calculations is for $10 \ m^3$ tank. The influence of the surface decreases the termo-oxidative and thermochemical stability by a factor of 0,12.

CONCLUSIONS

1. The investigations prove the destabilizing effect of LCG, although in relatively low concentrations, on the thermo-oxidative and thermo-chemical stability of diesel fuels.

2. The presence of some metal surface intensifies the proceeding of the processes pointed above.

3. It has been found that in the presence of LCG and steel surface the additives studied by us can not eliminate their deteriorating influence.

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Table 1. Components content and physico-chemical characteristics of the samples A and B of the diesel fuel tested.

Components	Sample A (Content in vol %)	Sample B (Content in vol %)
1	2	3
Light Diesel Fraction (LDF)	35	35
Heavy Diesel Fraction (HDF)	10	10
Hydrogenizate (HG)	33	32
Denormalizate (DN)	15	12
Fraction from hydro-purification (DFHP)	7	5
Light Catalytic Gas-Oil (LCG)		6
Parameters of the physico-chemical characteristics		
1. Relative Density (d^{20})	0,836	0,847
2. Fractional Content °C ; Initial Boiling Point	164	172
10 % vol.	208	213
50 % vol.	272	270
90 % vol.	348	346
End Boiling Point	375	366
3. Kinematic Viscosity at 20 °C, mm^2/sec.	4,8	4,6
4. Total Sulfur Content mass. %	0,23	0,26
5. Mercaptan Sulfur - mass. %	0,01	0,0096
6. Acidity, mg KOH per 100 cm^3	0,58	0,72
7. Resins , mg/100 cm^3	6	8
8. Bromine Number, g Br/100 g.	3,5	5,1
9. Dienes, mass. %	abs.	0,2
10. Coke in 10 % residue, mass. %	0,044	0,048
11. Nitrogen, ppm	167	181
12. Poup point, °C	-8	-10
14. Corrosion on Copper Plate	no	no

1	2	3
15. Hydrocarbons in vol. %		
- Alkanes & cycloalkanes	68,2	67,7
- Alkenes & cycloalkenes	1,4	10,7
- alkylarenes	3,7	7,3
- arenes	26,7	24,6
16. Ash, mass. %	abs.	abs.
17. Flammability °C	58	48
18. Iodine Number, g I/100 g	1,5	4,5

Table 2. Results of acceletated ageing of samples A and B according to the modified ASTM-D2274-80, in the kinetic region at 368 K.

Sample	[ROOH]$_0$	[ROOH]$_t$	(Acidity)$_0$, mg.KOH/100 ml	(Acidity)$_t$, mg.KOH/100 ml	Total Insolubles, mg/100 ml	Colour ASTM-D 1500	
						oxidized	non-oxid.
A	0	0	0,6	3,2	9,62	3,0	4,5
B	0	0	0,7	6,1	12,56	3,0	5,0
B + 0,01 mass.% addititve I	0	0	0,7	4,3	9,06	3,0	4,0
B + 0,01 mass.% addititve II	0	0	0,7	5,3	3,68	3,0	3,5
B + 0,01 mass.% addititve III	0	0	0,7	3,1	8,28	3,0	3,5
B + 0,04 mass.% addititve III	0	0	0,7	2,8	9,43	3,0	4,0
B + 0,01 mass.% DTBP	0	0	0,7	7,3	18,93	3,0	4,0
Light Catalytic Gas Oil (LCG)	0	0	1,6	33,4	21,61	4,0	5,0

Table 3. Results of acceleted ageing of samples A and B according to the modified ASTM-D2274-80, in the kinetic region at 368 K.

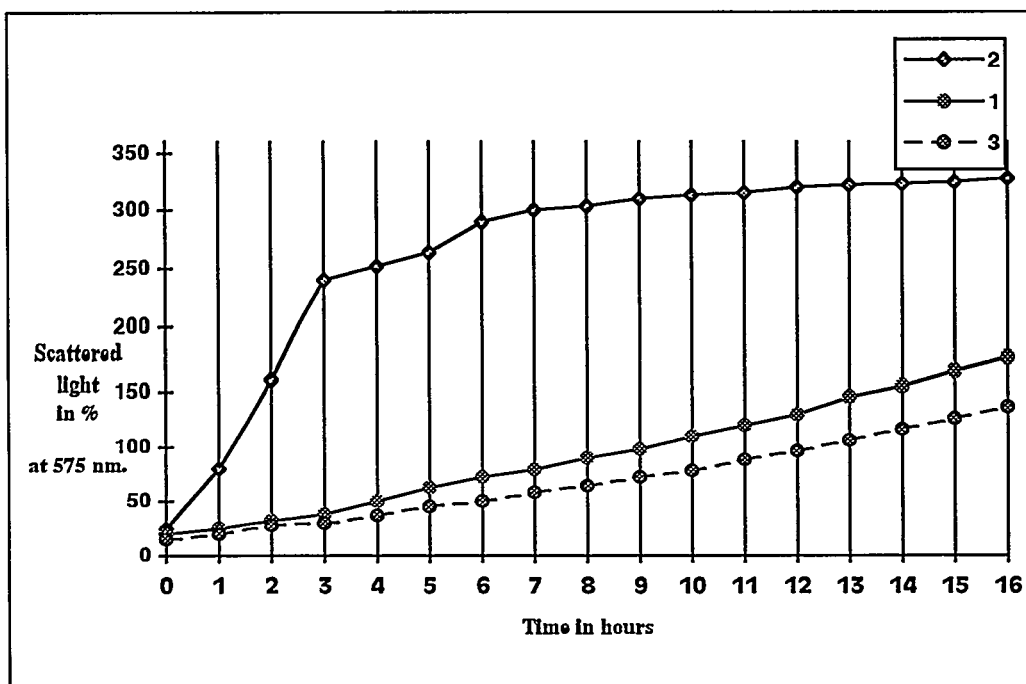| Sample	$E_a \pm 2$ kJ/mol.	ln g$_o$	r^2 correl. coeff.	Predicted total ins. at 368 K, mg/100 ml	Predicted storage term at 284 K for reaching the boundary values in months according to: (in months)		Predicted storage term at 284 K for reaching the boundary values in 10 m^3 tank, according to: (in months)	
					ASTM- 2274 1,5mg/100 ml	Russian GOST 5mg/100 ml.	ASTM- 2274 1,5mg/100 ml	Russian GOST 5mg/100 ml
A	48,28	14,53	15,66	10,35	6,2	19,4	-	-
B	39,17	15,66	0,99	18,81	6,6	20,5	-	-
B + 0,01 mass.% addititve I	42,30	15,57	0,99	15,59	11,5	35,8	-	-
B + 0,01 mass.% addititve II	33,81	12,79	0,98	12,58	5,0	15,5	-	-
B + 0,01 mass.% addititve I + steel plate	24,84	10,72	0,93	21,75	2,2	3,8	2,1	3,4
B + 0,01 mass.% addititve II + steel plate	24,57	10,39	0,98	18,46	2,2	3,8	3,4	4,0

Figure 1. Dependence of the total insolubles formation versus time at 413 K, (determined nephelometrically) for the sample B (basic diesel fuel + 6 % LCG) - curve 1; pure LCG - curve 2; sample A (basic diesel fuel) - curve 3. The wavelength is 575 nm.

STUDIES ON GUM FORMATION TENDENCIES OF MIDDLE DISTILLATE DIESEL FUELS

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The rapid growth in transportation fuel demand is compelling greater use of severe processing like catalytic cracking, visbreaking, coking etc, which results increased contents of olefines & aromatics and consequently less stable processed fuels. Total gum formation in coker kerosene (191- 454°C), straight run gas oil (156-477°C) available from an Indian refinery and their blends were determined using UOP-413 method and correlated with their composition. Effect of hydrocarbon type composition, bromine no. sulphur and nitrogen content, maleic anhydride and diene value and also of boiling range on formation of sediment and adherent gum in these blends was investigated. Composition has been observed to play an important role in the degradation of these distillate fuels.

INTRODUCTION

In order to meet increasing demand of middle distillate fuels, refiners have resorted to blending significant proportions of cracked stocks of middle distillate fuels as extenders. The cracked stocks have less stability than straight run distillates [1-2]. These unstable cracked components, although diluted by blending in diesel oil formulations, still exert a strong influence on stability behaviour during long storage periods [3].

The presence of coke and fouling material or cracked stocks in the fuel can cause engine operating difficulties. These materials form deposits on heat exchanger surface. Solids in engine combustion nozzels result in reduction in the efficiency of the heat transfer surface areas in heat exchangers ultimately leading to malfunction of the fuel system [4-6]. Injector fouling in compression ignition engine may be troublesome in engine operation and reduced fuel spray quality. Injector coking has greatest effect on pilot injection. Engine noise, excessive smoke, loss

of power, poor fuel economy degraded emmissions and poor drivability have also been cited as problems arising from injector coking [7].

Several authors [8-10] have reported that the formation of insolubles in cracked stocks is due to the presence of hetero compounds and some of them has explained the phenomenon using phenalene and indole as model componds. The formation of insolubles is a complex process in which many compounds of the cracked stocks are involved. Malhotra et al [11] have reported that polynuclear aromatic hydrocarbons are also an important source of gum formation in cracked middle distillate fuels.

The aim of present paper is to examine the effect of some of the properties like bromine no.,maleic anhydride value, diene value, (all representing unsaturation of the fuel), total nitrogen, basic nitrogen, total sulphur and the concentration of different types of aromatics in straight run and its blends on with the insoluble formations.

EXPERIMENTAL TECHNIQUES & PROCEDURES

Straight run and coker kerosene derived from an Indian refinery were taken for this study. Different blends in the ratio 50:50, 70:30 and 30:70 were made from them. Table 1 presents their physico-chemical characterstics.The concentration of different types of aromatics viz mononuclear ranges between 15-28 percent by wt, dinuclear ranges between 14-16 percent by wt, and poly nuclear ranges between 4-6 percent as determined by UV spectroscopy in these samples and are also reported in Table 1.Distillation data of these samples showed the boiling ranges between 156-480 °C, were determined using ASTM D-2887 and are presented in Table 2 . Stability of these samples determined by UOP-413 method are reported in Table 3.

The insolubles formation in these samples were correlated with their hydrocarbon composition and heteroatoms (nitrogen & sulphur) concentration.

RESULTS AND DISCUSSION

The density of these fuels and their blends varied from 0.8881 to 0.8751 and their molecular weight ranges from 231 to 246. Distillation data of these samples show the boiling range between 156-480 °C.

Almost all the properties, which affects the stability are higher in coker kerosene than straight run product. Their values in the blends show appropriate trends with reference to their compositions.

Fuel deterioration is observed to occur under long term, low-temperature storage conditions (storage stability) as well as short term, high temperature stress (thermal oxidative stability i.e.UOP-413).

Effect of total nitrogen concentartion on gum formation of these fuels is shown in (Fig 1). It is observed that the increasing the concentration of nitrogen the tendency of gum formation increases linearly. However, basic nitrogenous compounds takes active role upto a certain concentration, after that their effectiveness in the gum formation slows down (Fig 2). From the comparison of Figs.1 and 2, it is evident that not only the basic, but non basic nitrogen compounds also play a role in gum formation, particularly at higher concentrations. Similar observations were observed in a study on the effect of indoles and pyrroles on gum formation tendencies [15]. Lacy et al [14] have also reported that pf !nfirmed by GC MS and nitrogen compoudnds type analysis of the methanol extract of cracked middle distillate from a Germany oil refinerey using GC/FPD detector [15].It has been reported that basic nitrogen compounds are much less prone to sediment formation than non basic compounds [7].

The effect of total sulphur on gum formation tendencies is shown in Fig.3. The effect is not linear but sulphur compounds are effective upto a certain concentration and then their effectiveness becomes slower. Mushrush [16] studied the type of sulphur compounds which are responsible for deterioration of fuel samples. He has confirmed that condensed thiophenes, but

not benzothiophenes, are deleterious in terms of fuel stability. Thiophene compounds reported in the literature with reference to fuel instability have included thiophene, tetrahydrothiophene, alkyl substituted thiophenes and condensed thiophenes such as benzo and dibenzothiophenes [18]. Our observations are in close agreement to the results of earlier workers [12] who have indicated that fuels low in sulphur content are relatively more stable to those having high sulphur content. However prediction of fuel stability can not be made on the basis of total sulphur and total nitrogen content alone because reactivity of their compounds depend upon the chemical structure [13].

Active olefines are generated during thermal cracking processes. The presence of oxygen or active oxygen species such as hydroperoxides will greatly accelerate degradation as well as significantly lower the temperature at which undesirable reaction (auto oxidation) will occur. Consequently the degradation of fuel blended with the cracked stocks is frequently dependent upon the nature of the potential autooxidation pathways, which can occur. Reactive species in fuels which may be involved are not only nitrogenous and sulphur compounds but the unsaturation in the fuel system also play an active role. Diene value, bromine no. and maleic anhydride value which are indication of unsaturation in the fuel also affect the fuel stability as shown in Figs. 4 and 5. With the increase of diene value and MAV, the amount of total gum or insolubles formation is more and show the trend like basic nitrogen and total sulphur compunds. Mushrush [16] examined hydroperoxides and oxygen induced oxidation of alkyl and aromatic sulphides, thiols, disulphides, substituted thiophenes, and the co-oxidation of thiols with the active olefines. The diene value and MAV confirm the presence of active olefines, which on co-oxidation, increase the value of total gum.Isobutylenes or other similar degradation products would provide active olefines that can further be involved in oxidation reaction. Not all the olefinic compounds are involved in the degradation of the fuel samples which is confirmed by our study of diene value and MAV that insoluble formation increases upto a ceratin extent and then stabilze. Mushrush [16] explained that substituted thiophenes gave sulphoxides, sulphones and the Dies-Alder product from these reactive species.From the co-oxidation of thiophenoles with styrene, the major product was 1-phenyl -(2-phenyl thiyl) ethane. Other products included: 1-phenyl-(1phenylthiyl) ethane and the oxidised products phenyl-(2-phenylethyl) sulphoxide and

phenyl thiolsulphonate. For indene, the major addition products included the 2-phenylthiyl indan. Oxidation product included the 2-phenylthiyl-1-indanol and indanon [16].

The present study on coker kerosene and its blends with straight run product showed that the increase in mononuclear type compounds in fuels decreases the gum formation (Fig.6). This could be due to the higher solvency power of monoaromatics for compounds forming the degraded products (gum).

Earlier study have shown that dinulear type compounds like phenalene reacts with the indoles after auto-oxidation [8,19] and form the insolubles in the form of alkylbis(indolyl)phenalene.This study was done in LCO. In case of coker kerosene the dinuclear aromatics concentration are found to reduce the gum formation tendency (Fig.7). From this, it may be inferred that the compounds like phenalene, senstive to auto-oxidation are not present in the coker kerosene fuel. The trend shown in Fig.7 supports the view that dinuclears present in the fuels are not participating in gum formation, but only play a role of solvent for degraded products. Thus, it is expected that the nature of dinuclear aromatics may depend on the type of cracking processes such as FCC,Coking and Visbreaking employed. Fig.8 indicates that in cokerkero the polynuclear compounds are most senstive to cause instability of the fuel sample. It shows that increasing the concentartion of polyaromatics the total gum formation increases.Hence it may be possible that in coker kerosene polynuclear structures play a role in the formation of degraded products by condensing and forming bigger molecules which separate out with gums. Similar observations i.e presence of polyaromatics in gum/sediments has been reported using FTIR technique in diesel fuels [20].

CONCLUSIONS

Straight run and coker kerosene were characterized for their physico-chemical characteristics and stability behaviour. The trend of the effect of basic nitrogen, sulphur, diene value and MAV on gum formation are similar. Poly aromatics take part in gum formation, while mono and diaromatics act as solvents for reducing the gum formation.

