5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7, 1994

THE EFFECT OF SOME METALS ON THE OXIDATIVE AND STORAGE STABILITY OF GASOLINE

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ABSTRACT

The catalytic action of transitional metal compounds on the oxidation of organic substrates with atmospheric oxygen has received considerable attention in the literature. The effect of metal surface (Fe and Zn) on the oxidation processes and storage terms of motor gasoline containing fraction from catalytic cracking have been investigated. Both metals are chosen because they are the main construction material of the fuel tanks. On the basis of the kinetic data the correction coefficient k_m evaluating the influence of metals on the oxidation processes of gasoline has been determined.This correction coefficient is included in the calculation for prediction of the real storage terms of gasoline.

INTRODUCTION

The catalytic action of transitional metal compounds on the oxidation of organic substrates has received considerable attention. One can reasonably expect that the oxidation processes proceeding within the fuel should be influenced by metals and their compounds. The accelerating effect exhibited by these metal contamination (Fe, Cu, Cr, Mn, Co)[1-6] is closely related to the oxidation and storage stability of various fuels and lubricants. In Ref. 6 the kinetics of oxidation of standard jet fuels T-64 RT, in the presence of construction materials: alloys, steel and pure metals which are part of the composition of these alloys, has been studied. It was proved that the catalytic action of the metals is due to their impact on hydroperoxides decomposition to free radicals. Many works emphasising research on hydrocarbon fuels has yielded some information regarding the effect of certain metals, but a quantitative assessment of this influence in the literature is lacking.

In the present paper we have investigated and quantified the effect of metal surfaces (Fe and Zn) on the oxidation process and the storage terms of motor gasoline (MG) containing up to 50 % catalytically-cracked fraction (CCF). We have chosen Fe and Zn, because they are the main construction material of the fuel tanks. On the basis of the kinetic results we have evaluated quantitatively this influence on the storage terms of gasoline determined according to Ref.7.

EXPERIMENTAL

The oxidation tests were carried out on commercially available gasoline - trade mark A-86, containing 40 and 50 % CCF and 0,02 % ionol (AC-86). The experiments were performed in the presence of zinc powder (Fluka puriss - p.a. > 98 %) with total surface 2 $m^2/gr.$ and iron plate (steel-5) with total surface - 11,14 cm^2. The oxidation stability of AC-86 was determined on an autoclave "Multiclave" [8] and UOSUG [9], at 393 K and oxygen pressure 1 MPa. The hydroperoxide content in the oxidates was determined iodometrically. The carbonyl and hydroxyl containing compounds were detected with the help of IR-spectroscopy. Their total quantity was determined in the following way:

$$C_{O.C.C.} = C_{abs.ox.} - C_{C.A.} - C_{ROOH}$$

where: $C_{O.C.C.}$ is the concentration of oxygen-containing compounds (mainly carbonyl and hydroxyl containing organic substances), mol/l.;

$C_{abs.ox.}$ is the concentration of the absorbed oxygen in mol/l;

$C_{C.A.}$ is the concentration of the carboxylic acids in mol/l;

C_{ROOH} is the concentration of the hydroperoxides in mol/l.

The prediction of the gasoline (AC-86) storage term was performed on a PC according to a method given in Ref.7.

RESULTS AND DISCUSSION

In Figure 1 is shown the kinetic curve of the absorption of oxygen during oxidation of gasoline A-86 in the presence of steel plate. The curve is characterised by three macrokinetic stages: induction period (1); intensive absorption of oxygen (2) and autoretardation (3). In order to predict the storage terms of gasoline we have used the induction period. The latter is practically not influenced by side effects. The oxidation in the presence of metals is typical heterogeneous process and it should be expected an influence of diffusion factors. The fact that the logarithmic plot of the induction periods versus 1/T correspond to the Arrhenius equation, discussed below, and the values of the activation energies measured, prove that the experiments are carried out in the kinetic region and the diffusion factors do not influence the process..

The catalytic activity of transitional metals is usually related to the additional generation of active radicals resulting from their interaction with hydroperoxides[10 - 12]:

$$ROOH + Me^{2+} \longrightarrow RO^{\cdot} + OH^{-} + Me^{3+}$$

$$\underline{ROOH + Me^{3+} \longrightarrow RO_2^{\cdot} + H^{+} + Me^{2+}}$$

$$2ROOH \xrightarrow{Me^{2+}} RO_2^{\cdot} + RO^{\cdot} + H_2O \qquad 1)$$

The marked lowering of the activation energy of this interaction (compared to the activation energy of the thermal decomposition process of hydroperoxides) results in the essential increase in the oxidation rate, in the presence of metals and their compounds[1]. The oxidation rate W_{ox} in this case is given by the following equation:

$$W_{ox} = \frac{k_p \,.\, [RH]}{\sqrt{k_t}} \,.\, \sqrt{W_i} \qquad 2)$$

where: k_i, k_p, k_t - are the rate constants for the initiation, propagation and termination steps of the oxidation process; [RH] -is the concentration of the "average" molecule of the hydrocarbon -fuel. The initiation rate W_i can be expressed by

$$W_i = k_i \,.\, [O_2]^x \,.\, [RH]^y \,.\, F^z \,.\, S^z \qquad 3)$$

where: x, y, z are the partial orders of the reaction with respect to gasoline, oxygen and metal, respectively ;

F is a coefficient connecting the concentration of the active centers with the metal surface for strong reagent adsorption;

S is the contact surface of the metal per unit volume of gasoline.

In the literature[13-17] is assumed that this process (see equation 1) is the only source for generation of free radicals, during oxidation of organic substrates with homogeneous catalysts. However, in the presence of heterogeneous catalysts[18] (for instance metals, metal oxides) the generation of free radicals can proceed on the metal surface according to:

$$[RH]_{ads} + [O_2]_{ads} \longrightarrow RO_2^{\cdot}, R^{\cdot}, H_2O_2 \qquad 4)$$

The desorption of the radicals in the liquid phase results in initiation of a radical chain reaction. At the beginning of the oxidation process, when the concentration of the hydroperoxides formed is very low, the process, described by eqn.(4) can be regarded as a main source of free radicals. Thus, the catalytic action of metal surface on the gasoline oxidation can also be due to the oxygen activation as a result of its interaction with the active species on the solid phase [19]. The duration of the induction period and the value of the oxidation rate have been selected, as basic kinetic parameters for evaluation of the influence of the metal surface. In the case of thermal initiation, proceeding only in the volume of the liquid phase, the oxidation rate is defined as follows:

$$W_T = \frac{k_p \,.\, [RH]}{\sqrt{k_t}} \,.\, \sqrt{W_i^T} \qquad 5)$$

where: W_i^T is the rate of thermal initiation; the other parameters have the same meaning as in equation (2).