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TABLE-1

PHYSICO-CHEMICAL PROPERTIES OF FUEL SAMLPES

PROPERTIES	SR. AS SUCH	COKER KERO.	SR+COKER KERO BLEND (70:30)	SR+COKER KERO BLEND (50:50)	SR+COKER KERO BLEND (30:70)
DENSITY $D^4{}_{20}$	0.8881	0.8751	0.8854	0.8819	0.8790
SP.GRAVI. 60/60 oF	0.8918	0.8718	0.8891	0.8856	0.8827
SULPHUR % BY WT.	0.21	0.34	0.23	0.25	0.28
TOTAL NITROGEN, PPM	176.6	588.4	345.4	383.1	476.0
BASIC NITROGEN PPM	57.3	312.6	127.9	152.5	221.6
MAV, mg/100gms.	1.13	10.86	2.72	4.55	5.97
DIEN VALUE	0.3	2.8	0.70	1.18	1.55
MOLECULAR WT.	246	232	234	245	231

HYDROCARBON TYPE ANALYSIS (BY UV)

MONONUCLEAR AROMATICS	27.7	15.1	21.3	20.6	18.5
DINUCLEAR AROMATICS	16.1	14.0	14.2	15.1	14.6
POLYNUCLEAR AROMATICS	4.5	5.7	4.6	5.1	5.4

TABLE 2

DISTILLATION CHARACTERISTICS OF FUEL SAMPLES
(ASTM D-2287)

| SAMPLES TEMP,°C	STRAIGHT RUN (SR)	COKER KEROSENE	SR+COKER KERO. BLEND (50:50)	SR+COKER KERO. BLEND (70:30)	SR+COKER KERO. BLEND (30:70)
IBP	156	191	174	172	162
DISTILLATE, VOLUME %					
5	213	219	217	216	217
10	226	241	234	231	236
20	244	263	254	250	258
30	261	278	312	268	276
40	277	290	284	281	288
50	291	303	300	296	303
60	307	319	317	313	320
70	330	333	334	331	336
80	357	349	352	353	353
90	394	366	377	383	374
95	421	382	401	412	393
FBP	477	454	467	480	464

TABLE-3

## STABILITY BEHAVIOUR OF FUEL SAMLPES

STABILITY

UOP-413 METHOD	SR. AS SUCH	COKER KERO.	SR+COKER KERO BLEND (70:30)	SR+COKER KERO BLEND (50:50)	SR+COKER KERO BLEND (30:70)
SEDIMENTS, mg/100 ml	2.4	82.3	41.6	46.9	81.5
ADHERENT GUM, mg/100 ml	1.8	41.7	14.8	32.1	26.1
TOTAL GUM,mg/100 ml	4.2	124.0	56.4	79.0	107.6

FIG.1
EFFECT OF TOTAL NITROGEN ON TOTAL GUM IN BLENDS OF STRAIGHT RUN & COKER KEROSENE

TOTAL GUM, mg/100ml

TOTAL NITROGEN,PPM
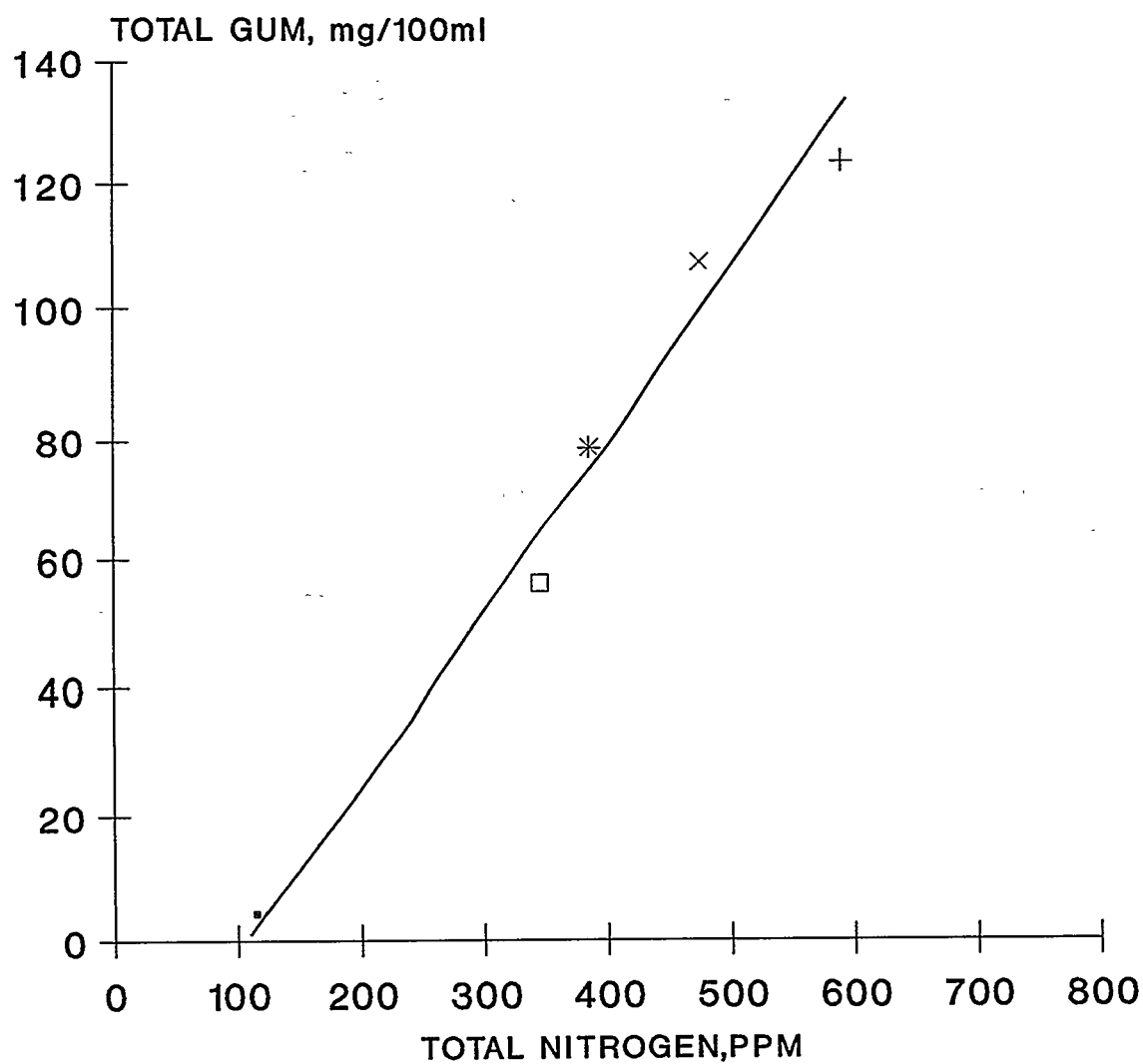
— ST.RUN (SR)   —+— COKER KERO (CK) SR+CK,50:50

—▢— SR+CK,70:30   —✕— SR+CK,30:70

FIG.2
EFFECT OF BASIC NITROGEN ON TOTAL GUM

TOTAL GUM, mg/100ml

BASIC NITROGEN,PPM
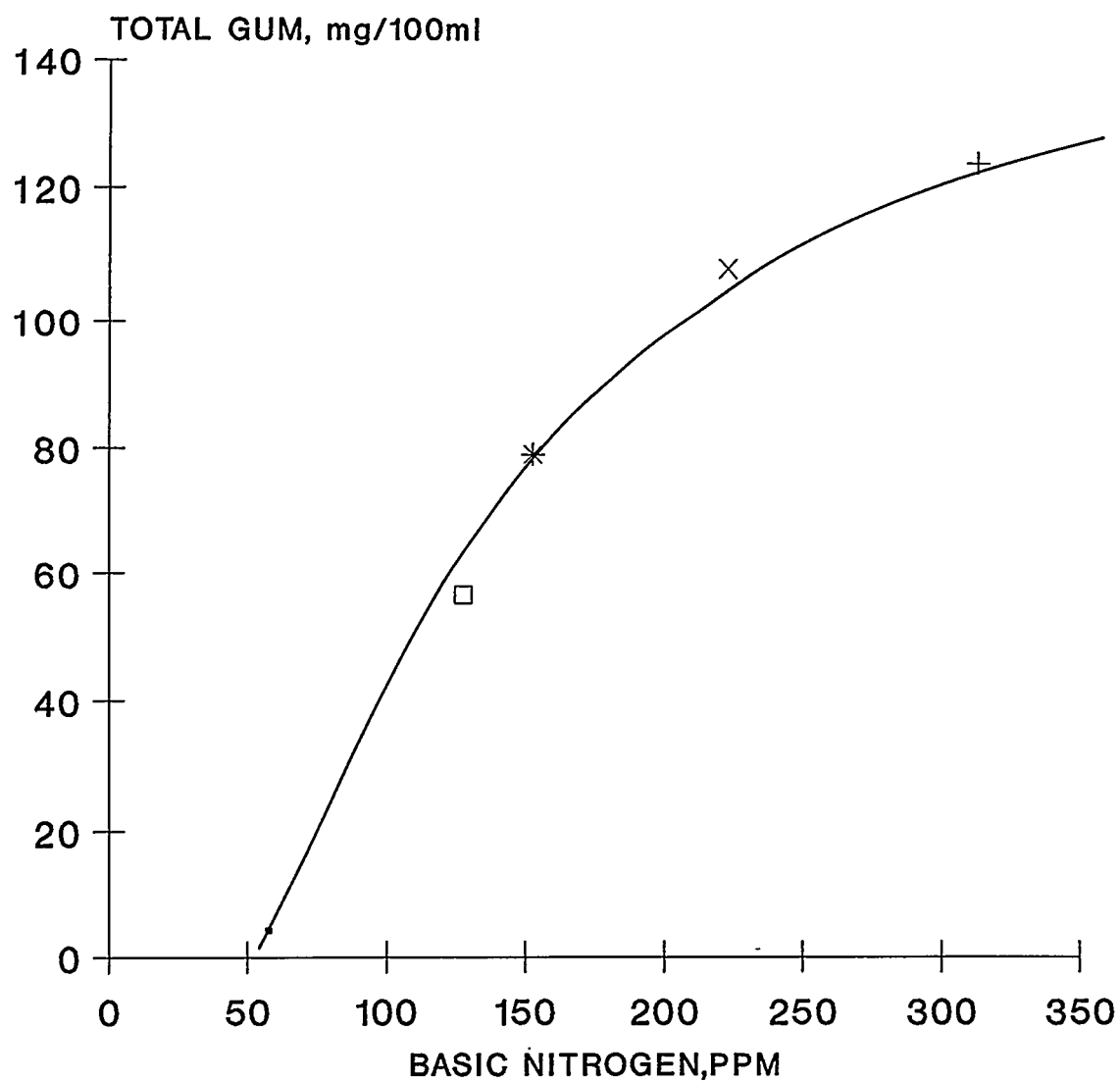
- ST.RUN
- COKER KERO
- SR+CK,50:50
- SR+CK,70:30
- SR+CK,30:70

BLENDS OF SR & KEROSENE

FIG.3
EFFECT OF TOTAL SULPHUR ON TOTAL GUM
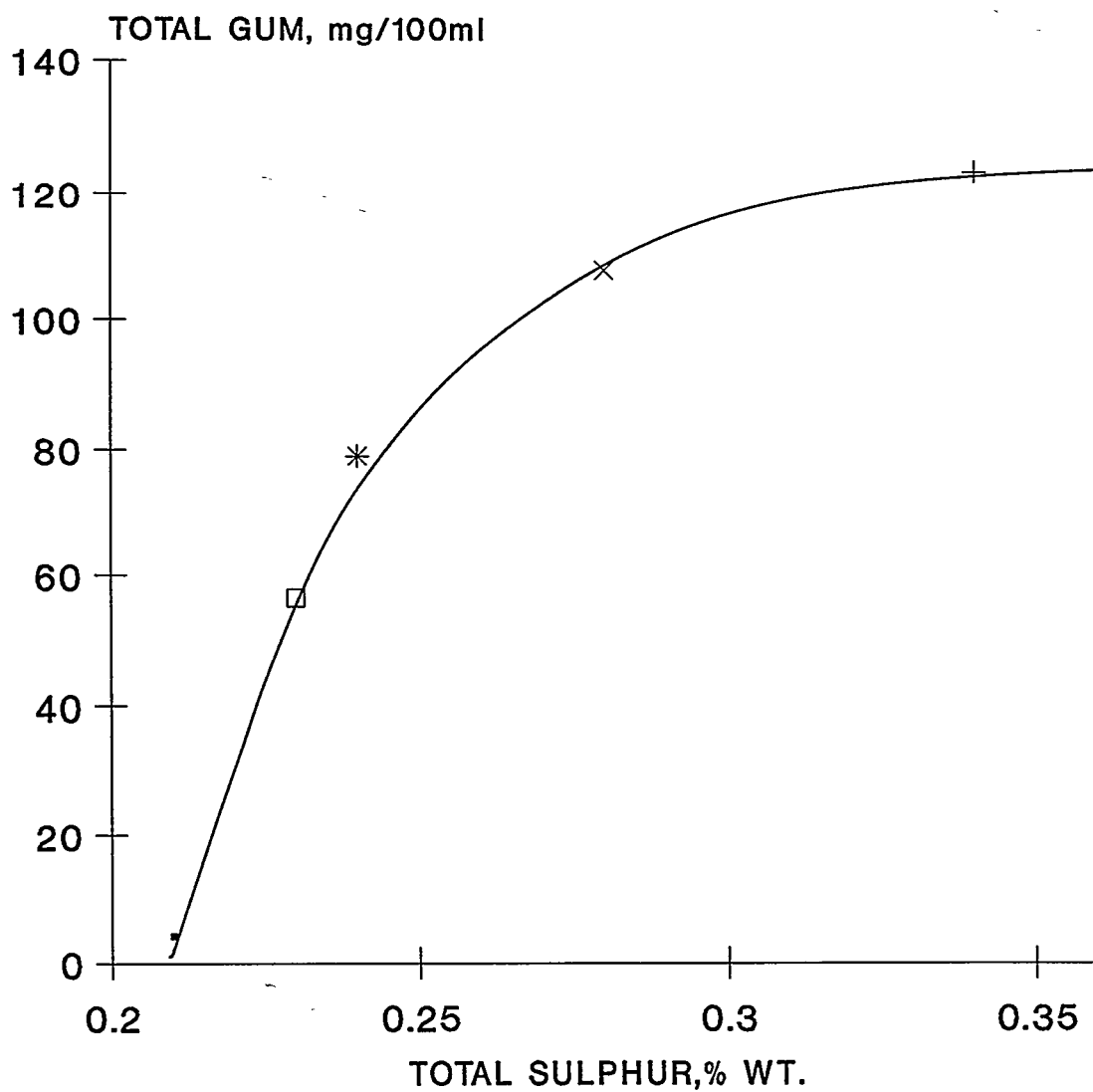
BLENDS OF SR & KEROSENE

FIG.4
EFFECT OF DIEN VALUE ON TOTAL GUM
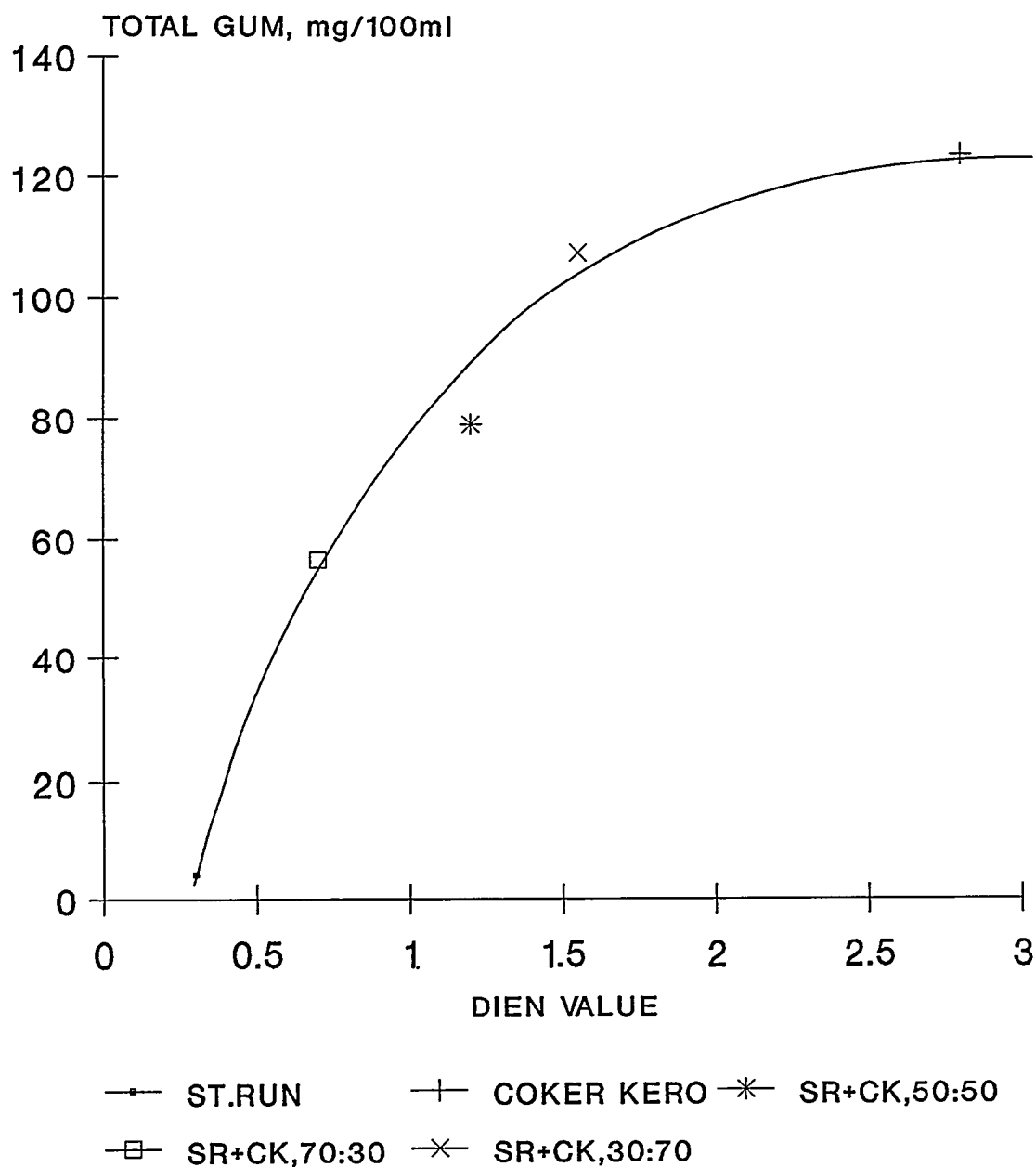
BLENDS OF SR & KEROSENE

FIG.5
EFFECT OF MAV VALUE ON TOTAL GUM

TOTAL GUM, mg/100ml

MAV,mg/100gms.

—•— ST.RUN   —+— COKER KERO —*— SR+CK,50:50

—▫— SR+CK,70:30   —×— SR+CK,30:70

BLENDS OF SR & KEROSENE

712
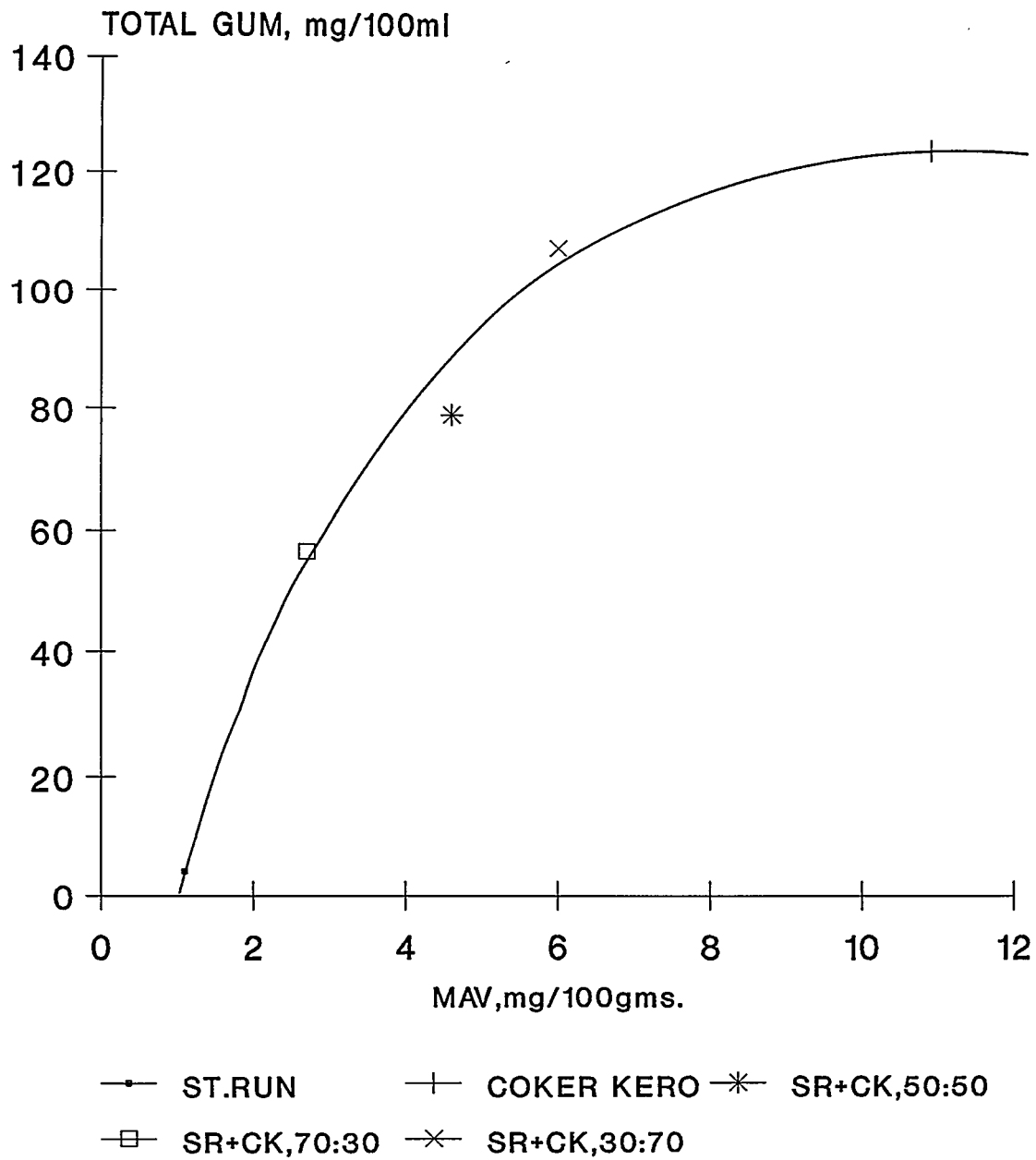
FIG.6
EFFECT OF MONOAROMATICS ON TOTAL GUM

TOTAL GUM, mg/100ml

MONOAROMATICS % VOL

—■— ST.RUN   —+— COKER KERO —✳— SR+CK,50:50

—▫— SR+CK,70:30 —✗— SR+CK,30:70

BLENDS OF SR & KEROSENE

713
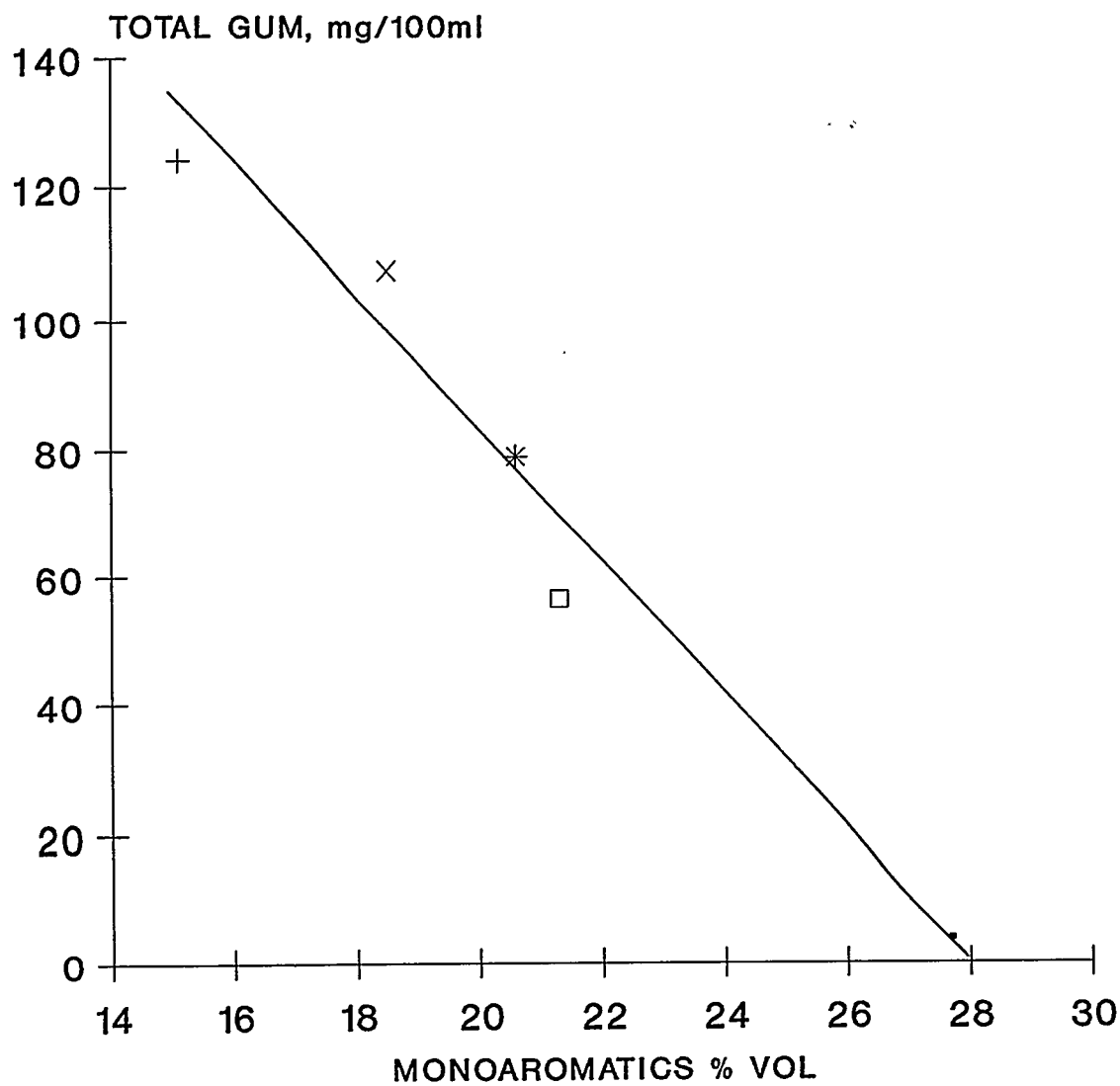
FIG.7
EFFECT OF DINUCLEAR AROMAT.ON TOTAL GUM

TOTAL GUM, mg/100ml

DINUCLEAR AROM.% VOL

—•— ST.RUN	—+— COKER KERO	—*— SR+CK,50:50
—□— SR+CK,70:30	—×— SR+CK,30:70	

BLENDS OF SR & KEROSENE

714
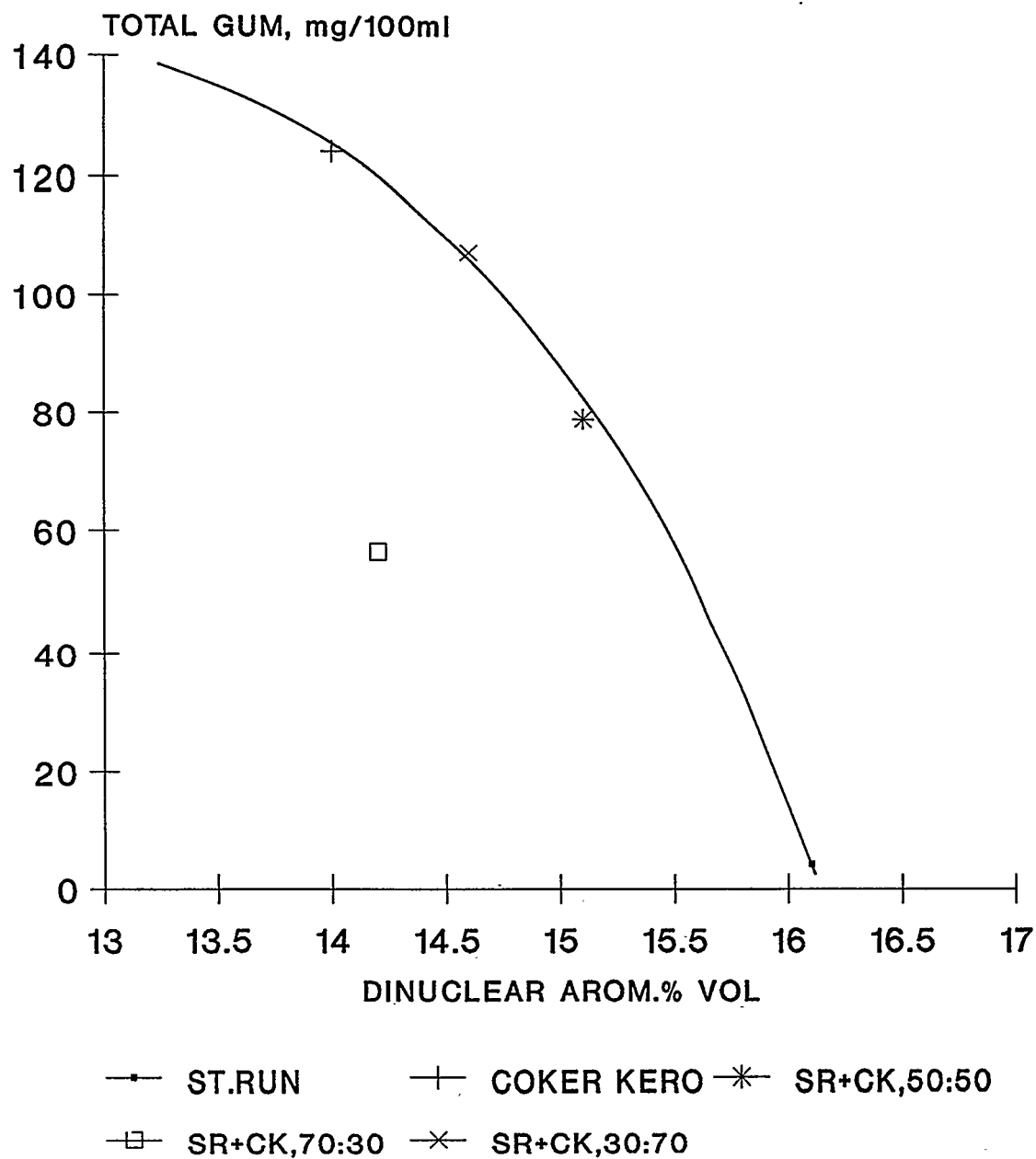
FIG.8
EFFECT OF POLYNUCLEAR AROM.ON TOTAL GUM
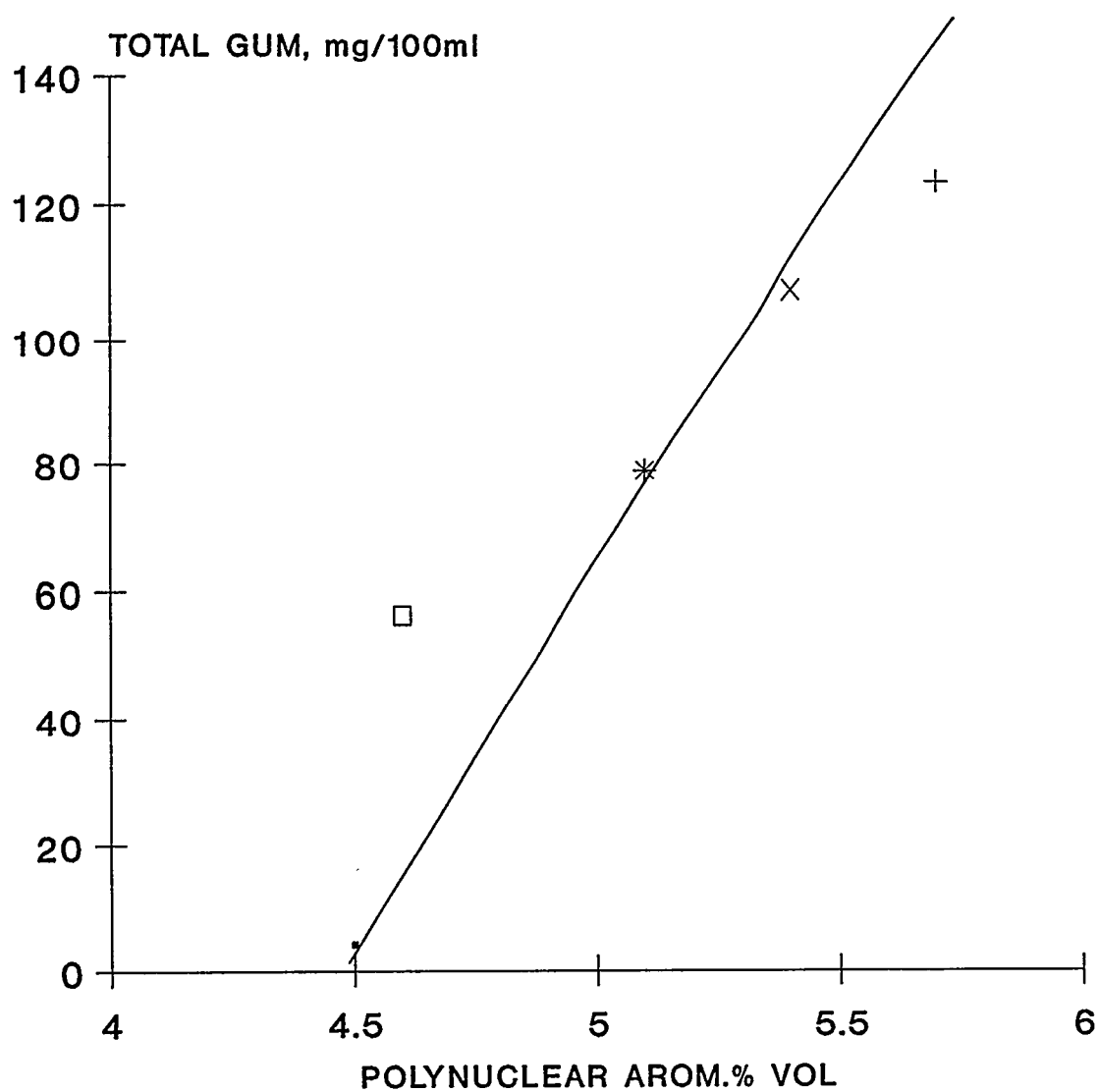
TOTAL GUM, mg/100ml

POLYNUCLEAR AROM.% VOL

ST.RUN   COKER KERO   SR+CK,50:50

SR+CK,70:30   SR+CK,30:70

BLENDS OF SR & KEROSENE

A BIT OF HISTORY - THE DEVELOPMENT OF STORAGE STABILITY TESTS FOR MIDDLE DISTILLATE FUELS SINCE WORLD WAR II

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ABSTRACT

After World War II, refiners in need of a viable outlet for by-product middle distillate stocks from cracking operations found that such stocks could be blended to a limited degree into burner fuels, distillate diesel fuels, and similar products. However, when long term storage was required, the buyer had to be certain the fuel would be usable at the end of the storage period. This led to extensive studies of the stability of such fuels and to the development of accelerated stability tests which ultimately evolved into ASTM, IP, ISO and other standard test methods. This paper summarizes those developments and examines their limitations. This encompasses work by the U. S. Bureau of Mines and by the U. S. Navy in the 1950's, and the standardization of ASTM Test Methods D2274 (the 95°C/16 hour test), D4625 (the 43°C test), and D5304 (the oxygen overpressure method).

INTRODUCTION AND BACKGROUND

During World War II, the armed forces required vast quantities of fuels. Fuels for jeeps, trucks, tanks, landing craft, naval ships, transports, and aircraft had to be produced in quantities much greater than those required for the peacetime economy, an economy, moreover, that was just emerging from the Big Depression of the 1930's. Further, the fuel for the propeller-driven military aircraft of those days was a gasoline with octane numbers in excess of 100, i.e. much higher than the octane level supplied by your friendly neighborhood service station for the automobiles of that era. Those familiar with aviation history will recall that it was only in the waning days of the war that the Luftwaffe activated the first jet-propulsion aircraft.

Although rationing of fuel and tires was a fact of life for the automobile owner during the war years, military requirements could not be met by rationing alone. New refineries had to be built, refineries replete with the most modern processes such as fluid catalytic cracking, alkylation, isomerization, and thermal and catalytic reforming to meet the volume and octane requirements of military machines. When

the war ended, these large, modern refineries replaced the less economical, lower throughput prewar refineries often referred to as "tea kettles." In the United States, these old tea kettles had been designed around sweet U.S. crudes and consisted largely of distillation operations augmented by thermal or Houdry fixed-bed cracking and by a limited amount of other processing.

In the United States, the postwar gasoline market was driven by the automobile manufacturers who filled the backlog of demand with products powered by engines having higher and higher compression ratios, thus forcing refiners to make continual adjustments to the octane levels of gasolines. In those days, gasolines were marketed in two grades with the lower octane grade designed to satisfy the needs of about 80 percent of the cars on the road and with the premium grade designed to satisfy another 15 percent. In the mid-1950's, a third grade was added to satisfy a further 3 percent of the cars. The remaining 2 percent could not be satisfied by any octane level because they were out of tune or had excessive deposits in their cylinders.

While gasoline requirements drove refinery processing, changes were also occurring in the home heating market. My own experience is indicative. While I was growing up in the 1920's and 1930's, my parent's home was heated by coal, - more specifically by anthracite. A popular radio program of the era was "The Shadow Knows" sponsored by Blue Coal, since coal was the major home heating fuel in the eastern United States. Shortly after the war, my father had the old coal furnace converted to a gun-type oil burner to reduce expenses and to eliminate having to take the ashes out on a routine basis.

SYMPOSIUM ON STABILITY (June 1958)

The conversion to the use of no. 2 fuel oil and the problems associated with the use of cracked stocks in that fuel proceeded at such a rate that, in June 1958, the American Society for Testing Materials held a symposium on the Stability of Distillate Fuel Oils, sponsored by Technical Committee E of Committee D-2. The papers were issued as STP 244 in February 1959.

Elmquist[1] reported that the total number of domestic oil burners had increased from 2.5 million in 1945 to over 9 million by the end of 1957 and that the annual domestic consumption of distillate fuels, exclusive of kerosine, increased roughly threefold from 219 million barrels in 1945 to over 604 million barrels in 1957. During the same period, the increase in the use of diesel engines resulted in an increase in diesel fuel consumption from 65 million barrels to over 180 million barrels. The increased volumes of

distillate fuels had been provided not only by increasing refinery throughputs but also by increasing the yield of distillate from a barrel of crude, from about 14.5% in 1945 to over 23% in 1957.