In the presence of metal surface exhibiting catalytic effect, the oxidation rate is:

$$W_S = \frac{k_p \,.\, [RH]}{\sqrt{k_t}} \,.\, \sqrt{W_i^T + W_i^S} \qquad 6)$$

where: W_i^S is the initiation rate in the presence of metal surfaces. The quantitative assessment of the increase in the oxidation rate under the initiation action of the metal surface (W_s) is given by equation (7), obtained by combining of eqns. (2), (5) & (6).

$$W_s^2 = W_T^2 + a.S^z \qquad 7)$$

where "a" is defined as:

$$k_p^2 \,.[O_2]^2 \,.[RH]^2 \,.\, F^z \,.k_i \,.[RH]^y \qquad 8)$$

According to the literature data [21, 22] the order z can be accepted to be equal to 1, e.g. equation (7) is as the follows:

$$W_s^2 = W_T^2 + a.S \qquad (9)$$

From the intercept and the slope of the kinetic curve in Figure 2 showing the dependence of W_s^2 versus S one can calculate W_T^2 and the parameter "a", respectively. Thus, knowing the contact metal surface in the experiment one is able to determine the coefficient referring to the extent of acceleration of the oxidation rate under the influence of the metal. Since the contact surface of the Fe plate (11.1 cm^2), under our experimental conditions was much smaller than the real contact surface (98 cm^2) we have obtained practically equal values for the oxidation rates of AC-86 in the absence of iron plate and in its presence (3.27 and $3.36.10^{-5}$ l/mol.sec, respectively). That is the reason why, we have tried to evaluate the catalytic initiation caused by the metal surface by measuring the induction period during the inhibited by ionol gasoline oxidation both in the absence (τ_T) and presence (τ_S) of initiating metal surface. This effect is demonstrated by the following equations:

$$\tau_T = \frac{f \, . \, [InH]}{W_i^T} \qquad 10)$$

$$\tau_S = \frac{f \, . \, [InH]}{W_i^T + W_i^S} \qquad 11)$$

After some transformations and substitution of W_i (eqn. 3) one can easily obtain the expression:

$$\tau_T = \tau_S \ (1 + b.S^z) \qquad 12)$$

where:

$$\text{“b”} = \frac{k_p \, . \, [O_2]^x \, . [RH]^y \, . \, F^z}{W_i^T}$$

Since according to literature data[7] z = 1, equation 12 is transformed as follows:

$$\tau_S = k_m \, . \, \tau_T \qquad 13)$$

where: $k_m = 1/(1 + b.S)$ 14)

Equation (15) demonstrates that the increase of the initiating metal surface results in the decrease of the induction period. In Figure 3 is given the dependence (15), obtained by simple transformation of equation (13):

$$1/\tau_S = 1/\tau_T + (b/\tau_T) \qquad 15)$$

The intercept of the straight line in Figure 3 gives the ratio $1/\tau_T$ and the slope - b/τ_T . Thus, calculating the value of "b" according to eqn. 12 on the basis of kinetic data and considering the contact area of the metal surface per unit of gasoline one can determine the coefficient k_m. We have applied eqns. (13) and (14) for calculation of k_m and for prediction of the storage terms of gasoline AC-86, taking into consideration the real performance factors[9].

The theoretical considerations pointed above allowed us to assess quantitatively the effect of metal surface on the predicted storage terms of the studied gasoline.

In Figure 4 are presented the kinetic curves for the gasoline oxidation (AC-86) in the absence and in the presence of steel plate and zinc powder, consequently. The values of the induction periods and the calculated maximal rates of oxidation are summarised in Table 1. There are presented the maximum amounts of the absorbed oxygen and the data concerning the composition of the oxidates: acid number, hydroperoxides, neutral oxygen containing compounds. It seems that these analyses do not concern the prediction of the storage terms but they are giving an idea for the state of the fuel after its oxidation under our experimental conditions. The obtained results show that the addition of Zn powder to the gasoline, results in significant change in the distribution of oxygen-containing compounds (higher concentration of the ROOH and neutral oxygen-containing compounds than in the basic sample), while the steel plate does not influence this distribution.

The data from Figure 4 and Table 1 show that the value of the induction period decrease in the presence of the metals tested. The plate area was 11,1 cm^2 , the sample volume submitted to oxidation 100 ml, and therefore the value of S = 111 cm^2 /l. The calculated parameter "b" equals to 3,55.10 l.cm^2 and the value of k_m (equation 14) has been determined to be 0,72.

It should be noted that for each separate case, the value of the parameter k_m can be determined according to eqn. (14). For instance, if 10 m^3 of gasoline are stored in a tank with diameter 171,2 cm and height 480 cm, the contact area should be S = 30,4 cm^2 /l. and k_m equals to 0,9.

The decrease in the predicted gasoline storage terms under the catalytic action of metals is estimated according to the following expression:

$$\tau = \tau_{chem} . k_m \qquad 17)$$

where: τ is the predicted storage term of AC-86 concerning the influence of the metal surface; τ_{chem} is the predicted storage term of gasoline AC-86 according to Ref.7 and it amounts to 4,5 years; k_m is a correction coefficient evaluating the effect of the metals and it equals to 0,72 for steel.

Thus, the predicted storage terms of the sample AC-86 we have investigated is 3 years. These results were confirmed in Ref. 9 whereby is made a comparative evaluation between the predicted and the real storage terms of gasoline for a 5 years period.

CONCLUSIONS

1. On the basis of the kinetic data the correction coefficient k_m evaluating the influence of metals on the oxidation process of motor gasoline has been determined.

2. The correction coefficient k_m gives us the possibility for more proper prognosis of the gasoline storage terms which are close to the real storage term.