A number of papers presented at the symposium dealt with fuel storage stability problems and how efforts by refiners and by oil burner manufacturers was reducing the number of maintenance calls. Gray[2], Editor of FUELOIL AND OIL HEAT, raised the question of whether a stability specification was needed for no. 2 heating oil and concluded that such a specification was needed if there was a practical and not too costly method to achieve it. It is interesting to note that a stability requirement has never been added to the ASTM specifications, although it has been discussed many times. However, the fuel specifications of the Army and of the Navy do have stability test requirements, since longer storage periods are involved.

The symposium also addressed test methods that had surfaced by that time. MacDonald and Jones[3] listed some 26 programs studying the stability problem and noted the conditions of testing and the characteristics measured as indicative of instability. Test periods ranged from 90 minutes for a 300°F test open to the atmosphere to "variable times" meaning 12 weeks or more under ambient temperatures. The characteristics measured included insolubles, soluble gums, light transmission, solids, color, filterability, screen clogging, discoloration of filter paper, pressure drop across a woven felt pad, injector sticking time, particle size, and acid flocculated materials. Although the popular means of supplying oxygen to the system was by venting or by leaving the test vessel open to the atmosphere, some use was made of aeration, of 100% oxygen, and of ultraviolet light under nitrogen. Some use had been made of rigs simulating heating oil systems or a diesel engine injector system. In short, if you could think of it, it was tried!

Clinkenbeard[4] commented that there were probably as many test methods are there were oil companies. He noted that long-time, low-temperature storage tests tended to correlate well with field experience but took too long to be useful as a quality control test, whereas the shorter, higher temperature tests used correlations that were limited to specific fuel composition and additive content.

Clinkenbeard also summarized the existent knowledge of the chemistry of fuel instability as being the product of oxidation and chemical reactions involving unsaturated hydrocarbons and reactive organic compounds of sulfur, nitrogen, and oxygen. He noted that there were considerably higher concentrations of those heteroatoms in the resulting sediments than there were in the parent fuels. The ensuing years

have not added that much to our knowledge except, perhaps, a better concept of the reaction mechanisms involved.

Ward and Schwartz[5] reported on work conducted at the Petroleum Experiment Station, Bureau of Mine, on the effect of blending distillate fuels. (This group has evolved into the present-day NIPER). Starting with 34 base fuels, they produced 250 blends which were subjected to storage in pint-size glass bottles at 110°F for 6 to 39 weeks. They found that the storage stability of a blend could not be predicted from the storage stability of its components. About 30 years later, the David Taylor Research Center in cooperation with the Naval Research Laboratory also obtained information on distillate blends as a byproduct of a stability additives study. White[6] confirmed that the blending of two fuel stocks may not result in sediment formation that is a linearly proportional to the sediments produced by each fuel stock alone.

FACTORS IN FIELD STORAGE

Accelerated tests for evaluating fuel stability may or may not be able to predict what will be found in large-scale field storage tanks. Storage tanks are usually constructed of various metals, although steel probably predominates, but plastic tanks, concrete tanks, salt caverns, and rock caverns have also been used.

The largest steel tanks are usually built above ground as right circular cylinders. Such tanks are subjected to the effects of atmospheric heating and cooling and of solar heating. Heating will cause the circulation of product because, as the material close to the tank walls is heated, it becomes less dense than the bulk volume and will rise to the surface. There, it is enriched with oxygen from the air, and eventually cools and descends. Diurnal cooling after the sun sets can result in atmospheric air being drawn into the tank. If the air is highly humid, moisture can condense out. Underground steel tanks are usually horizontal cylinders. The temperatures are more uniform but such tanks are subject to corrosion and leakage of ground waters into the tank, if care is not taken to preclude such effects.

If the steel tank walls are penetrated by pipes of copper or its alloys, there is the possibility of copper being dissolved and catalyzing the oxidative reactions thought responsible for instability reactions. If the internal tank walls or fittings have rusted, the iron oxide may serve as a catalyst (as postulated by some), although White and Bowen at the David Taylor Research Center[7] failed to find a statistically significant effect in a few limited tests.

In summary, fuel in a storage tank may contain filterable insolubles (sediment) and gums from a variety of sources, specifically, from leakage or rusting, from catalyzed or uncatalyzed instability reactions, or even from air blown silt. It is impossible for an accelerated test to simulate all the real life situations so, by necessity, such tests can only evaluate the "inherent stability" of a fuel.

There are two further ways in which accelerated tests can fail to produce the same results as field storage. First, any effort to obtain a fully representative sample from a large storage tank may be doomed to failure. Mixing of contents prior to sampling may be inadequate as there are often dead spaces in a tank. Further, structural members in a storage vessel may trap sediment thus rendering samples from the vessel lower in sediment than the true average value. John MacDonald (Naval Engineering Station) told the author he had seen accumulations of sediment in emptied barges used in a joint Bureau of Ships/Coordinating Research Council test program in the early 1950's.

Second, the average temperature to which the contents of a storage tank are exposed affect the speed with which instability reactions occur. In work at the Naval Ship Research and Development Center[8] starting in the late 1960's, four fuels/fuel stocks were stored outdoors in 4-liter Pyrex glass bottles at locations in Maine, at Annapolis, and in Florida. After 24 months of storage, fuels stored in Maine on average produced less total insolubles than those stored at Annapolis, and those stored in Florida produced more insolubles.

ACCELERATED STABILITY TESTS

Over the years, three accelerated stability test methods for middle distillate fuels have been standardized by ASTM, specifically:

- Test Method D 2274 Oxidation Stability of Distillate Fuel Oil (Accelerated Method)
- Test Method D 4625 Distillate Fuel Storage Stability at 43°C (110°F)
- Test Method D 5304 Assessing Distillate Fuel Stability by Oxygen Overpressure

An attempt was also made to standardize a 300°F/90 minute filter pad test, but interlaboratory testing yielded such poor repeatability and reproducibility that a decision was made not to publish this method. As reported in another paper in this International Conference, John Bacha is attempting to resurrect the method using improved technology to preclude subjective examination of the filter pads.

Test Method D 2274 was standardized in 1964. IP 388 and ISO 12205 are comparable standards. It was based on a method developed in the course of stability studies started at the Navy's

Engineering Experiment Station, Annapolis, MD, in 1950 – 1951. Both air and pure oxygen were tried, with the latter being found superior. Using oxygen, a 350 mL sample of fuel was held at 210°F for 16 hours while 5 +/- 0.5 L/hr of oxygen were bubbled through the fuel. At the end of that time, the total insolubles were determined. In the course of the standardization effort, the temperature was changed to 95°C and the oxygen flow rate was reduced to 3 +/- 0.3 L/hr. The standardized test has been used in the U.S. Army and Navy fuel specifications to preclude acquisition of unstable fuels. Total insolubles levels of 1.5 to 2.5 mg/100 mL of fuel have been used as the maximum allowable levels.

Test Method D 4625 (IP 378/87) was not standardized until 1986. It is an outgrowth of a large number of tests conducted in sealed or vented bottles of various sizes or in open beakers under controlled temperatures. MacDonald and Jones[3] mentioned tests in pint bottles, in quart bottles, and in beakers with temperatures controlled at 80° to 275°F, with 110°F being the most common. Storage periods ranged from 2 hours at 275°F to 12 weeks at 110°F. As standardized, Test Method D 4625 stores 400 mL of fuel in a 500 mL borosilicate glass bottle fitted with a vent in an oven at 43°C (110°F) for periods of 0, 4, 8, 12, 18, and 24 weeks. After the contents of a bottle have been cooled to room temperature, the filterable and adherent insolubles produced during the storage period are determined.

Test Method D 5304 was not standardized until 1992. It grew out of coordinated studies at the David Taylor Research Center and the Naval Research Laboratory on using oxygen under pressure to accelerate the instability reactions. The use of oxygen under pressure is not new. MacDonald and Jones[3] mention the use of 100 psi oxygen in one of the tests they cited and, in a 1954 paper, Nixon and Cole[9] reported using 100 psig oxygen in a pressure vessel held at 212°F for a study of JP-3 aircraft jet engine fuel stability . In fact, ASTM Test Method D 525 Oxidation Stability of Gasoline (Induction Period Method), which was originally published in 1939, also uses 100 psi oxygen.

In Test Method D 5304, a 100 mL aliquot of filtered fuel is placed in a borosilicate glass container, which is then placed in a pressure vessel preheated to 90°C. The pressure vessel is pressured with oxygen to 800 kPa absolute (100 psig) for the duration of the test. The vessel is placed in a forced air oven held at 90°C for 16 hours. After aging and cooling, the total amount of fuel insoluble products is determined gravimetrically and corrected by use of a blank determination.

USES AND LIMITATIONS OF THE THREE STANDARD METHODS

Test Method D 2274 provides a basis for the estimation of the inherent storage stability of middle distillate fuels. It has been used for many years as the stability control test in the U.S. Naval Distillate Fuel specification, MIL-F-16884. As previously mentioned, the original breakpoint between acceptable and unacceptable fuel was 2.5 mg/100 mL. However, as the refiners dug more deeply into the bottom of the crude barrel, components in the fuel changed and D 2274 limits had to be reduced to 1.5 mg/100 mL to preclude the acceptance of unstable fuels. In the current MIL-F-16884J, Test Method D5304 using oxygen overpressure has become the referee method with D 2274 accepted as an alternate if the time at 95°C is extended from 16 hours to 40 hours.

Throughout its life, Test Method D 2274 has suffered from poor precision. The 1997 Annual Book of ASTM Standards[10] shows a repeatability of 0.60 mg/100 mL and a reproducibility of 1.17 mg/100 mL at a total insolubles level of 1.5 mg/100 mL. Moreover, the scope of the test method has been limited to middle distillate fuels and stocks from petroleum, so that any residual components or stocks from non-petroleum sources such as oil shale renders the test method invalid.

Over the years, a number of studies have been conducted to ascertain the reasons for the poor precision associated with the D 2274 procedure. At the 2nd International Conference held in San Antonio, Texas, in July/August 1986, it was noted [11] that some laboratories were departing from the specified procedure. Oxygen purities from "lab filtered compressed air" through 99.5% oxygen were in use; solvents other than those specified were being employed; filter media other than the specified glass-fiber filter paper and filtration areas greater than that of the specified Gooch crucible were noted; and a wide variety of methods for cleaning the glassware were in use. Also, wide variations in the ability of individual analysts to reproduce their results, as indicated by standard deviations from eight replicates of a single fuel, were noted. However, minor variations in the control of the three main variables (oxygen flow rate, fuel temperature, and time in bath) were found to have little effect on the results obtained. Finally, it was suggested that a single period of time is inadequate for identifying a fuels instability due to induction periods varying from fuel to fuel.

Also at the 2nd International Conference, Lee and Stavinoha[12] reported on sources of error in accelerated stability tests. They concluded that, if the procedure is followed, the gravimetric determination of filterable insolubles should not cause significant variation in results, but that the use of other filter media could cause variations. They also found that a single test time at one temperature may not give a true

indication of a fuel's instability, so they suggested the use of more than one time period or the time required to reach 4 mg/100 mL level of insolubles. Finally, they noted that the size and quantity of particulate matter formed during the cooling period following the oxidation stage of the test may be a function of the cooling temperature.

At the 3rd International Conference in London, in September 1988, White and Bowen[6] examined a number of test variables that might affect D 2274 test results. The basic experimental approach was to change a single test variable to a much greater degree than would be expected as the result of chance, and to ascertain whether this change produced a significant change in the results. The more significant findings were:

(1) Air yields significantly lower quantities of insolubles than pure oxygen and should not be used as a substitute.

(2) A number of substances catalyze oxidation during a D 2274 determination, particularly copper; fuels should not be shipped in unlined metal containers.

(3) Ultraviolet radiation catalyzes oxidation, so fuels to be tested by D 2274 should not be exposed to sunlight or to other sources of UV radiation.

(4) Different temperature baths can yield different results in a D 2274 test; this may be a major reason why reproducibility for the test is so poor. The test method should be revised to control bath differences. (NOTE: Although this matter has been discussed, no controls on bath responsiveness have been added to the procedure.)

(5) The one-hour drying time for filterable insolubles following the isooctane rinse was found inadequate with the glass fiber filters specified at that time. A 2.5 hour period of drying at 99°C was required before filters reached constant weight. (NOTE: Changes have been incorporated in D 2274, which now dries matched pairs of 47 mm cellulose ester filters for 30 minutes at 80°C.)

Test Method D 4625 is primarily used as a research method because the test temperature of 43°C (110°F) is so little above ambient that the reactions and products produced are very similar to those produced in field storage. In general, a week of storage at 43°C is approximately equivalent to a month of storage under ambient conditions. However, those who chose to use this generality should be warned that ambient conditions vary as we reported[8][13] at several ASTM symposia.

Because the test periods are long (4 to 24 weeks, or longer), the method is not suitable for quality control. In an effort to speed up the accumulation of results, a number of researchers have used essentially

the D 4625 method at higher temperatures. Thus, Milsom and Rescorla[14] stored fuel in bottles held at 110°, 150°, 180°, and 212°F and used the time required to reach the 2 mg/100 mL level of insolubles as their measure of fuel stability. They found that, above the 2 mg/100 mL level, the rate of insolubles formation increased. Moreover, they found a linear relationship existed between the time for a fuel to reach 2 mg/100 mL and the reciprocal of the absolute temperature in degrees Rankine.

Researchers at the Naval Research Laboratory have, at times, used temperatures of 65°C and 80°C in vented and unvented containers. Thus, at the 2nd International Conference in 1986, Beal et al[15] reported using 43° and 80°C in a study of the effects of shale-derived polar compounds on diesel fuel stability. Later, at a 1987 symposium on hydrocarbon oxidation held by the American Chemical Society, Hazlett[16] reported, in a paper on acid/base phenomena in oxidative stability of distillate fuel, that he had used 65° and 80°C. Again, at the 3rd International Conference held in 1988, Hardy et al[17] reported using bottle tests at all three temperatures for their evaluation of commercial stability additives for Naval Distillate Fuel. These three references are, of course, only a sampling of the many reported by Naval Research Laboratory research personnel and by other investigators around the globe.

Test Method D5304, the oxygen overpressure procedure, provides a means of ranking a specific fuel sample against other specific fuel samples or standards, with or without additives. Like other stability test methods, the insolubles produced should not be considered an indication of solids production in field storage, because storage conditions vary so greatly. The standard covers a procedure for assessing the inherent stability of middle distillate fuels such as ASTM D975 Grades 1-D and 2-D diesel fuels, comparable burner (D396) and gas turbine (D2880), and stocks from which such fuels are made.

Test Method D 5304 is specified as the referee stability test in the Navy's MIL-F-16884J Naval Distillate Fuel with a total insolubles limit of 1.5 mg/100 mL with test conditions of 90°C for 16 hours with an initial oxygen pressure of 800 kPa absolute (100 psig). The published precision of D 5304 at the 1.5 mg/100 mL limit is a repeatability of 0.32 mg/100 mL and a reproducibility of 0.84 mg/100 mL, i.e. slightly lower than the precision of Test Method D 2274 at the same 1.5 mg/100 mL level.

The D 5304 test method evolved from studies on the effects of oxygen pressure conducted independently at the Naval Surface Warfare Center (NSWC, Annapolis) and at the Naval Research Laboratory (NRL, Washington). At NSWC, we used the rotating pressure vessel system of ASTM Test Method D 2272 Oxidation Stability of Steam Turbine Oils by Rotating Bomb. NRL personnel used the pressure vessel described in ASTM Test Method D 525 Oxidation Stability of Gasoline (Induction Period

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Method) in the early stages of their work, then changed to the use of an improved pressure vessel capable of conducting 20 or more tests simultaneously. The two laboratories soon began a coordinated program and, in May 1986, they began a joint study to evaluate the effects of time, temperature, and oxygen pressure on the results. Hardy et al[18] presented the results of this early work and of a mini round robin at the 3rd International Conference in London.

Standardization

Bear in mind that the three test methods we have discussed are living entities. As ASTM standards, they must be reviewed at intervals of not more than five years and then balloted for reapproval, for reapproval with changes, or for withdrawal. ASTM Committee D02 on Petroleum Products and Lubricants, has jurisdiction with Subcommittee E on Burner, Diesel, Non-Aviation Gas Turbine, and Marine Fuels having direct responsibility. Anyone finding an error in one of these methods or wishing to suggest changes should contact Section E-5 on Cleanliness and Stability. IASH's Harry Giles is also chairman of that Section.

Committee D02 maintains close relations with two other standardization bodies, specifically the Institute of Petroleum (U.K.) and Technical Committee 28 of ISO (Geneva). Therefore, it is not surprising that both the IP and the ISO have standards similar to Test Method D 2274, and that IP has a standard similar to Test Method D 4625.

SYMPOSIA ON MIDDLE DISTILLATE STORAGE STABILITY

In this brief history of the development of test methods for evaluating the inherent storage stability of middle distillate fuels, a number of sources of information have been noted. There are obviously more sources than I have been able to incorporate. The following provide some core reading on the subject.

First, the Conference Proceedings of the five international conferences sponsored by IASH, plus the Proceedings of this conference when they are issued:

- Conference on Long Term Storage Stabilities of Liquid Fuels, Tel Aviv, Israel (July 1983)

- 2nd International Conference on Long-Term Storage Stabilities of Liquid Fuels, San Antonio, TX, July/August   1986

- 3rd International Conference on Stability and Handling of Liquid Fuels, London, U.K., September 1988

- 4th International Conference on Stability and Handling of Liquid Fuels, Orlando, FL, November 1991

- 5th International Conference on Stability and Handling of Liquid Fuels, Rotterdam, the Netherlands, October 1994

Second, there were a series of symposia sponsored by the American Society for Testing and Materials, Committee D02, and published as Special Technical Publications (STP's). I have mentioned these in the course of my remarks, specifically:

- STP 244 Symposium on Stability of Distillate Fuel Oils, June 25, 1958.

- STP 751 Symposium on Distillate Fuel Stability and Cleanliness, June 24, 1980.

There were also a few papers on fuel stability in the following:

- STP 531 Manual on Requirements, Handling and Quality Control of Gas Turbine Fuel, June 1972.

- STP 878 Marine Fuels, 7 - 8 December 1983.