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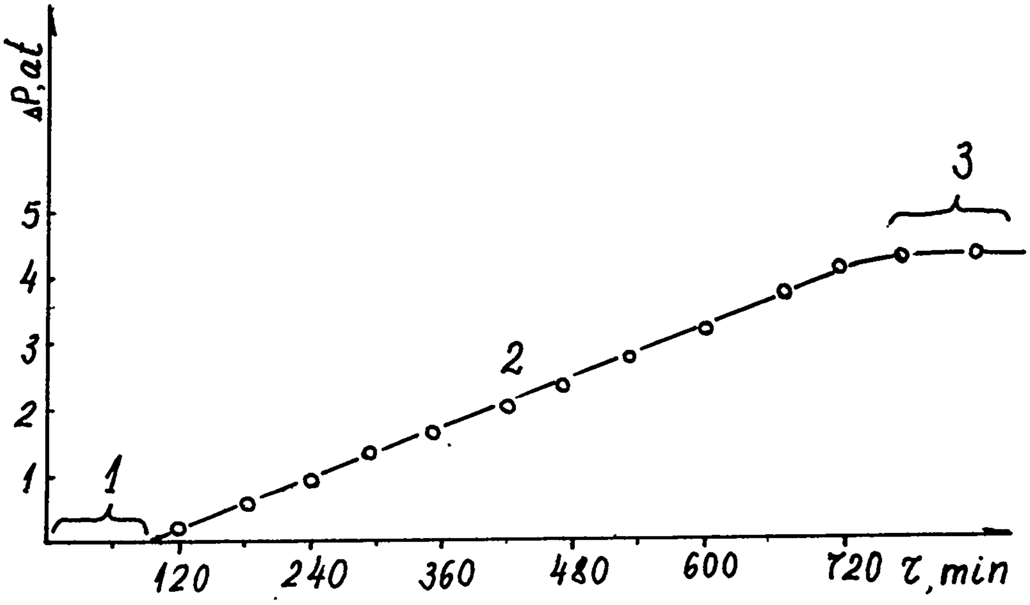

Figure 1. Kinetic curve of oxidation of A-86 in the presence of steel plate at 393 K. 1 - induction period ; 2 - maximum rate of oxygen absorption; 3 - autoretardation.

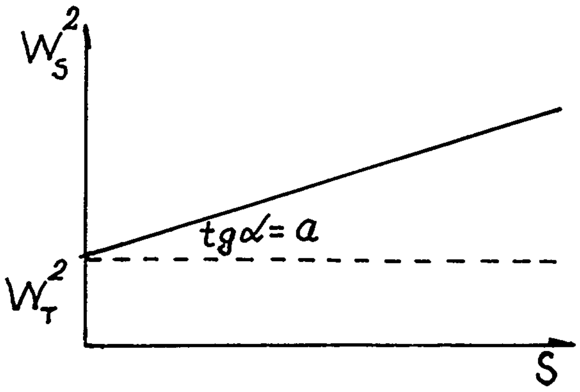

Figure 2. Dependence of the maximum oxidation rate of gasoline A-86 versus the contact metal area.

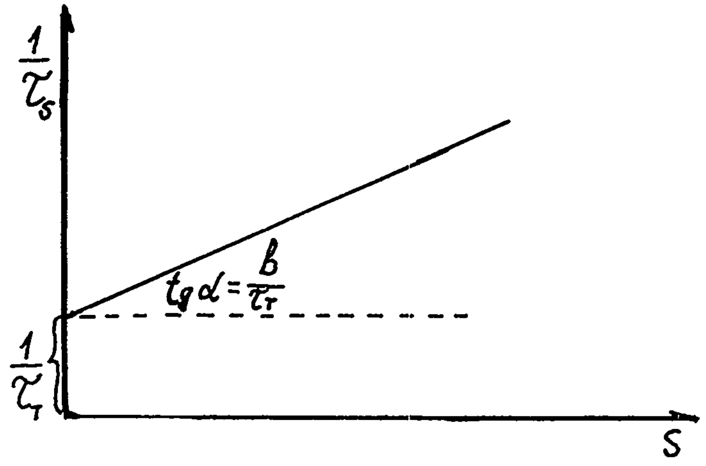

Figure 3. Dependence of the induction period versus the contact metal area during the oxidation of gasoline A-86.

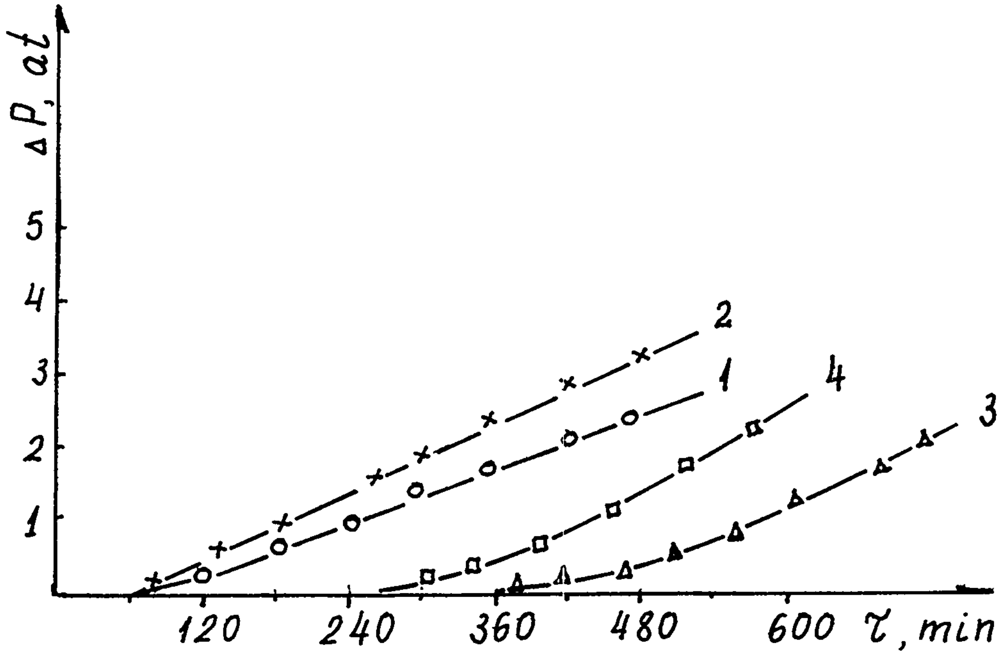

Figure 4. Kinetic curves of oxidation, at 393 K of:

1.A-86 containing 40% CCF;

2.A-86 containing 40% CCF and 0,0012 % wt. zinc powder;

3.A-86 containing 50% CCF;

4.A-86 containing 50% CCF\ in the presence of iron plate.

TABLE 1

Experimental data for gasoline oxidation at 393 K.

SAMPLE	τ_{ind} min	$W_{max} . 10^5$ mol/l.sec	Maximum amount of O_2 absorbed mol/l	ROOH mol/l	Acid number in mgr. KOH/gr.	Acids in mol/l	Other O-contn. compounds in mol/l.	Notice
A-86 contn. 40 % CCF	138	0,67	0,19	0,0186	520	0,0927	0,0787	no deposits
A-86 contn. 40 % CCF + 0,02 gr./l Zn powder	96	0,83	0,40	0,124	250	0,0446	0,2314	no deposits
A-86 contn. 40 % CCF	460	3,27	0,55	0,180	628	0,112	0,262	no deposits
A-86 contn. 40 % CCF + Fe plate	330	3,63	0,57	0,190	712	0,127	0,195	occurrence of deposits

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GUM FORMATION TENDENCIES OF OLEFINIC STRUCTURES IN GASOLINE AND SYNERGISTIC EFFECT OF SULPHUR COMPOUNDS

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ABSTRACT

The high octane gasoline pool contains varying amounts of cracked naphthas as an important ingredient in formulating high octane lead free gasoline. The cracked naphthas are largely from Fluidised Catalytic Cracking (FCC) units and to lesser extend from thermal cracking units. While the role of olefinic unsaturation in gum formation during storage of gasoline has been extensively studied, there is little published work on contribution of individual olefin types in storage stability and gum formation tendency of gasoline containing these compound types.

In the present work we report our results on storage stability and gum formation tendency of different olefin types present in cracked naphthas through model compound matrix. It is found that cyclic olefins and cyclic diolefins are the most prolific gum formers. We have also studied the role of sulfur compounds present in the gasolines on gum formation tendency of olefins. While thiols enhance gum formation from all olefinic types, sulfides and disulfides interact depending on the structure of olefins. These can have either an accelerating, or inhibiting effect on gum formation.

INTRODUCTION

In order to meet the market demands and the octane requirement of gasoline, dependence on secondary conversion schemes has been increasing in recent years. The cracked naphthas going to gasoline pool are largely from Fluidised Catalytic Cracking (FCC) units and to lesser extent from thermal cracking units such as visbreaking and coking (Table 1 & 2).

These cracked naphthas are likely to be predominant in different types of olefinic hydrocarbon types due to difference in process conditions, which are likely to have different level of gum formation tendencies during storage and handling. Micro - constituents such as sulphur, nitrogen and copper enhance the gum formation.

Two classes of antioxidants viz. phenylene diamine (PDA) and alkylated phenols are being used in gasoline to counter the gum formation reactions. PDA type additives are favoured at high levels of olefininc unsaturation. [1]

In the present work reported here gum formation tendencies of the two different types of cracked naphthas (FCC and thermal cracking) vis-a-vis their composition have been studied as well as their relative effectiveness to the two types of antioxidants investigated. Synergistic effects of sulphur compounds with olefins in gasoline are also investigated.

EXPERIMENTAL

Materials

Typical FCC and visbroken naphthas boiling in gasoline range, were collected from operating refineries. For studies on pure compounds mixtures of analytical grade chemicals were used. 2-6 di-tert-butyl phenol and N,N'- di sec-butyl- p-phenylenediamine of >99% purity as representative phenolic and amine type of antioxidents were taken.

Procedure

Naphtha samples were analysed by standard test techniques [2]. Silica gel adsorption technique described elsewhere [3] was used to study the effect of olefininc structures on oxidation stability and additive response.

Combination of catalytic hydrogenation over Ni catalyst and capillary gas chromatography, high resolution mass spectrometery (KRATOS-MESSO with data station and DS-90 software) and nmr spectrometery (JEOL FX 100 FT, nmr) were used to generate useful compositional information on the naphthas particularly olefinic structures.

Oxidation stability studies were carried out by potential gum method, 4 hrs aging, ASTMD 873 [2]. For accurate additive doping, stock solutions in toluene were prepared.

DATA & DISCUSSION

Seven of the 12 Indian operating refineries have FCC units and five refineries have thermal cracker (Table - 1,2). The proportion of the FCC naphtha in gasoline pool ranges from 45 to 90% wt. While upto 8% of thermal cracking naphtha is accommodated in gasoline pool. Physico-chemical characterisation of typical FCC naphtha and thermal cracking naphthas are listed in table 3 and the boiling range depicted in Fig.1. These naphthas as such have very poor stability characteristics, However stability characteristics do not directly correlate with olifinic levels shown in table 4.

The aromatic content values in the cracked naphthas as determined by mass spectrometery range from 6.0 to 11.1% vol. The percentage of olefins in FCC naphthas are substantially higher (55.1 and 52.4 in FCC naphtha A and B respectively) as compared to thermally cracked naphthas (ranging from 32.1 to 35.9 vol). While FCC olefins are predominant in mono-olefins the olefins in thermally cracked naphthas contain relatively higher amount of olefins grouped as cyclo-olefins+diolefins+acctylenes (34.3 to 38.8% vol). Relatively higher proportions of Tri-olefins + cyclo-diolefins are present in thermally cracked naphthas.

Analysis of olefinic concentrate by ^1H nmr shows that thermal cracking naphthas contain relatively more <-olefins as compared to internal ones. For carrying out GLC analysis the olefinic concentrates were saturated over reduced Ni catalyst under hydrogen pressure. The saturation was controlled by Bromine number measurement. The data shows that while FCC naphthas are predominant in iso-olefins the thermal crackates are predominant in straight chain and cyclic structures.