The American Chemical Society has published many papers on fuel stability, both in its Division of Petroleum Chemistry, Inc., and in its Division of Fuel Chemistry. The following are a few of the symposia that contain such papers:

- Symposium on Hydrocarbon Oxidation, Preprint Div. Pet. Chem., Vol 32 (#4), August 1987

- Symposium on Stability and Oxidation Chemistry of Middle Distillate Fuels, Preprint Div. Fuel Chem., Vol 35 (#4), August 1990

- Symposium on Stability and Oxidation Chemistry of Liquid Fuels, Preprint Div. Fuel Chem., Vol 39 (#3), August 1994

Finally, I would be remiss if I failed to mention the book STABILITY PROPERTIES OF PETROLEUM PRODUCTS authored by the late Nahum Por, one of the founding fathers of IASH, and published by the Israel Institute of Petroleum and Energy.

SUMMARY AND CONCLUDING REMARKS

In summary, as a result of refinery construction during World War II and of a spurt in home oil heating following the war, the need to meet demand and to find an outlet for cracked stocks led to the marketing of fuels with poorer storage stability than the straight-run distillates before the war. To preclude the marketing of unsuitable fuels, many test methods were proposed, each empirical in nature. These have evolved into three standard test methods capable of comparing the inherent stability of middle distillate fuels and stocks. However, any relationship between the results obtained by these tests and the instability reactions that occur with a specific fuel in a specific storage situation is purely empirical and limited in applicability.

This paper was written with the thought that the older generation which witnessed the developments just described is gradually retiring from the field and leaving to a new generation the task of continuing the advancements we have made. We have left our marks in the technical literature, so remember, before you rush into the laboratory, review that literature. You may find we have been there, we've done that!

To the new generation of chemists armed with the marvels of the instrumented laboratory, we leave the problems of defining the mechanisms of instability, and of relating the specific chemistry of a fuel and its storage system to the instability reactions which will occur. We leave also the need for a more rapid means of identifying unstable fuels. Even the 16 hour tests we have developed leave much to be desired and are much too long for good quality control. In Australia and in the United Kingdom, some work has been done on colorimetric tests. We leave it to you to develop these into standard test methods!

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STABILITY OF DIESEL FUELS WITH IMPROVED LOW TEMPERATURE CHARACTERISTICS.

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Diesel fuels with low sulfur content (below 0.05 %) belonging to the so called " green fuels", are preferred for exploitation in the big cities, but the interest towards the conventional fuels with higher sulfur content (up to 0.1 - 0.2 %) has not ceased. These types of fuels are characterised by increased storage terms and are used for military purposes. Studying the processes of total insolubles formation in Diesel Fuels, with higher content of sulfur compounds, it is possible to throw light on the mechanism of their formation in an inert atmosphere as well as in the presence of oxygen. In the present paper the total insolubles formed after tests of accelerated oxidation, are studied with the help of gel-permeation chromatography, NMR, IR and other physical methods. The tests are performed in different conditions: diffusion, diffusion-kinetic and kinetic and the effect of metal surfaces is investigated. The obtained data make it possible to evaluate the ways for improvement of the low temperature characteristics of motor diesel fuels for military purposes.

The problems concerning the low temperature characteristics of motor diesel fuels is very important for the countries in Europe, North America and others with severe climate during the winter[1]. These problems are extremely important for the exploitation of military machines during the winter. In Republic of Bulgaria in December, January and February, although for relatively short periods are registered temperatures below minus 20°C. The latter necessitates the production of motor diesel fuels

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with cold flow plugging point (CFPP) under minus 25°C. During the production of low sulfur highway diesels some difficulties arise in securing their low temperature characteristics especially the CFPP and the pour point (PP) [2,3].

For the production of motor diesel fuels with improved low temperature characteristics, can be used components giving them satisfactory CFPP and PP and also low sulfur content (under 0,2 %). These fuels can be used by the military vehicles out the high ways and on off- high ways.

Motor diesel fuels are produced in Bulgaria from several basic components obtained by the petrol processing industry. Their types and basic characteristics are given in Table 1.

The data in Table 1 show that, if the motor diesel fuel is compounded in a suitable way from Light Diesel Fraction (LDF) with hydrogenizate (HG- light) from the fraction 170 - 300°C or denormalizate (i.e. the same light hydrogenizate from which the n-paraffins have been separated by molecular sieve) we can obtain fuels with very good CFPP and PP properties and relatively low sulfur content. When the fuel is compounded with 10 % vol. LDF or its denormalizate (DN) are obtained diesel fuels fulfilling the contemporary requirements for highway diesel fuels with sulfur content less than 0,05 % wt. The compounding of 20, 30, 40 % vol. of LDF with 80, 70 and 60 % HG or DN results in the obtaining of motor diesel fuels with sulfur content of 0,08, 0,12 and 0,14 wt. % , respectively. All these fuels have very good low temperature characteristics and can be used for military purposes during the winter. When 20 % vol. LDF are combined with 80 % of heavy HG a fuel is obtained with low sulfur content (below 0,2 wt. %). It has relatively good low temperature characteristics.

In the present paper are studied the chemical and oxidative stability and the tendency for total insolubles formation of industrial samples with improved low temperature characteristics or of their initial components (Table1). The volume of the oxygen absorbed, the concentration of hydroperoxides, carboxylic acids and carbonyl compounds have been determined for these fuels. The investigations were carried out both in the kinetic and the diffusion regions and the storage terms are prognosticated on the basis of the obtained results. The total insolubles obtained during the oxidation of the diesel fuel containing 20 % wt LDF and 80 % wt. HG-light have been also analyzed. The kinetic studies have been performed in a manometric apparatus[4], in apparatus for accelerated determination of the oxidative stability of distillate fuels[5] and in.DK-2 NAMI apparatus[6] . The analysis of the oxygen-containing products was carried out according to standard procedures. The composition of the isolated

total insolubles was determined by gel-permeation chromatography ("Waters" Ltd), IR, and NMR spectroscopies. The kinetics of their formation was followed in an apparatus according to ASTM-D 2274-80 as well as by means of nephelometric method by measuring the intensity of the reflected light in the region of 500 - 700 nm in an apparatus "Spekol".

Total unsolubles formation in the kinetic region

The results of the accelerated ageing of diesel fuels with improved low temperature characteristics are summarized in Table 2. These data have been obtained following the procedure according to ASTM-D 2274-80 which is modified for investigations in the kinetic region. The results presented in Table 2 were obtained after 16 hours ageing at 413 K. They show undoubtedly that the tendency towards total insolubles formation in the kinetic region is the highest in the case of the pure hydrogenizate, followed by the denormalizate. The lowest ability to total insolubles formation in the fuel is registered by the blend with component ratio of 20 % wt LDF and 80 % wt hydrogenizate, or of 20 % wt LDF and 80 % wt. denormalizate. The dependence of the amount of total insolubles formed on the content of LDF (Fig. 1A)(which is symbatic to the sulphur content in the fuel) proves the existence of extremum of sulfur content in the both components of 0.084 % wt. (Fig.1B, compare also the data of Tables 1 and 2).

Recently in a previous paper[7] we have shown that the distillate diesel fuels from Dolni Dubnik petroleum (North Bulgaria, "Neft i Gaz" Refining) which are characterized by a very low sulfur content - 0.066 % wt. possess very good lubricating properties and decrease soot and coke formation on the nozzles. They are also stable at storage and reduce the total insolubles formation. Thus the sulfur content in the diesel fuels in the range of 0.07 - 0.085 % wt is of special importance for the thermooxidative stability of the fuel and for ensuring good lubricity.

Total insolubles formation in the diffusion-kinetic region

The results of the studies in the diffusion region, carried out in NAMI apparatus at 413 K in the presence of copper plate, are presented in Table 3. This method makes possible the evaluation of the corrosion activity of the fuels and determination of the amount of deposits on the metal surface as well as the acidity of the samples.

The results obtained are quite surprising. The total insolubles formation is the lowest in the case of hydrogenizate and denormalizate, while their acid numbers are the highest. The hydrogenizate is characterized by the highest corrosion activity. LDF has high acid number, high level of total insolubles

formation and the highest loss of plate weight. These results, which simulate the exploitation conditions in the engines, show that the hydrogenizate diesel fraction can exert strongly negative effect on the metal parts of the diesel engines mainly due to their high acid numbers (their ability to accelerated oxidation is evident) and corrosion activity.

Oxygen absorption in manometric equipment in the kinetic region

In Table 4 are summarized the data of the oxidation of the same fuel samples or of their components in a manometric apparatus including the duration of the induction period (in min) and the value of the maximum oxidation rates (in mol/l s). In addition are also given the results of the IR -spectral analysis of the structural group composition, as well as the content of nonsaturated compounds for some samples. The data reveal that hydrogenizate and denormalizate absorb oxygen with a rate by an order higher than that of the samples containing LDF. The oxidation processes of HG and DN proceed without an induction period. Their oxidates are characterized by a higher olefin content. The samples containing 10 % LDF only, i.e. those which correspond to the requirements as ecological fuels with low sulfur content, are characterized by short induction periods but with surprisingly low maximum oxidation rates.

The effect of metal surface and inhibitors

In Table 5 are shown the results from the oxidation of diesel fuels with good low temperature characteristics in the presence of metal surfaces (heterogeneous catalysts) and inhibitors or suppressants of total insolubles formation. The data justify the fact that the presence of metal surfaces (200 cm^2/l) accelerates the total insolubles formation. The application of additives in some cases (Inhibitor No 3) results in suppressing their formation, in abrupt increase of the induction period and minimum corrosion towards copper surface. The other additives have various effects. Thus inhibitor No 1 increases significantly the induction period but does not improve the total insolubles formation tendency and the corrosive resistance of the fuel towards copper.

Analysis of the isolated sediments

The oxidation of hydrogenizate results in the highest amount of total insolubles formed. This product has been subjected to analysis by gel-permeation chromatography, IR.-spectral analysis, elemental analysis and NMR spectroscopy. The data from gel-permeation chromatography show that the molecular mass distribution in the total insolubles is as follows: 6100 D - 28 %; 6200 D - 16 %; 19200 D - 19 % and 21500 D - 37 %, for the soluble in tetrahydrophurane part of it.

The IR-analysis prove the occurrence of broad bands in the region of 2400-3200 cm^{-1} and intensive bands at 1710 and 1770 cm^{-1} which are assigned to the presence of -COCH groups; band at 3540 cm^{-1} - the presence of -OH groups and intensive bands at 1180 and 1290 cm^{-1} which are ascribed to the presence of -C-O- groups. The intensive band observed at 1046 cm^{-1} is indicative of the presence of >S=O group.

The element analysis has been carried on two fractions of the total insolubles. The first fraction, which is tetrahydrofuran unsoluble, contains 5.43 % sulfur, 71.76 % carbon, 9.53 % hydrogen and 13.28 % oxygen. The second one that is tetrahydrofuran soluble is characterized by the following composition: 8.85 % H, 63.63 % C, 0.93 % S, 1.24 % N and 25.35 % O.

The NMR spectral analysis of the total insolubles (^{1}H NMR spectra were registered on Bruker WM - 250 MHz in $CDCl_3$) shows the presence of three weak signals in the region of 0.8-1.3 ppm, which are assigned to the occurrence of alkyl groups; the relatively intensive signal at 3.4 ppm is ascribed to -OH groups and the intensive signal at 8.25 ppm is indicative of the presence of heterocycles with conjugated double bonds (of thiophene and pyrene type). The presence of aromatic protons is ascertained by the appearance of the weak intensive signal at 7.2 ppm.

The presence of heterocyclic compounds containing nitrogen or sulfur atoms is demonstrated by the ^{13}C NMR spectrum whereby is observed an intensive signal at 78 ppm. The same spectra proves also the presence of carbon atoms included in >CO, aromatic and aliphatic groups.

The data obtained from the analysis of the total insolubles show undoubtedly their complex composition including heterocyclic compounds of sulfur and nitrogen and oxygen-containing compounds.

Conclusion

The present investigations confirm that high quality motor diesel fuels with improved low temperature properties and low content of sulfur and aromatic hydrocarbons can be successfully obtained from the appropriate compounding of industrially available components from middle distillate fractions. These fuels are distinguished by high stability at their compounding with the initial nonhydrogenized distillate fractions. The metal surfaces deteriorate the fuel quality. Some additives can be effective in prolongation of the storage terms of the fuels.

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Table 1. Physico-chemical characteristics of different types of components used for motor Diesel Fuels.

Sample	d^{20}_4	Fractional Content					Sulfur	Viscosity at 20°C or 40°C	Aromatic Hydrocarbons	CFPP	PP
		Init. Boiling Point, °C	10% vol., °C	50% vol., °C	90% vol., °C	End Boiling Point °C	% wt	mm²/s	vol.%	°C	°C
Light Diesel Fraction (LDF)	0,805	160	183	216	260	283	0,3	2,1(20°C)	20,1	<-35	<-35
Heavy Diesel Fraction (HDF)	0,818	193	238	285	344	372	1,0	3,8(40°C)	34,5	-1	-6
Hydrogenizate (HG) Source for Normal Paraffins	0,857	215	238	279	343	370	0,1	3,6(40°C)	33,2	-2	-6
Normal Paraffins - 170-300°C	0,825	182	218	244	278	302	0,47	3,1(20°C)	26,1	-30	-34
Hydrogenizate of cut 170-300°C	0,820	188	214	243	275	301	0,03	3,1(20°C)	25,3	-31	-34
Denormalizate cut 170-300°C (mol. sieve)	0,830	183	215	245	277	302	0,03	3,2(20°C)	24,3	-35	-35

Table 2. Results of accelerating ageing of fuel samples in the kinetic region according to the modified ASTM-D2274-80 at 413 K

Sample	Oxygen atmosphere					Argon atmosphere	
	Tot.insol. mg/100 ml	Acid number mg KOH/100ml	Peroxides mol/l	Nephelometry at λ $_{575}$ nm	λ $_{600}$ nm	ASTM D2274 tot.insolubles mg/100 ml	ind.period for tot. insoluble formation h
Light Diesel Fraction (LDF)	36.50	48.2	1.2×10^{-3}	285	126	-	0
10% LDF + 90% light HG	9.60	0	0	160	40	-	1.5
20% LDF + 80% HG	4.30	0	0	30	11	0.70	0
30% LDF + 70% HG	5.20	0	0	38	6	-	0.5
40% LDF + 60% HG	12.7	0	0	155	71	0.40	3.0
Hydrogenizate (HG)	2321.4	836	18.6×10^{-3}	5000	2900	-	2.5
10% LDF + 90% DN	39.80	0	0	155	59	-	1.5
20% LDF + 80% DN	6.80	0	0	50	8	0.40	0
30%LDF + 70% DN	15.20	0	0	170	70	-	0
40% LDF + 60% DN	16.0	0	0	175	65	-	1.2
Denormalizate (DN)	833.0	306.2	0	2400	1450	-	0.5

Table 3. Oxidation in apparatus DK-2-NAMI at 413 K (GOST-8245-56) in air atmosphere in the presence of copper plate at a surface/volume ratio 95.5cm^2/l for 24 h.

Sample	Total insolubles mg/100 ml	Deposits (+) on metal plate or losses (-) g/m^2	Corrosion by BSS -14369-77	Acid number mg KOH/100 ml
LDF	80.0	-5.4744	4C	137.0
10% LDF + 90% HG	79.2	2.3973	4C	0
20% LDF + 80% HG	82.4	1.2655	4A	0
30% LDF + 70% HG	72.7	2.4400	4B	0
40% LDF + 60% HG	37.1	2.5400	4B	0
HG	4.9	0.7016	2D	93.3
10%LDF + 90% DN	91.9	3.3050	4A	0
20%LDF + 80% DN	68.2	1.6072	4A	48.4
30% LDF + 70% DN	85.7	3.5900	4B	
40% LDF + 60% DN	68.2	2.1963	4A	46.2
DN	31.6	1.2337	3B	228.0

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Table 4. Kinetic results from the oxidation in manometric apparatuse, at 473K

Sample	Induction period min	Maximum rate of oxygen absorption mol/ls x 10^5	Content of nonsaturated compounds in the oxidates, 413 K (Margolis method)		Structural group analysis by IR spectroscopy at E^{1610} and E^{1720}		
			unoxidised sample, % M	oxidised sample, % M	C aromatic %	C paraffinic. %	C naphthenic, %
LDF	16.0	3.55	-	-	-	-	-
10% LDF + 90% HG	4.0	1.74	-	-	-	-	-
20% LDF + 80% HG	18.0	1.86	0.0010	0.0021	27.15	68.01	4.84
30% LDF + 70% HG	17.0	1.98	-	-	-	-	-
40% LDF + 60% HG	20.0	1.25	-	-	-	-	-
HG	0.0	14.9	0.0015	0.0117	23.21	68.63	8.44
10%LDF + 90% DN	13,5	1.75	-	-	-	-	-
20%LDF + 80% DN	26.0	1.01	0.0018	0.0025	26.52	60.38	13.10
30% LDF + 70% DN	13.0	2.33	-	-	-	-	-
40% LDF + 60% DN	12.0	4.02	-	-	-	-	-
DN	0.0	38.7	0.0016	0.0129	26.68	58.33	14.99