Olefinic concentrates separated from typical FCC and visbroken Naphtha were blended in different proportions in two straight run naphthas having variation in hydrocarbon types. Potential gum determined by aging these blends by ASTM D 873 for 4 hrs. are plotted in figures 2 and 3 respectively. Potential gum generated in the blend containing visbreaking naphthas olefins are invariably higher than generated in the blend containing olefins from FCC Naphtha indicating that olefinic species present in visbreaking naphthas tend to generate more gum content as compared to olefins from FCC naphtha. Another interesting observation is that upto 10% olefin content, increase in potential gum content is slow, while above that the increase in potential gum is almost proportional to the percentage of olefins in blends containing visbreaking naphtha olefins. On the other hand the curve tends to flatten after certain percentage of olefins in case of blends containing FCC olefins.

Effect of additives 2,6, di-tert butylphenol (DTBP) and N,N'-di sec-butyl-p-phenylenediamine (BPDA) on the blends of olefins from FCC and visbreaking naphtha studied through ASTM D 873, 4 hrs aging taking 40 ppm additive doses is depicted in figure 4 and 5. While in case of FCC naphtha olefin blends, the effect of two additives is comparable, amine type of additive having marginally better effect at lower concentration, the effect of phenolic additive has certainly better effect on the blends containing olefins from visbreaking naphtha throughout the concentration of olefins studies.

The studies carried out on model olefin compounds in known sample matrix have helped in further understanding the gum formation tendencies of the olefinic structures. Different olefin compounds were taken in varying proportions in a mixture of equal volumes of n-heptane, methyl cyclohexane and toluene and potential gum (ASTM D 873 4, hrs) aging was determined. Figures 6 and 7 show the gum - formation tendencies of the different types of olefininc structures. With increase in molecular weight of straight chain alpha olefins, the gum forming tendency also increases. However, in case of iso-olefins the position of isomerisation also plays an important role. Iso-olefins containing alkyl radicals at different carbon atoms have higher gum forming tendency as compared to the straight chain olefins with substituents at single carbon atom such as 3,3-di-methyl butene. Cyclic olefins produce much more gum as compared to straight chain as well iso-olefins and the cyclo-diolefins such as 4-vinyl -1- cyclohexene (Figure 7) are the most prolific gum producers in motor gasoline.

Conjugated diolefins even in small concentration have been identified as one of most deleterious species for stability of fuels as they are known to initiate the gum formation reactions due to their high reactivity. The synergistic effect of cis-trans -2,3, - hexadiene in a concentration range of 1 to 3% concentration of 1-Octene and 2-methyl-2-butene in known sample matrix are plotted in figure 8. ; With 1-Octane, 1% conjugated diene have relatively lesser effect while 2 to 3% of the diolefin significantly increase the gum content. With 2-methyl-2 butene, even 1% diene have substantial effect indicating enhanced effect with iso-paraffins, predominantly present in FCC gasoline.

Synergistic Effect of Sulphur Compounds

Extensive studies have been carried out to investigate the role of sulphur compounds in sediment formation in gasoline. Thomson et at [4] reported that elemental sulphur and disulphide act as natural inhibitors while aliphatic mercaptons and sulphides had slight effect on oxidation stability. Gureev et al [5] reported that organic sulphur compounds including marcaptans react with peroxides to inhibit the gum formation. Frankenfeld et al [6] also reported similar observations.

In the present work effect of mercaptan sulphur, sulphides and disulphide with different types of olefins, straight chain, iso-and cyclic-olefins blended in a known sample matrix have been studied through ASTM D 873, 4 hrs. aging. Test data is presented in figure 9.

On addition of 100 ppm of 2-methyl-2- butylthiol to 1-Octene 30% vol. in the sample matrix, the total gum content has increased from 10.9 to 26.0 mg./100 ml. On the other hand 100 ppm of diethylsulphide and di-tert-butylsulphide the total gum content has decreased (8.3 and 4.8 mg/100 ml) indicating inhibiting effect of sulphide and disulphide.

With 2-methyl -2- butene there is increase in total potential gum on addition of all the three types of sulphur compounds studied, with the thiol, increases is maximum [23,8 to 156,5 mg/100 ml].

Cyclic - olefins have higher gum forming tendencies as compared to straight chain and iso-olefins and the presence of sulphur compounds including sulphide and disulphide sulphur considerably enhance the gum forming tendencies. ; Combination of cyclo-hexene with 2-methyl -2- butyl thiol have produced maximum gum contents (304.8 mg/100 ml) Increase in gum content is relatively lower in presence of sulphide and disulphide.

Sulphur compounds produce relatively more insoluble gum in presence of iso-olefins and cyclo-olefins as compared to their blends with straight chain olefins. The ratio of insoluble to soluble gum in case of 1-octene and the thiol is 0.48 while these ratios are 0.93 and 0.96 respectively when thiol is combined with 2-methyl -2 butene and cyclohexene respectively.

CONCLUSION

Compositional studies of FCC and thermal cracking naphthas show that FCC naphthas are predominant in iso-olefins and n-olefins and cyclo - olefins are present in lower extent while vis breaking naphthas are rich in n-olefins and contain relatively more cyclic olefins as well cyclo-diolefins.

The olefins separated from visbreaking naphthas are found to have higher gum formation tendencies.

The pure compound studies show that iso-olefins have higher gum formation tendencies as compared to n-olefins and cyclic compounds have still higher gum forming tendencies. Diens and particularly cyclo diolefins are the most prolific gum producers.

The additive response is olefinic composition dependent and not on olefinic level dependent. In thermal cracking naphtha, phenolic antioxidants are favored.

There is a synergism in sulphur compounds and olefinic types in gum formation tendency. While thiols enhance the gum formation tendencies with all olefinic types, sulphide and disulphide inhibit the gum formation in n-olefins and enhance gum formation in iso-and cyclic olefins to a lesser extent as compared to thiols.

Acknowledgment

Authors are thankful to Dr. T S R Prasada Rao, Director, Indian Institute of Petroleum for permission to present this paper in 5th International Conference on Stability and Handling of Liquid Fuels.