Table 5. The effect of the metal surfaces and of total insolubles supressants and inhbitors during the oxidation of diesel fuels with improved low temperature characteristics

| Sample	Total insolubles formation by ASTM D227480 at 413 K or by nephelometry			Oxygen absorption in mano- metric apparatus, 473K		Oxidation in DK-2-NAMI in the diffusion- kinetic regime at 413 K		
	total insolubles	maximum extinction λ_{575} nm	maximum extinction λ_{600} nm	induction period	max.rate of absorption	total insolubles	deposits (+) losses (-)	corrosion by
	mg/100ml			min	mol/l s x 10^5	mg/100 ml	g/m^2	BSS 14365-77
20% LDF + 80%HG	4.3	30	11	18	1.86	82.4	1.2655	4A
20% LDF + 80% HG + steel 5	12.2	-	-	-	-	-	-	-
20% LDF + 80% HG + galvanized sheet iron	11.8	-	-	-	-	-	-	-
20% LDF + 80% DN	6.8	50	8	26	1.01	68.2	1.6072	4A
20% LDF + 80% DN + steel 5	11.8	-	-	-	-	-	-	-
20% LDF + 80% DN + galvanized sheet iron	12.9	-	-	-	-	-	-	-
20% LDF + 80% DN + 0.01% Inhibitor 1	7.2	84	8	150.0	0.27	130.4	10.93	4C
20% LDF + 80% DN + 0.01% Inhibitor 2	33.9	134	82	1.0	8.56	82.1	10.83	4C
20% LDF + 80% DN + 0.01% Inhibitor 3	2.8	19	6	130.0	3.72	116.4	-1.2456	4A
20% LDF + 80% DN + 0.01 % Inhibitor 4	15.6	59	22	20.0	3.55	45.1	1.5600	4C
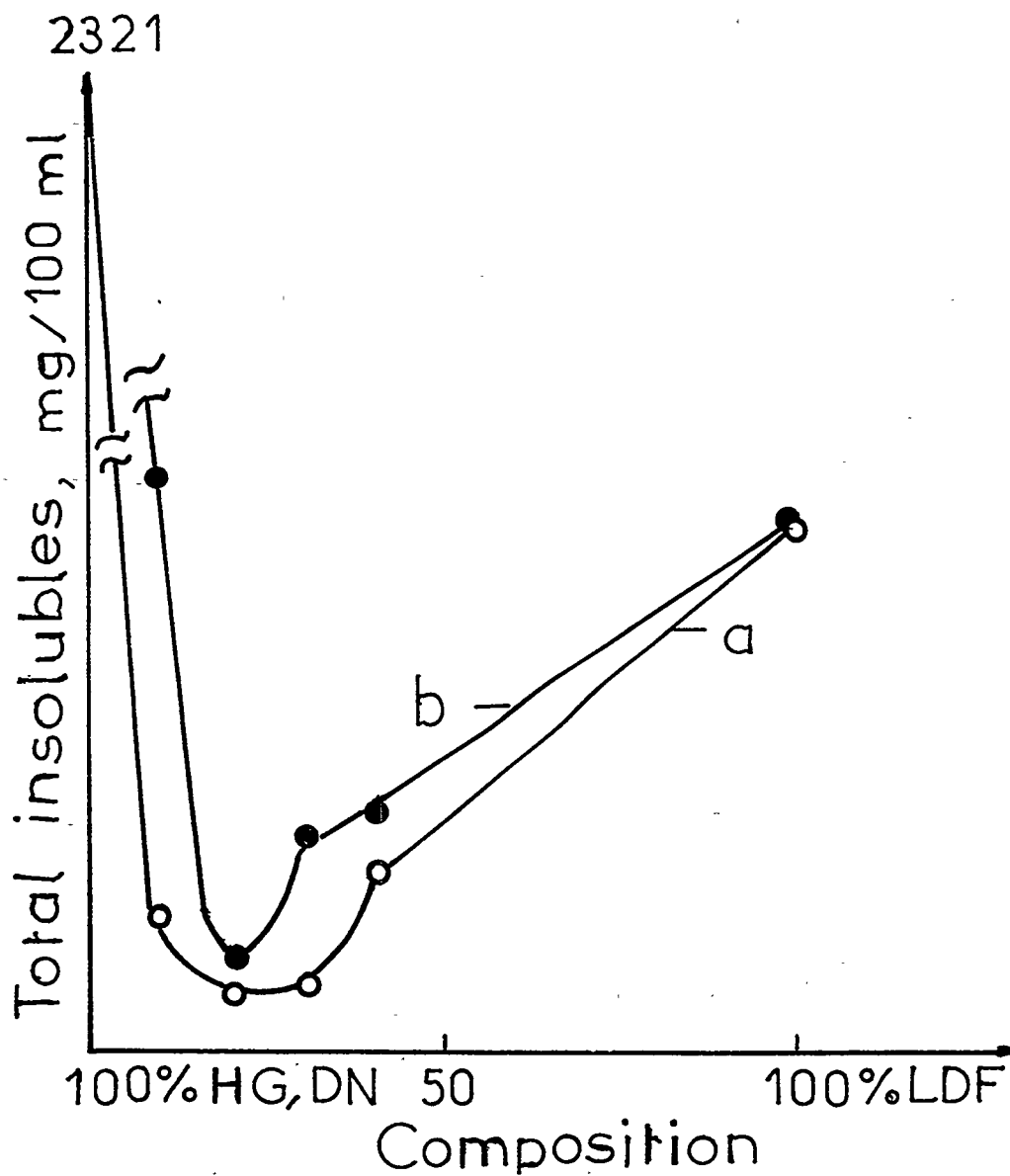
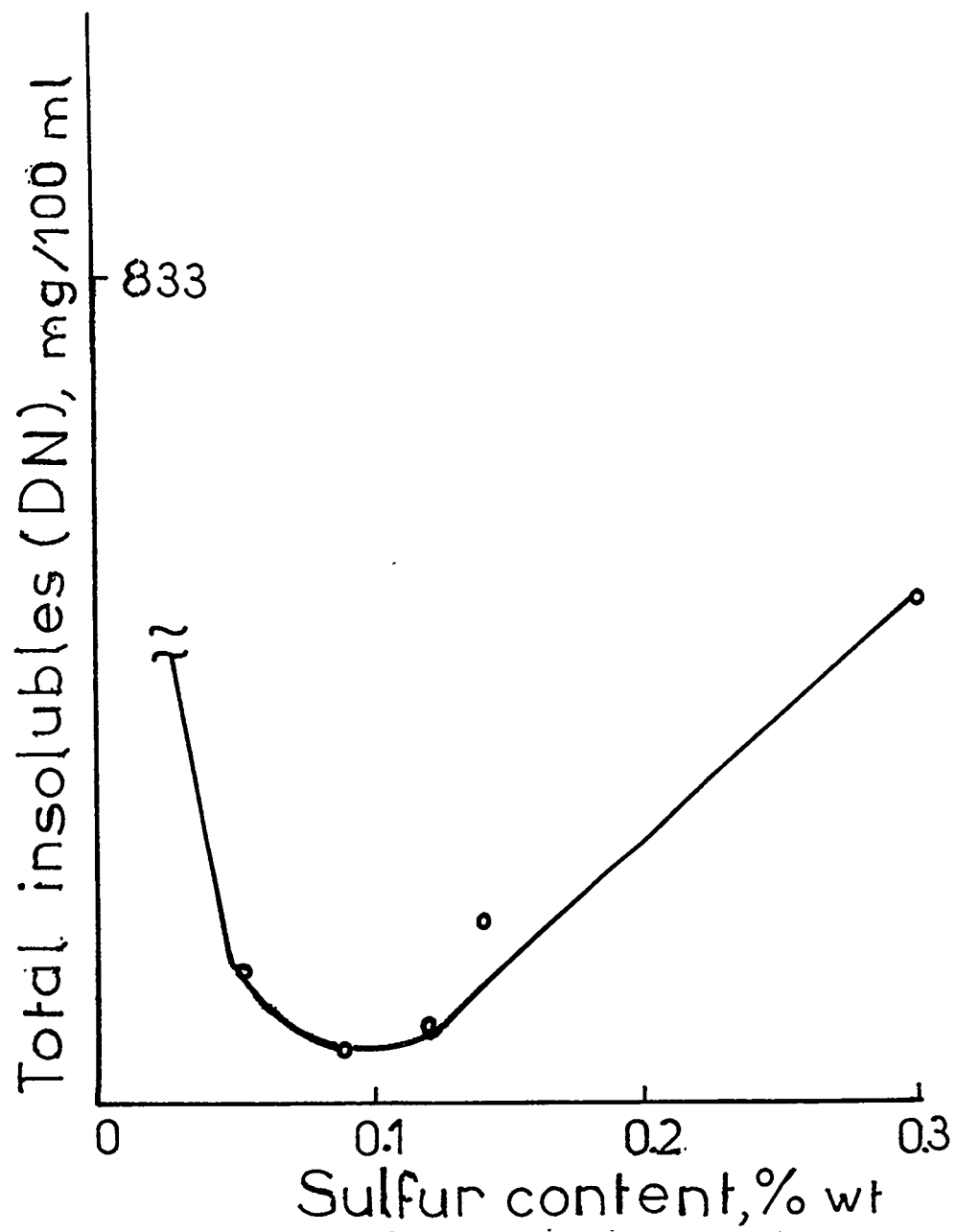**Fig.1A.** The dependence of total insolubles in the samples on diesel fuel composition

Fig.1B. The dependence of total insolubles in DN on sulfur content

IMPROVEMENT IN DIESEL FUEL QUALITY THROUGH ADDITIVES

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Out of a number of quality requirements for high speed diesel (HSD), stability characteristics is considered to be an important criteria for HSD blended with cracked streams. Stability behaviour of an Indian HSD and its blends with a cracked stream (Visbreaker gas oil-VBGO) as such and in presence of three stabilizing additives has been studied with a view to maximize the HSD production. Test methods UOP-413 (16Hrs.) and three months storage IP-378 (modified) have been followed. It has been found that blending of VBGO to HSD adversely affect the stability. However, by using a suitable stabilizing additive, VBGO in concentration range of 2-4% can be accommodated in HSD pool and finished blend meet the Indian HSD specification IS: 1460-1995. Attempt has also been made to examine the relationship between UOP-413 and IP-378 (modified) test data and between 45 days and 90 days data of IP-378 (modified) test by linear regression analysis technique. The correlation coefficient in the range of 0.96-0.98 has been found, showing very high degree of reliability in predicting the total sediment value of IP-378 (modified) test either from UOP-413 or 45 days test data of IP-378 (modified) test. Considering the better acceptability of IP-378 test limit, more stringent pass limit of 0.8 mg/100 ml of HSD has been proposed for UOP-413, as against the specified limit of 1.6 mg/100 ml of HSD.

INTRODUCTION

High Speed Diesel (HSD) fuel is mainly used in automotive engines for public and commercial transport and in DG sets for power generation. Demand of HSD is increasing at an alarming rate all over the world excepting USA. In India, HSD fuel requirement was 27.7 MMT in 1995-96 and likely to increase to 40.4 MMT by 1999-2000. To meet the increasing demand, conventional approach of incorporating the cracked streams from secondary refinery processes like FCC, coker and visbreaker in diesel fuel is being followed world wide. This approach has main disadvantages of imparting instability in the fuel leading to poor quality. Out of a number of properties required for assessing the performance of HSD, stability is considered to be an important requirement.

Instability of distillate fuels is characterized by colour degradation and formation of organic insoluble gums during storage. These gums serve as binding agents for water ,dirt , rust and other corrosion products found in fuel distribution systems[1,2].The resulting sludge can clog fuel filters and cause malfunctioning of oil burners,nozzles and diesel injection systems. It is generally agreed that 2 mg. of gum per 100 ml. of fuel[3] is the maximum amount that can be tolerated without encountering unsatisfactory field performance .

The gum products in diesel fuel appear in two forms[4] i.e. insoluble gum and soluble gum. The fuel insoluble gum , precipitates from the fuel and can be separated by filtration. The fuel soluble gum can be recovered only by evaporating the fuel. In diesel fuel, soluble gum forms first followed by insoluble gum. Formation of soluble gum in fuel is indicated by dark brown colour. Insoluble gum is considered to be the main concern for the performance of HSD. Brinkman and Bowden[5] determined the elemental composition and molecular wt. of the gum formed in the diesel fuel in an effort to understand the mechanism of gum formation. The gum consisted mainly of carbon (85%) and hydrogen (13%) and rest was nitrogen, oxygen and sulphur. The exact mechanism of involvement of sulphur and nitrogen compounds in gum formation is not known, however , it is believed that the free radicals (R$^•$ & H.$^•$) attack the compounds of sulfur and nitrogen and forms the gum[6] . Brinkman and Bowden[5] determined the molecular wt.of diesel fuel gum components which was found to be in the range of 100 to 5000, whereas the molecular wt. of a typical diesel fuel range from 170 to 220. This indicated that gum consisted of combination of decomposition ,oxidation (low molecular wt.) and polymerisation (high molecular wt.) products . Thiopheonols are the most reactive compounds[7] and among organic nitrogen compounds , pyrroles are believed to be the biggest contributor to fuel instability[8].

Investigation have shown that the major cause for instability is the esterification reaction which was later confirmed[9]. Typical chemical species identified in sediment formed by esterfication are aromatic hydrocarbons, cyclic nitrozen compounds and sulfur compounds such as thiophenes, cyclic sulphides etc. Reaction time for esterification can require a few weeks or months to reach completion. Similarly, the presence of only few parts per billion level of metals can accelerate sediment formation e.g. copper will accelerate both oxidation and esterification reaction. Copper contamination can occur by contact with copper alloy valves, fittings and contaminated tank bottoms.

Schrepfer et. al [10] observed that certain chemical tests may be used to predict potential fuel instability or to determine which process streams is contributing to the instability of a blended

fuel. Table-1 gives some of the chemical tests which are useful in predicting the fuel stability, corrosivity and treatment scheme. These tests are not required as daily controls, rather they are utilized to check new blend ratios, process streams from different units or the potential effect of changing feedstocks. For example, a major change in FCC severity could increase the level of thiophenolic as well as pyrrolic nitrogen compounds in the light cycle oil (LCO). LCO which is high in pyrrolic nitrogen, when mixed with a stream containing benzenethiol, will result in an unstable fuel.

The stability of distillate fuels can be improved by adopting appropriate refinery processes to remove the compounds responsible for gum formation or by the use of additives, or by combination of both the approaches[11,12]. The use of additives is considered to be simple, effective and economical means to improve the stability of fuel. The three types of additives component used are antioxidants, dispersant and metal deactivators to perform specific role in improving stability of fuel. The antioxidant inhibits the formation of gum, dispersants suspends it in a finely divided form to allow it to pass through filters and metal deactivator chelates metal ions to prevent their catalytic action. It is common practice to combine two or three of these type of additives into package known as stabilizers, to achieve maximum effectiveness .

In India, Indian specifications IS:1460-1995 covers quality requirements of HSD which defines the stability characteristics in terms of sediment value determined by UOP-413 test method. The present study was undertaken to maximise HSD pool by blending with available streams derived form secondary processing and improving the stability of the blend through the use of additives. Also to examine relationship between the sediment data generated by laboratory stability screening test (UOP-413) and long storage stability test IP-378 (modified).

EXPERIMENTAL
Fuels:

Following two fuels were used in the study.

- Base HSD fuel
- Visbreaker Gas Oil (VBGO)

The base HSD fuel was a finished refinery product, blended from straight run gas oil, total cycle oil from FCC, hydrocracker gas oil and light vacuum gas oil in desired ratio. The base HSD fuel and VBGO were collected from one of the Indian Refinery. The physico-chemical

properties of base HSD and VBGO are given in Tables 2 and 3 respectively. It may be observed from the Tables that base HSD meets requirements of IS:1460-1995 specification. As expected, the VBGO stream has been found to have higher values of sediment and olefin content. Since one of the objectives of the study was to maximize the HSD production, blends of base HSD and VBGO containing VBGO concentration from 2 to 6% were prepared.

Stabilizer Additives :

Three commercial diesel stabilizers marked as A,B and C were used in the study. Stabilizers A and C were mainly amino phenol type while stabilizer B was based on hindered phenol. The base HSD and HSD-VBGO blends were doped with stabilizers in the dosages of 25 and 50 ppm. concentration.

Evaluation Methodology:

A number of tests have been reported for assessing the stability characteristics of HSD. Table - 4 gives brief details of the six most commonly used methods, covering their evaluation criteria and acceptability with respect to field performance. It may be observed from the Table that test methods, namely, UOP-413 (16hrs) and IP - 378 (3 months storage) reported to have reasonably good correlation (over 90%) with field storage. Therefore, these two methods were followed for the present study. The IP-378 test method was modified in terms of storage temperature . The brief description of the procedure followed for these methods are given as under:

- UOP- 413/82 Test Method

In the UOP- 413 test, the pre-filtered (through 0.8 micron filter membrane), 150 ml.sample of the fuel was aged at 100deg.C under oxygen atmosphere in a specified pressure bomb for 16 hrs. Aged sample was then cooled and filtered through pre-weighed 0.8 micron filter membrane. The amount of filterable sediments was reported as total sediments in mg/100 ml.

- IP-378/87 (modified) Test Method

The standard IP-378/87 method was modified for ease of operation in terms of storing the fuel at ambient temperature in place of specified test temperature of 43 deg.C In this test, 400 ml. of the pre-filtered (through GF/A Glass fibre filter pads) fuel sample was aged by storing in a 500 ml.borosilicate glass container at ambient temperature (30-35 deg.C) for a period of 45 and 90 days. After ageing for 45 and 90 days, samples were removed from storage and analysed for filterable insolubles and for adherent insolubles. Results were reported as total sediments in mg/100 ml.of HSD. Data during the middle of the test (45 days) were generated

to investigate the sediment build up process and also to develop possible correlation between 45 days and 90 days test data.

RESULTS AND DISCUSSION

Effect of VBGO Blending on Stability :

Effect of VBGO blending at 2, 4 and 6% concentration on the stability of base HSD in terms of total sediment values determined by UOP-413 and IP-378 (modified) test methods is given in Table-5. It may be seen from the data that as expected, the blending VBGO with base HSD adversely affects the stability of the HSD. The sediment values in both the tests have been found to increase by about 2 times at 4-6% conc. level of VBGO. In general, the sediment values determined by 3 months ambient storage IP-378 (modified) test were found to increase by about 2 times in comparison to those determined by UOP-413 test. However, the rate of increment of sediment value was slower beyond 45 days.

It may also be noted that addition of VBGO in 4% and above concentration to the HSD resulted in failing the stability criteria of HSD as per IP-378 (modified) test.

Response of Stabilizing Additives in HSD-VBGO Blends:

Tables-6 and 7 give the response of three stabilizing additives on total sediment values of HSD-VBGO blends determined by UOP-413 and IP-378 (modified) tests respectively. It may be seen from Table-6 that all the three additives reduced the level of total sediment in UOP-413 test significantly. In base HSD, the additives could reduce total sediment values by 42-71%. As expected, the level of response of additives in HSD-VBGO blends was found to reduce in comparison to noticed in base HSD and was marginally dependent on amount of VBGO present in the blend. In these blends, containing VBGO in 2 - 6% concentration, the values of total sediment could be reduced by 33-66%. Except few, improvement in additive response (by 12-50%) with increasing additive concentration from 25 ppm.to 50 ppm.was noticed. The study revealed that with the help of stabilizing additives, VBGO can be accommodated even upto 6% in the HSD pool with total sediment values in the range of 0.5 - 0.8 mg/100 ml.as against the specified UOP-413 limit of 1.6 mg/100 ml.