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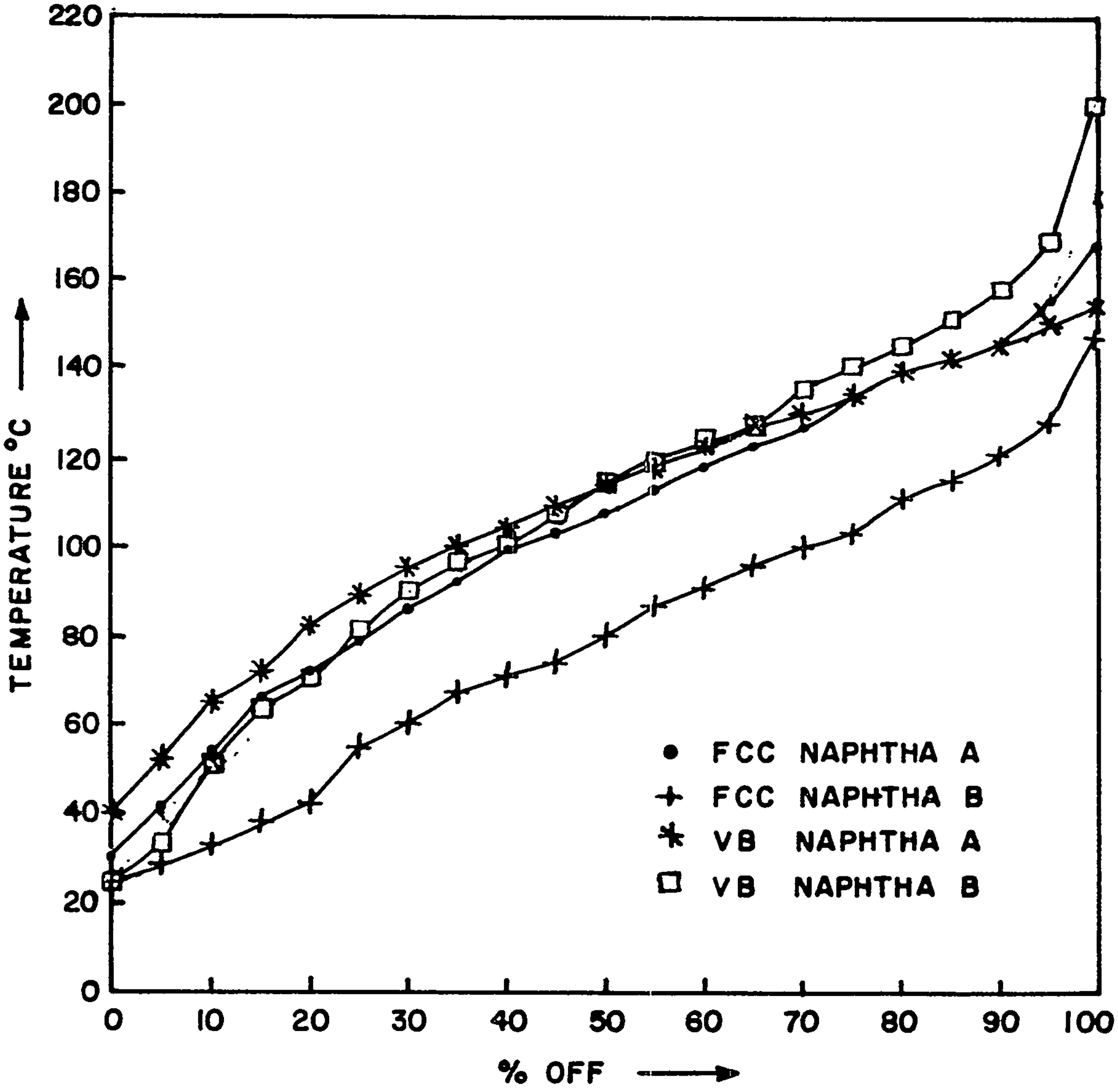

FIG. I : SIMULATED DISTILLATION CURVES OF CRACKED NAPHTHAS.

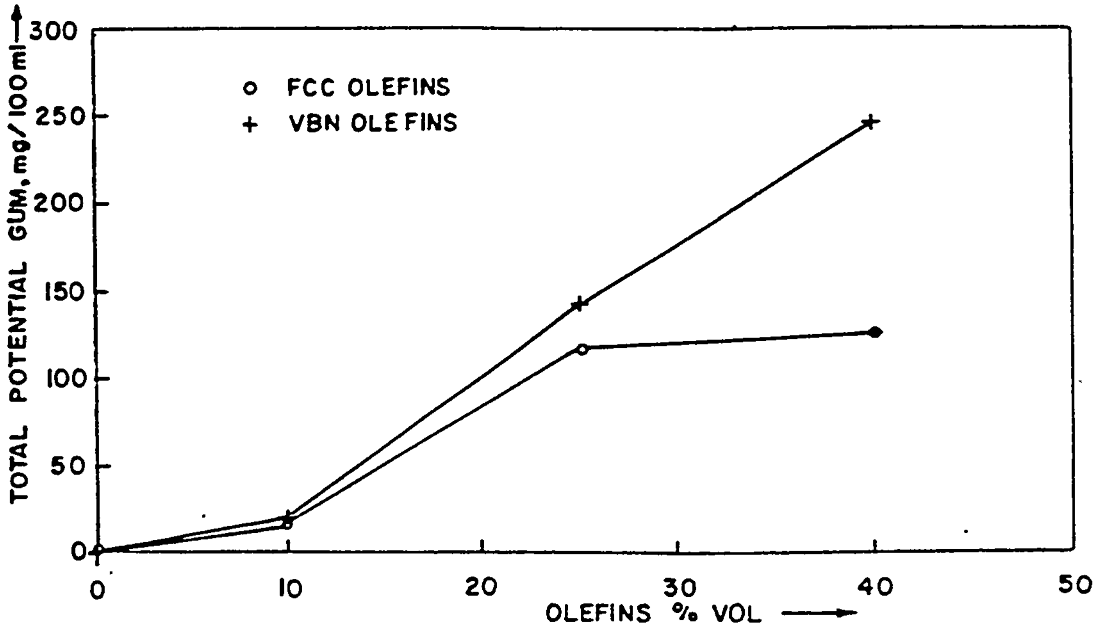

FIG. 2 - TOTAL POTENTIAL GUM Vs % OLEFINS IN STRAIGHT RUN NAPHTHA A

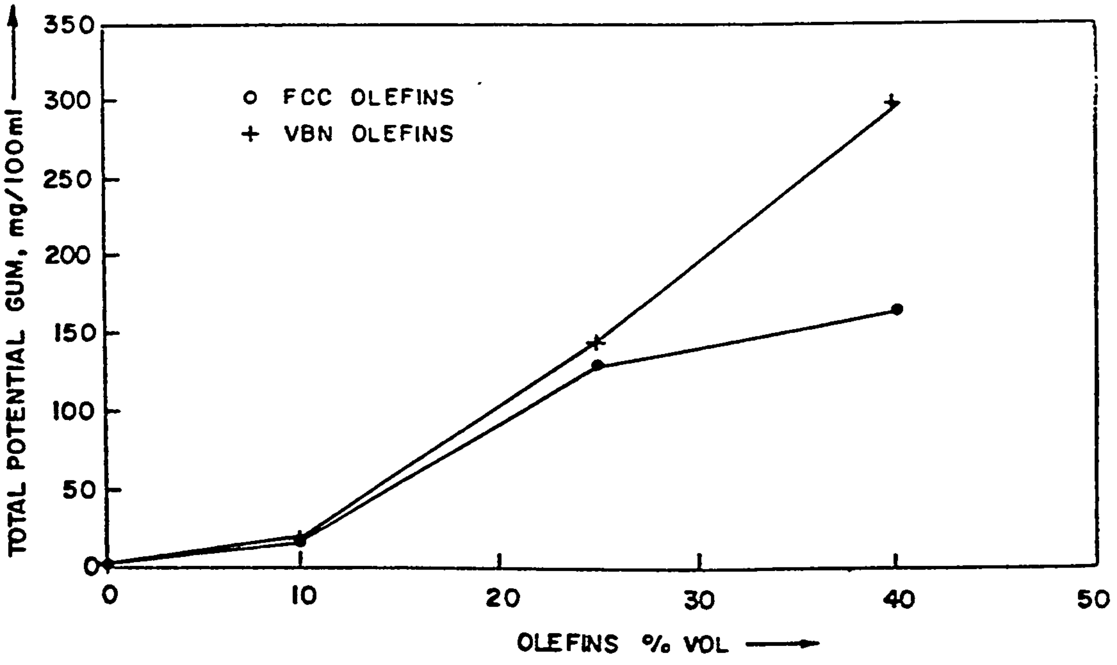

FIG. 3 - TOTAL POTENTIAL GUM Vs % OLEFINS IN STRAIGHT RUN NAPHTHA B.