Similar observation was also noticed in case of the data generated by IP-378 (modified) test (Table-7). However, the level of additive response was slightly lower. The reduction in total sediment values of HSD-VBGO blends containing VBGO in 2-6% concentration, was in the range of 16-45% after 90 days of test duration. The results revealed that for maintaining safe limit of 2.0 mg/100 ml.of total sediment, VBGO upto 4% can be blended to HSD pool with the use of additive.

Relationship between UOP-413 and IP-378 (modified) Tests Data :

The total sediment value data generated by UOP-413 and IP-378 (modified) tests were examined for the following aspects :

- to examine possible relationship between UOP-413 and IP-378 (modified) data and between 45 days and 90 days data generated in IP-378 (modified) test and

- review of the validity of acceptable limit of 1.6 mg/100 ml specified for UOP-413 test.

- IP-378 (modified) Vs UOP-413 Test Data

It has been reported earlier that UOP-413 test data correlate well with three months storage stability test data generated by IP-378 test. Therefore the data generated in the present study was examined for verification of the same and also to explore the possibility of reducing the time of three months storage stability test. For this, the UOP-413 and IP-378 (modified) tests data given in Tables-5-7 (28 nos.) were analyzed by linear regression technique which showed a correlation coefficient (R^2) of 0.96 between these two tests. Encouraged by the result, data generated on various HSD blends in the past were also included (total data 42 nos.) for further analysis. In this case also, a correlation coefficient (R^2) of 0.96 was obtained indicating very high degree of reliability. Figure -1 shows the plot between experimental and predicted values of IP-378 (modified) test which shows high degree of linearity. The relationship between the two parameters can be expressed as follows:

$$IP\text{-}378 \text{ (modified)} = 2.5546 \times UOP\text{-}413 \text{ -----------------(Eq.1)}$$

Similarly, relationship between total sediment data of 45 days and 90 days generated by IP-378 (modified) test were analyzed following the above methodology, which showed correlation coefficient of 0.98. Plot between experimental and predicated values of IP-378 (modified) test computed from the 45 days duration test data is given in Figure-2 which also shows linear relationship. This relationship can be expressed as under:

$$IP\text{-}378 \text{ (modified)} = 1.2651 \text{ } IP\text{-}378 \text{ (modified) 45 days data.-----(Eq. 2)}$$

Rationalisation of UOP-413 Test Limit

The acceptable limit of total sediment value determined by UOP-413 test for HSD is specified as 1.6 mg/100ml. Guided by the better acceptability of IP-378 test data with field performance, it was considered logical to review the present UOP-413 test data in relation to IP-378 (modified) test data. It may be observed from the data given in Tables-5 to 7, the specified UOP-413 tests value of 1.6 mg/100 ml of HSD appears to be less stringent and

requires adjustment. In cases where the values of total sediment crossed the limit of 2.0 mg/100ml. of HSD determined in IP-378 (modified) test, the corresponding UOP-413 test values are much lower than the specified limit. From the linear regression analysis (Eq.1), the total sediment value of 0.8 mg/100 ml. of HSD which corresponds to IP-378 (modified) test value of 2.0 mg/100 ml of HSD may be proposed as the pass limit for UOP-413 test. This limit not only will ensure the quality of HSD in terms of stability at the production end but also take care the trouble free performance of the fuel in the field.

CONCLUSION

♦ Blending of cracked streams from secondary processing to the HSD adversely affects the stability of HSD pool. However stability of such blend can be improved by use of suitable stabilizing additives. Study has shown that VBGO can be accommodated in HSD in the range of 2-4% by doping the product with additive.

♦ Short duration laboratory stability UOP-413 test data has good correlation with three months ambient storage stability IP-378 (modified) test data (correlation coefficient 0.96). The total sediment value for IP-378 (modified) test can be predicted from UOP-413 data with high degree of reliability.

♦ Similarly, total sediment value for IP-378 (modified) test of 90 days can possibly be predicted from the values determined after 45 days of test duration and therefore, has the potential of saving 50% of test duration. However, a large number of data need to be analyzed to establish the correlation firmly.

♦ Considering the acceptable reported total sediment value of 2.0 mg/100 ml. of HSD for IP-378, the specified value of 1.6 mg/100 ml. of HSD for UOP-413 test appears to be less stringent. A value of 0.8 mg/100 ml. has been proposed which will ensure better quality of HSD at production end and good field performance.

ACKNOWLEDGEMENT

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FIGURE-1

CORRELATION BETWEEN EXPERIMENTAL AND PREDICTED VALUE OF IP-378 (MODIFIED) TEST COMPUTED FROM UOP-413 TEST DATA

TOTAL SEDIMENT, mg/100ml. OF HSD

$R^2=0.96$
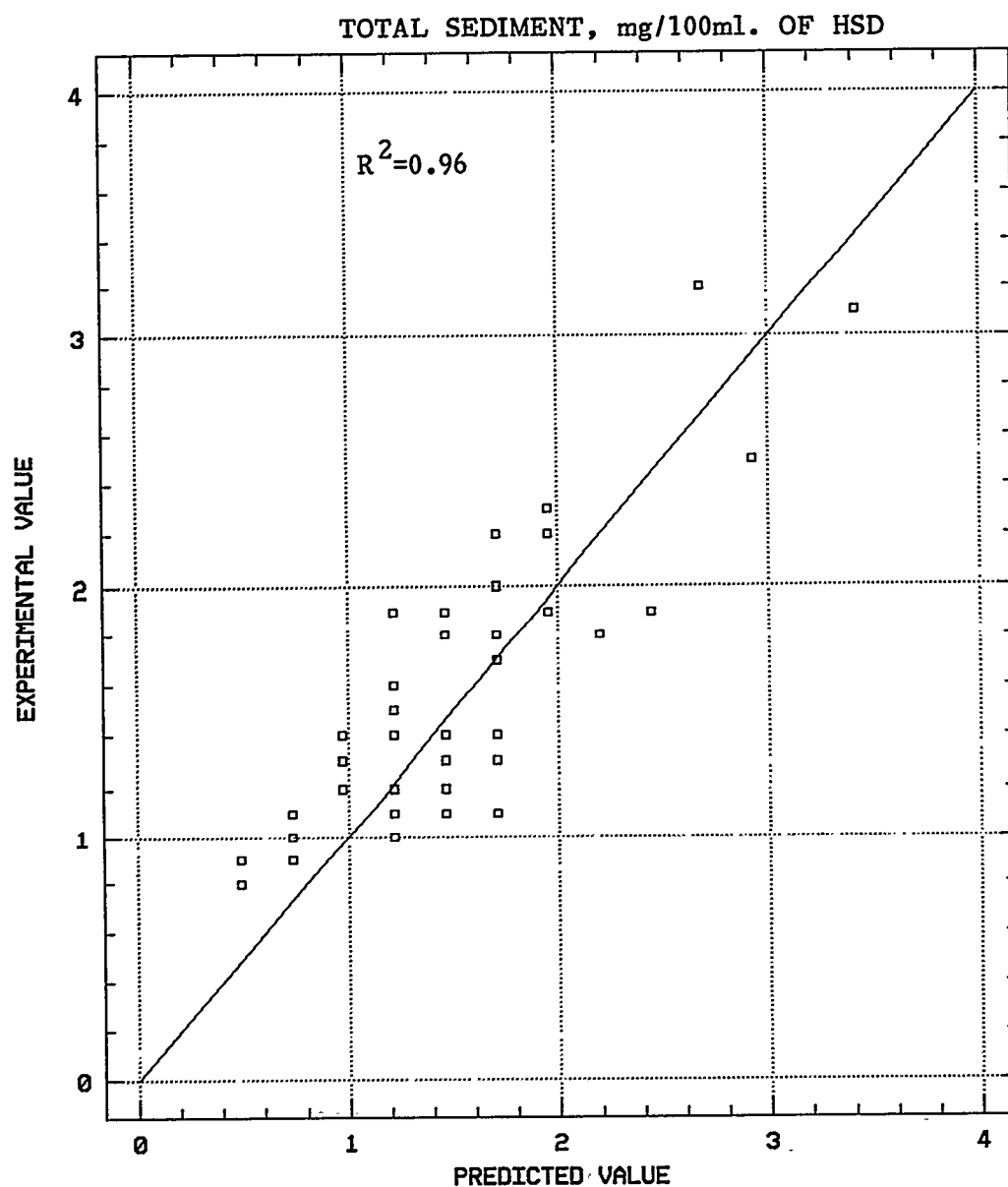
EXPERIMENTAL VALUE

PREDICTED VALUE

FIGURE-2

CORRELATION BETWEEN EXPERIMENTAL AND
PREDICTED VALUE OF IP-378 (MODIFIED) TEST
COMPUTED FROM 45 DAYS DATA OF IP-378 (MODIFIED) TEST

TOTAL SEDIMENT, mg/100 ml. of HSD

$R^2=0.98$

EXPERIMENTAL VALUE

PREDICTED VALUE
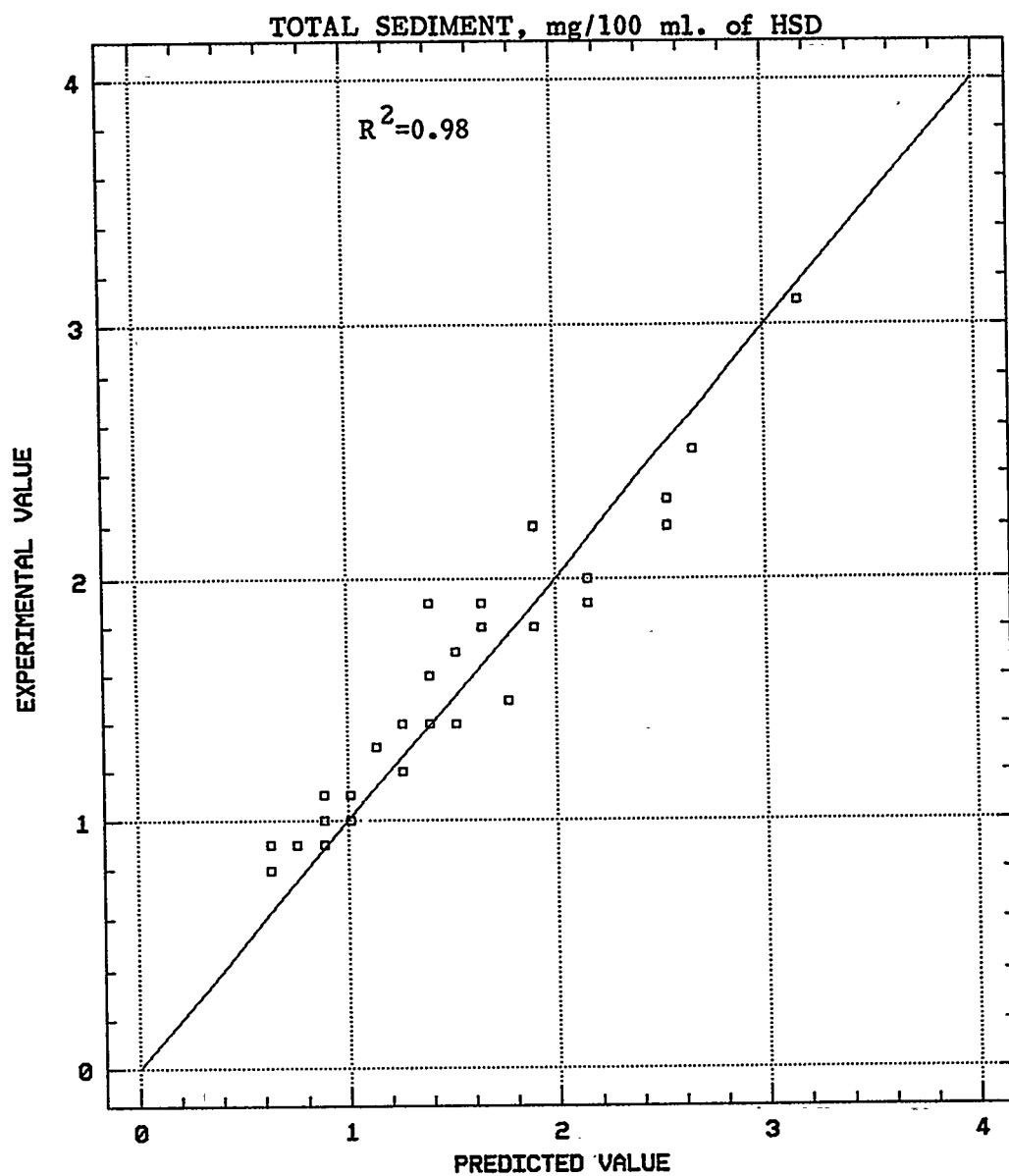
TABLE-1

CHEMICAL TESTS USEFUL IN PREDICTING FUEL STABILITY, CORROSIVITY AND TREATMENT SCHEME

TEST	METHODS
FIA	ASTM -D 1319
Bromine No.	ASTM -D 1159
Diene value	UOP-326
Copper (ppb)	UOP -144
Phenols & Thiophenols	UOP-262
Pyrrole Nitrogen	UOP-276
Acid NO.	ASTM - D 974
Free Sulfur (Mercury No.)	UOP - 377
Basic Nitrogen	UOP - 269

TABLE-2

PHYSICO-CHEMICAL PROPERTIES OF BASE HSD FUEL

S.NO.	CHARACTERISTICS	TEST METHOD	VALUES
1.	Density @ 15 deg.C, gm/ml	ASTM D -1298	0.8374
2.	KV @ 40 deg. C, cst	ASTM D -445	3.6
3.	Copper strip corrosion for 3 hrs at 100 deg.C	ASTM D -130	1
4.	Pour point, deg. C	ASTM D -96	+9
5.	Flash point, deg.C	ASTM D -1310	36
6.	Sulphur, % wt.	ASTM D -4294	0.59
7.	Total Sediment, mg/100 ml	UOP - 413	0.7
8	Distillation,	ASTM D -86	
	IBP, DEG. C		130
	10 ML Rec. at, deg.C		162
	50 ML Rec. at, deg.C		304
	70 ML Rec. at, deg.C		330
	90 ML Rec. at, deg.C		362
	FBP, deg.C		390
9.	Hydrocarbon Analysis, % wt. (by NMR)		
	- Aromatics		26.3
	- Naphthenes		17.2
	- Paraffins		56.2
	- Olefins		0.3

TABLE-3

PHYSICO-CHEMICAL PROPERTIES OF VB GAS OIL

S.NO.	CHARACTERISTICS	TEST METHOD	VALUES
1.	Density @ 15 deg.C, gm/ml	ASTM D - 1298	0.8097
2.	KV @ 40 deg. C, cst	ASTM D - 445	1.67
3.	Flash point, deg.C	ASTM D - 1310	65
4.	Sulphur, % wt.	ASTM D - 4294	0.76
5.	Total Sediment, mg/100 ml.	UOP- 413	4.6
6.	Distillation	ASTM D- 86	
	IBP, deg.C		157
	10 ML Rec. at, deg.C		172
	20 ML Rec. at, deg.C		179
	50 ML Rec. at, deg.C		203
	70 ML Rec. at, deg.C		218
	90 ML Rec. at, deg.C		245
	95 ML Rec. at, deg.C		225
	FBP, deg.C		275
7.	Hydrocarbon Analyses, NMR % wt.		
	- Aromatics wt. %		29.2
	- Saturates, wt. %		56.4
	- Olefins, wt. %		14.4

TABLE-4

VARIOUS STABILITY TESTS USED FOR DISTILLATE FUEL

TYPE OF TEST	TEST CONDITIONS	MAXIMUM ALLOWABLE SEDIMENT LIMIT	FIELD STORAGE CORRELATION	COMMENTS
- Field storage	Field , ambient, 1yr.	2.0 mg/100ml	100%	Best
- Lab storage IP-378/87	3 months 100 deg.F	2.0 mg/100 ml	90% +	Best
-ASTM D-2274	O^2 bubbled through fuel at 203 deg.F, sediment & colour determined	2.5 mg/100 ml	Non established	Repeatable but not reproducible
- DU PONT F 21-61	90 min. 300 deg.F, filter pad rated from 1-20	Refiners 7 pad rate Pipe lines 5 pad rate	Non established	Repeatable but not reproducible
- DEF 2000 T	16 Hrs, 99 deg. sediment and colour deter-mined	1.0 mg/100 ml.	None	None
- UOP - 413	16 Hrs. at 212 deg.F O^2 media, sediment and colour determined	1.6 mg/100 ml	90% with 110 deg. F storage (IP-378)	Very good

• May vary according to individual procure/producer/user requirements

TABLE-5

EFECT OF VBGO BLENDING ON STABILITY OF BASE HSD FUEL

HSD BLEND	Total sediment, mg/100 ml. Determined by :		
	UOP-413 After 0 day:	IP-378 (modified)	
		After 45 days	After 90 days
HSD	0.7	1.1	1.4
HSD + 2% VBGO	0.9	1.5	1.8
HSD + 4% VBGO	1.2	2.1	2.5
HSD + 6% VBGO	1.4	2.5	3.1

TABLE-6

RESPONSE OF STABILIZING ADDITIVES IN HSD - VBGO BLENDS DETERMINED BY UOP - 413 TEST

Stabilizer/ Dosages (ppm)	Total sediment, mg/100 ml. with VBGO conc. :			
	0%	2%	4%	6%
None	0.7	0.9	1.2	1.4
Stabilizer [A]				
- 25	0.3	0.4	0.6	0.7
- 50	0.2	0.3	0.5	0.5
Stabilizer [B]				
- 25	0.4	0.5	0.7	0.8
- 50	0.3	0.5	0.6	0.8
Stabilizer [C]				
- 25	0.3	0.6	0.6	0.8
- 50	0.2	0.3	0.4	0.7

TABLE-7

RESPONSE OF STABILIZER ADDITIVES IN HSD-VBGO BLENDS DETERMINED BY IP- 378 (MODIFIED) TEST

Doped blends	Total sediment, mg/100 ml obtained with additives conc.			
	AFTER 45 DAYS		AFTER 90 DAYS	
	25 PPM	50 PPM	25 PPM	50 PPM
STABILIZER - A				
HSD	0.7	0.6	0.9	0.9
HSD + 2% VBGO	1.0	0.7	1.2	1.1
HSD + 4% VBGO	1.3	1.1	1.8	1.6
HSD + 6% VBGO	1.5	1.1	2.2	1.9
STABILIZER - B				
HSD	0.9	0.8	1.3	1.0
HSD + 2% VBGO	1.4	1.2	1.5	1.4
HSD + 4% VBGO	1.7	1.7	2.0	1.9
HSD + 6% VBGO	2.0	2.0	2.3	2.2
STABILIZER - C				
HSD	0.5	0.5	0.9	0.8
HSD + 2% VBGO	0.8	0.7	1.1	1.0
HSD + 4% VBGO	1.0	1.0	1.4	1.4
HSD + 6% VBGO	1.3	1.2	1.9	1.7

MICROBIAL DETERIORATION OF HYDROCARBONS

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A wide range of bacteria, yeasts and filamentous fungi utilise hydrocarbons as their sole energy and carbon source. Microbial degradation of hydrocarbons has economic implications when spoilage of crude oil and petroleum products occurs, e.g. fuels, hydraulic oils, lubricating oils and machine tool coolants. As a consequence of microbial activity an oil product changes chemically and functionally and some components may disappear entirely. Metabolic products may cause severe corrosion or may be used as substrates by other microorganisms, e.g. sulphate-reducing bacteria whose products can in turn also cause damage. The biomass can clog pores and pipes. As spoilage can occur only in the presence of free water, good housekeeping is a prerequisite for preventing microbial degradation of hydrocarbons. The growth of anaerobic bacteria (e.g. sulphate-reducing bacteria) can be inhibited by introducing oxygen into the system. Coatings can be used to protect metals from corrosion.

1. Introduction

Microbial interaction with hydrocarbons has attracted the attention of various researchers looking for positive and detrimental activities in the biodegradation of hydrocarbons. The first report of microbial hydrocarbon utilisation is given in 1895 by a Japanese botanist, who reported that paraffin was attacked by the fungus *Botrytis cinerea*.[1] According to Quayle [2] the first classic papers on microbial oxidation of petroleum, paraffin and benzene were published in 1913 by Söhngen who noted that microbial decomposition of hydrocarbons " ... explains the disappearance of the petroleum, daily brought at the surface of canals by motor boats and in other ways".

Meanwhile enormous progress in petroleum microbiology has been made and the biodegradation of petroleum was found to be a widespread natural phenomenon.

2. Biodegradation of hydrocarbons

It has been reported that many microorganisms, bacteria as well as yeasts and filamentous fungi, can utilise hydrocarbons as a sole carbon and energy source [3-6]. It was found that aliphatic hydrocarbons are degraded and assimilated by a wide variety of microorganisms.

Other classes of hydrocarbons, including alicyclic, aromatic and heterocyclic compounds, may be oxidised but are assimilated by only a few bacteria. Saturated aliphatic compounds are degraded more readily than unsaturated ones, and straight chain compounds are degraded more easily than branched chain, alicyclic and aromatic ones.

Before biodegradation can occur, hydrocarbons have to enter the cytoplasm of the microorganism. Many microorganisms which can grow on hydrocarbons can adapt to this substrate. As a consequence of the utilisation of hydrocarbon substrates or in response to such substrates, they produce extracellular metabolites which act as surfactants (biosurfactants) and bring about the emulsification of the substrate into small droplets (macro-emulsion) or the " solubilisation" of hydrocarbon compounds in the medium (micro-emulsion). At present there is still some controversy about the mechanism for the uptake and transport of water-insoluble hydrocarbons into the cell [7].

The mechanisms of microbial hydrocarbon degradation have been investigated in detail and an enormous amount of literature has been published over the past few decades. It is beyond the scope of this presentation to go into details, but it should be emphasised that the first step in microbial oxidation of any hydrocarbon, i.e. the insertion of an oxygen atom into the hydrocarbon structure, is an aerobic reaction requiring molecular oxygen. The enzymes responsible for these reactions are called oxygenases and are essential for both aliphatic and aromatic hydrocarbon degradation. Once oxygen has breached the hydrocarbon structure anaerobic degradative pathways may operate. In this way phenols may be utilised by anaerobic microorganisms.

Recent studies however have demonstrated that mono-aromatic hydrocarbons such as benzene, toluene, xylene and alkylbenzenes can be biodegraded in the absence of oxygen [8-10]. There are now several strains of sulphate-reducing and nitrate-reducing bacteria shown to grow definitely on saturated hydrocarbons under strictly anaerobic conditions.

The first products of biooxidation are alcohols, aldehydes and carboxylic acids which can then be further modified by mono, di and subterminal oxidation processes, the final products being CO_2 and H_2O.

Most of the research work has been done using chemically defined hydrocarbons such as alkanes of specified chain length and chain configuration, pure aromatic compounds, and synthetic mixtures of hydrocarbons. Since the work of Jones & Smith [11] and Winters & Williams [12] microbial alteration of crude oils has become of special interest. The studies of Winters & Williams, confirmed by other investigators [13, 14], documented changes in the

chemical and physical characteristics of reservoir oils which suggested that biodegradation had taken place.

The microbial capability of utilising petroleum hydrocarbons is used in petroleum prospecting and recovery, for the biotransformation of individual hydrocarbons to valuable chemical products and for the disposal of petroleum waste and oil spills. Besides the beneficial aspects of microbial hydrocarbon utilisation however, there are also detrimental sides, particularly with respect to the deterioration of crude oil and its distillation and cracking products, as well as products containing them, e.g. lubricants, cooling and hydraulic fluids. Microbial degradation can lower the concentration of a substance or completely remove a class of substances. Degradation products, e.g. acids, can be corrosive, damaging metal surfaces they come into contact with. Under suitable conditions, the degradation products can serve as substrates for other microorganisms, e.g. sulphate-reducing organisms, whose products can in turn also cause damage. The biomass itself, as well as excreted polymers, can clog pores and pipes or form sludge.

3. Damages

As with all living systems, water is required for microbial activity. Although microorganisms can enter the oil phase and survive there for some time, growth and reproduction must take place in the aqueous phase. Small amounts of water are sufficient and water is often a product of the decomposition of the hydrocarbons. *Pseudomonas spec.* e.g. grows well in fuel water condensate, but in dry kerosene less than 0.01 % of the initial bacteria concentration survived after three hours of incubation [15]. In contrast spores of the filamentous fungus *Cladosporium resinae* survived even after 17 days of incubation in dry kerosene. The same fungus can grow in kerosene containing only 80 mg of free water per litre of kerosene. After four weeks of incubation at least 940 mg of water per litre of fuels was produced by metabolic processes.

3.1. Oil reservoirs and oil recovery

Oil reservoirs were once considered to be too hostile to support microbial life because of extreme environmental conditions such as temperature, pressure or salinity. However it is now well known that many oil reservoirs have active and diverse populations of microorganisms, even in extremely thermophilic or hypersaline reservoirs and their activities will affect natural oil constituents[16]. Water injection for the purpose of secondary and tertiary re-

covery stimulates microbial activity and sludge may be generated round a well impairing the oil production. Plugging of pores due to polymer and biofilm formation and lowering of the quality of the oil may be other detrimental effects. Aerobic microorganisms rapidly use up the oxygen in the water pumped into the reservoir, quickly leading to anaerobic conditions which permit the growth of sulphate reducing bacteria. Sulphate reducers on their part cause the souring of an oil reservoir directly linked to H_2S production. As consequences of souring, corrosion in production and injection wells, pipelines and other water-handling equipment, plugging by corrosion products, safety hazards due to high H_2S levels and increased costs to remove H_2S may occur which are expensive to the oil industry[16,17].

3.2 Long-term storage of petroleum and petroleum products

Crude oil and fuel can rarely be stored in tanks and underground caverns for long periods of time without any problem[18]. In the early forties large numbers of bacteria were reported to be in tank bottom water under stored gasoline and kerosene. Some years later sludge development in fuel storage tanks was recognised as being of microbial origin and it was shown that hydrocarbons in the range of C_{10} - C_{18} (kerosene) were utilised by a much wider variety of microorganisms and at a faster rate than C_5 - C_9 compounds (gasoline).

In general fuels are always associated with water and it is extremely difficult if not practically impossible to prevent or eliminate contamination of fuels by water. Water enters the fuels from a variety of sources during refinery processes and in storage. At the refinery gasoline and kerosene fuels are washed, often with river water. Although most of the water separates readily from the fuel, small amounts are transported to the storage facility where final separation of water and fuel will occur. Water may be used in petroleum product storage tanks to prevent loss of products by seepage at the bottom of the tanks. In some instances water is used for displacing storage products from the tank instead of directly pumping the product.

Microbial activity is influenced by a variety of environmental factors such as temperature, pH value, salinity of the aqueous phase, availability of oxygen and inorganic nutrients and of course mainly depends on the composition of hydrocarbon products. During long term storage some microorganisms may be adapted to changes in their environmental conditions, others, for instance, per se may grow at a wide range of temperatures. Oxygen is available by its rather high solubility in oil. Nitrogen and phosphate may be available when pressure additives and corrosion inhibitors are added to the oil product.

3.2.1 Storage in tank

The main problems most often associated with microbial contamination of hydrocarbon storage tanks are loss of fuel quality due to hydrocarbon degradation, plugging of filter and pipeline systems, sludge development and corrosion of storage tanks and pipelines.

In the case of gasoline storage the shorter-chain n-paraffins ($< C_9$) remained undegraded. The lack of utilisation is attributed to the toxicity of these hydrocarbons because of their greater solubility and their higher concentration in the aqueous phase. The reason for the toxic effect of short-chain alkanes is probably their disorganisation of the cytoplasmic membrane of microorganisms. Sludge development in gasoline tank bottom water has been found to be due to microbial utilisation of organic compounds added to the gasoline for preventing oxidation of gasoline constituents.

Stored kerosene fuel may undergo microbial degradation because kerosene contains many higher molecular weight hydrocarbons which are oxidised by a wide variety of microorganisms. Microbial growth results in the formation of sludge which, together with the physical presence of the microorganisms, may cause the plugging of filters and pipeline systems. Due to metabolic pathways production of organic acids may occur causing metal corrosion of the tanks.

Hydrocarbons utilising microorganisms primarily are aerobic organisms, that is they require oxygen for continued growth. During long-term storage of fuels oxygen-free areas develop underneath the layer of aerobic organisms giving rise to growth conditions for anaerobic sulphate reducing bacteria such as *Desulfovibrio*. These bacteria produce large amounts of hydrogen sulphide as a metabolic product effecting anaerobic corrosion of iron and steel. A seriously corrosive fuel was observed when sea water rich in sulphate ion and relatively rich in organic matter had been used for the clearance of the pipelines and had come into contact with the fuel.

The phenomena described in kerosene storage have also been noted in stock piling of gas oil, diesel fuel and heating fuel although the consequences have been less dramatic than in the case of aviation turbine fuels.

3.2.2 Underground storage

For several ecological and safety reasons, underground storage of liquid hydrocarbons has become increasingly attractive. In principle similar phenomena have to be expected in rock caverns as observed in tank storage and investigated under laboratory conditions. Of course environmental factors are more difficult to consider and additionally hydrostatic pres-

sure in deep caverns has to be taken into consideration. Availability of oxygen may be more critical, but contamination by water will be just as difficult to prevent or to eliminate. Condensation of atmospheric water may occur and also meteoric and groundwater may enter into the rock cavern.

The long-term storage of aviation fuel in rock caverns in Scandinavia is representative for various cases where damage due to microbial decomposition of hydrocarbons had happened[19,20]. A so-called "water curtain" was installed to seal the system. The slight contact of the fuel with the water initiated the growth of microorganisms that oxidise hydrocarbons. The pipes for the "water curtain" were soon clogged and a biofilm formed at the oil/water interface. The quality of the fuel deteriorated so badly that it could no longer be used as aviation fuel.

Storage in rock caverns sealed by coating obviously is a much better concept. But it should be emphasised that microbial deterioration of fuel tank linings also has been reported. For coating polymerised relatively inert organic materials were used. It was found that poly-sulphide polymers used for lining large concrete storage tanks were susceptible to microbial attack. Bacteria (*Bacillus, Flavobacterium*) as well as filamentous fungi (*Cladosporium, Fusarium*) were isolated from deteriorated coatings. Prior to employing coatings for use in hydrocarbon long-term storage the coating material should be subjected to rigid tests on its susceptibility to microbial deterioration.

For strategic purposes in several countries large volumes of crude oil have been stored in salt dome caverns for long periods of time without showing detrimental changes in the chemical and physico-chemical properties of stored products [21]. In some caverns, however, a viscous sludge layer was formed after some time at the oil-brine interface that could possibly be explained as the result of microbiological activity. As a matter of fact aerobic and anaerobic bacteria have been isolated from the oil, brine and oil-brine interface, most of these were spore formers and under laboratory conditions able to grow aerobically on oil. Nevertheless, because of oxygen deficiency, hypersalinity and low phosphate and nitrogen content in the brine, significant growth of microorganisms and spoilage of stored products seem to be unlikely, even during long periods of storage [22-24].

3.3 Fuels

Fuels contain very little water, the ratio of water to hydrocarbons is normally much lower than 1: 1000. Considerable problems however occur in the case of aviation fuels, owing

to the high proportion of long-chain saturated hydrocarbons (C_{10} - C_{18}). As a matter of fact chemical changes in the hydrocarbons are not the main problem. The damage is caused chiefly by the particular nature of the microorganisms which clog screens, filters and valves and by their metabolic products which corrode tanks. Microbial growth occurs only during flight interruptions; during a flight, growth is hindered by the low temperatures. The main problem organism is the fungus *Cladosporium resinae* which produces spores quickly and whose spores survive for months in the organic phase.

Microbial contamination of motor fuels and heating oil is quite common. The effects are less dramatic than for aviation fuel because the mostly shorter hydrocarbon chains (C_5 -C_9) are less easily decomposed. The main damage is caused by clogging of filters and pipelines.

Fuel for ships always contains considerable amounts of seawater, especially if seawater is used to rinse or fill empty tanks. Extensive corrosion is usually the consequence. *Cladosporium resinae* is the predominant microorganism here, sulphate-reducing bacteria can also play an important role[25].

3.4 Hydraulic oils and lubricating oils

Hydraulic oils and lubricating oils are used in closed systems. Not until there is a leak is microbial degradation possible. The pressures at which hydraulic oils are used guarantee sufficient oxygen for the microflora normally present. Decomposition of the individual components of the mineral oil, clogging of valves and corrosion are the usual consequences.

Lubricating oils in motor vehicles are subject to microbial degradation only after long periods of disuse, in which case severe damage is done to metal parts. The working temperature of lubricating oil in an internal combustion engine is normally about 90° C, thus sterilising the oil.

The situation is different for diesel motors on ships, where the working temperature of the lubricating oils is in the range of 40 - 45° C. If water contaminated with microorganisms enters the system, the microorganisms find ideal conditions for growth. Owing to the slightly alkaline conditions, bacteria predominate, particularly *Pseudomanonas spec.*. Yeasts and molds are generally found in much lower concentrations. A typically found mold is *Aspergillus fumigatus* which can cause considerable corrosion. In extreme cases, complete breakdown of the engine is the result. An early indication of damage is the formation of a stable water-in-oil emulsion, sludge formation, increasing acidity, clogged filters and rust formation[25].

3.5 Machine tool coolants

Machine tool coolants are oil-in-water emulsions, often containing a number of additives (emulsifiers, stabiliser, anti-foaming agents, anti-corrosion agents, odor neutralising agents, biocides). In newer products, many of the original components of the mineral oil have been replaced by synthetic products. Owing to their high water contents, machine tool coolants are particularly susceptible to microbial degradation. Although they are sterile when they are delivered, machine tool coolants are quickly contaminated with microorganisms, either from traces in old fluids when containers are refilled or by entry from the air. Because of the generally alkaline pH (about 8.5), bacteria predominate, e.g. *Alcaligenes, Achromobacter, Acinetobacter, Proteus* and *Pseudomonas*. At lower pH values, yeasts and molds occur more frequently and in the case of an oxygen deficit, sulphate-reducing bacteria begin to develop.

The kinds of damage that can occur are as different as the differences in composition of cooling fluids: e.g., foam formation, sludge formation, unmixing of the emulsion, viscosity changes, foul-smelling odors (H_2S, NH_3), lowering of pH and corrosion. In addition to the cost resulting from damage to materials, there is the cost of disposing of the fluid that is no longer useable.

As there is a direct contact of the user with machine tool coolants, the question arises as to the damage to the user's health. *Escherichia coli, Enterobacter aerogenes, Proteus vulgaris, Staphylococcus aureus* and *Klebsiella spec.* are often found in fluids containing mineral oils. The survival rate of pathogenic microorganisms in oil is considered to be very low. Infections by bacteria in aerosols from cooling fluids can irritate the eyes and lungs, serious infections have not been reported however [25].

4. Protection measures

4.1 " Good Housekeeping"

The reason for damage is always the presence of water. The most important measure is then the prevention of the entry of water. Residual water can be pumped off, followed by heat treatment. Tanks should be thoroughly cleaned before refilling.

4.2 Biocide additives

If " good housekeeping" does not help or when flooding with water is used, e.g. as a production measure or for transport, biocides can be used. These must fulfill a number of requirements:

a) They must be soluble in either water or oil, or both.

b) They must be toxic to the microorganisms at very low concentrations.

c) They must be of acceptable levels of toxicity to humans.

d) They must be stable with respect to changes in pH and temperature.

e) They must be biodegradable.

f) They must be affordable.

Numerous substances are used - from simple compounds such as chromate, formaldehyde or glutaraldehyde to complex compounds or mixtures [25, 26].The growth of anaerobic bacteria (e.g. sulphate-reducing bacteria) can be prevented if the system contains sufficient oxygen.

4.3 Physical measures

In addition to chemicals, various physical methods have been tested for inactivating or killing microorganisms [25]. Magnetic fields, UV or gamma radiation have been shown to be ineffective. Ultrasonic treatment was equally ineffective. These methods cannot be used on a large scale anyway. Thermal treatment has been shown to be effective in a pilot test with 1500 L of cooling fluid. Metals can be protected with a coating of a material that is resistant to microbial decomposition.

5. Conclusion

Microbial deterioration of hydrocarbons is a widespread phenomenon which has been studied for more than 50 years. There are multiple variations in microbial degradation of petroleum and petroleum products and as many are the final products and consequences of microbial degradation, most of them have economic implications. Various antimicrobial methods have evolved, others still have to be developed. Looking for protective measures these should not be selected only for economic reasons, but should also take the environmental impact into consideration.

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