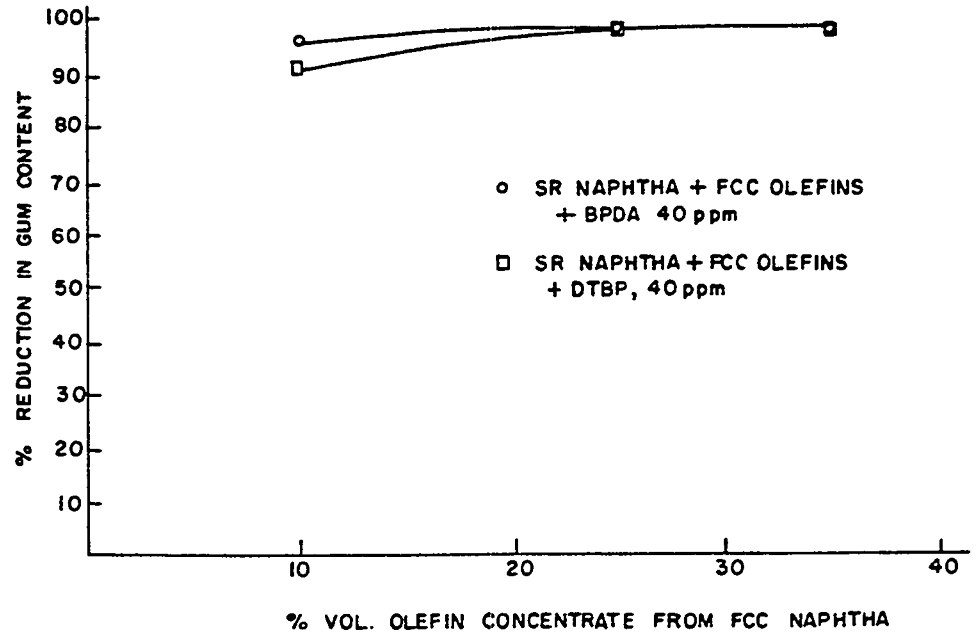

FIG.. 4 : EFFECT OF ADDITIVES ON BLENDS OF OLEFIN CONCENTRATE FROM FCC NAPHTHA WITH STRAIGHT RUN NAPHTHA B

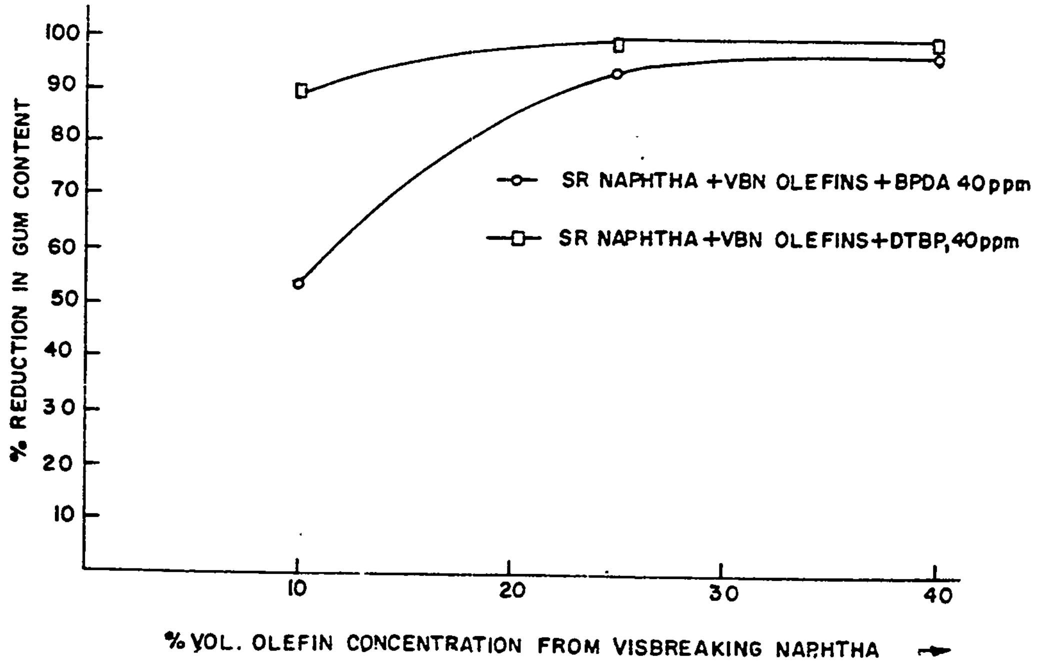

FIG. 5 : EFFECT OF ADDITIVES ON BLENDS OF OLEFIN CONCENTRATE FROM VISBREAKING NAPHTHA WITH STRAIGHT RUN NAPHTHA B

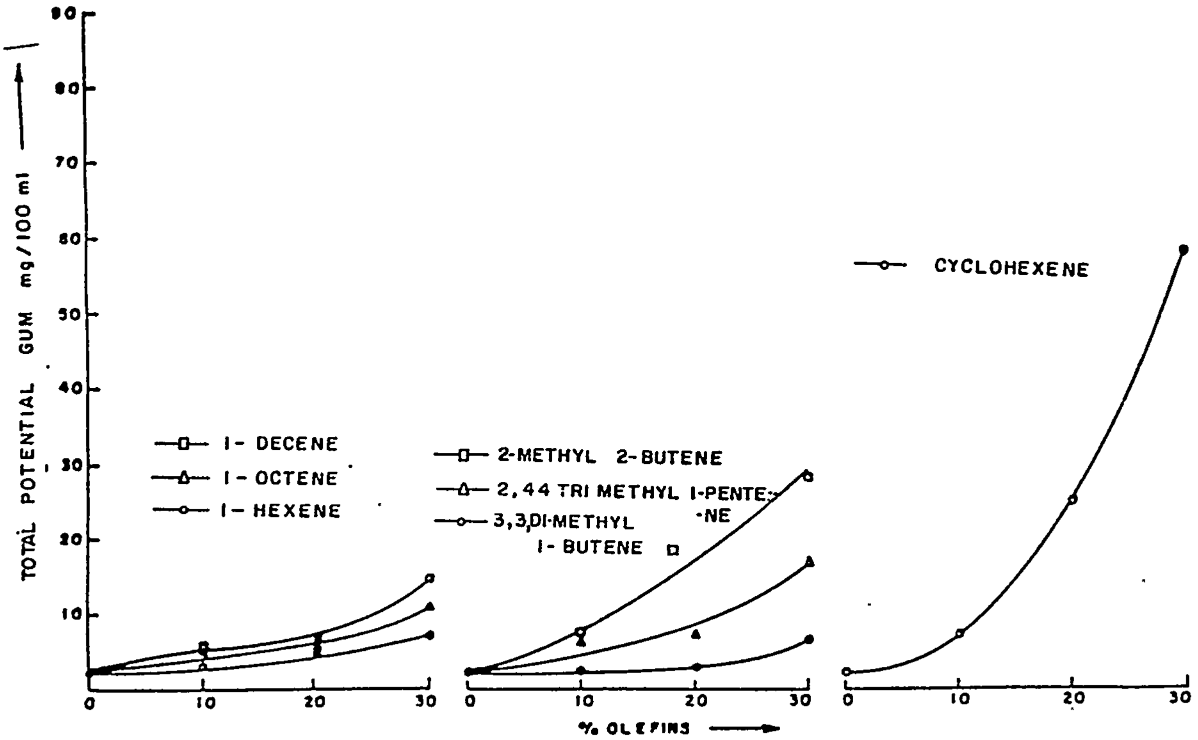

FIG. 6 - % OLEFINS IN KNOWN SAMPLE MATRIX Vs POTENTIAL GUM (ASTM D873, 4 Hrs. AGING)

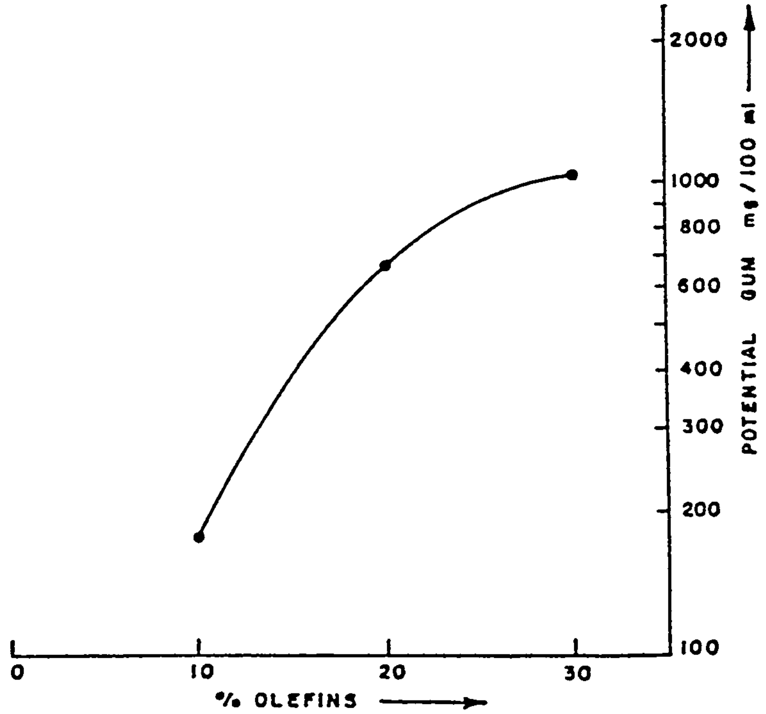

FIG. 7 — % OLEFINS IN KNOWN SAMPLE MATRIX Vs POTENTIAL GUM (ASTM D873, 4 Hrs. AGING) 4 - VINYL-1-CYCLOHEXENE.

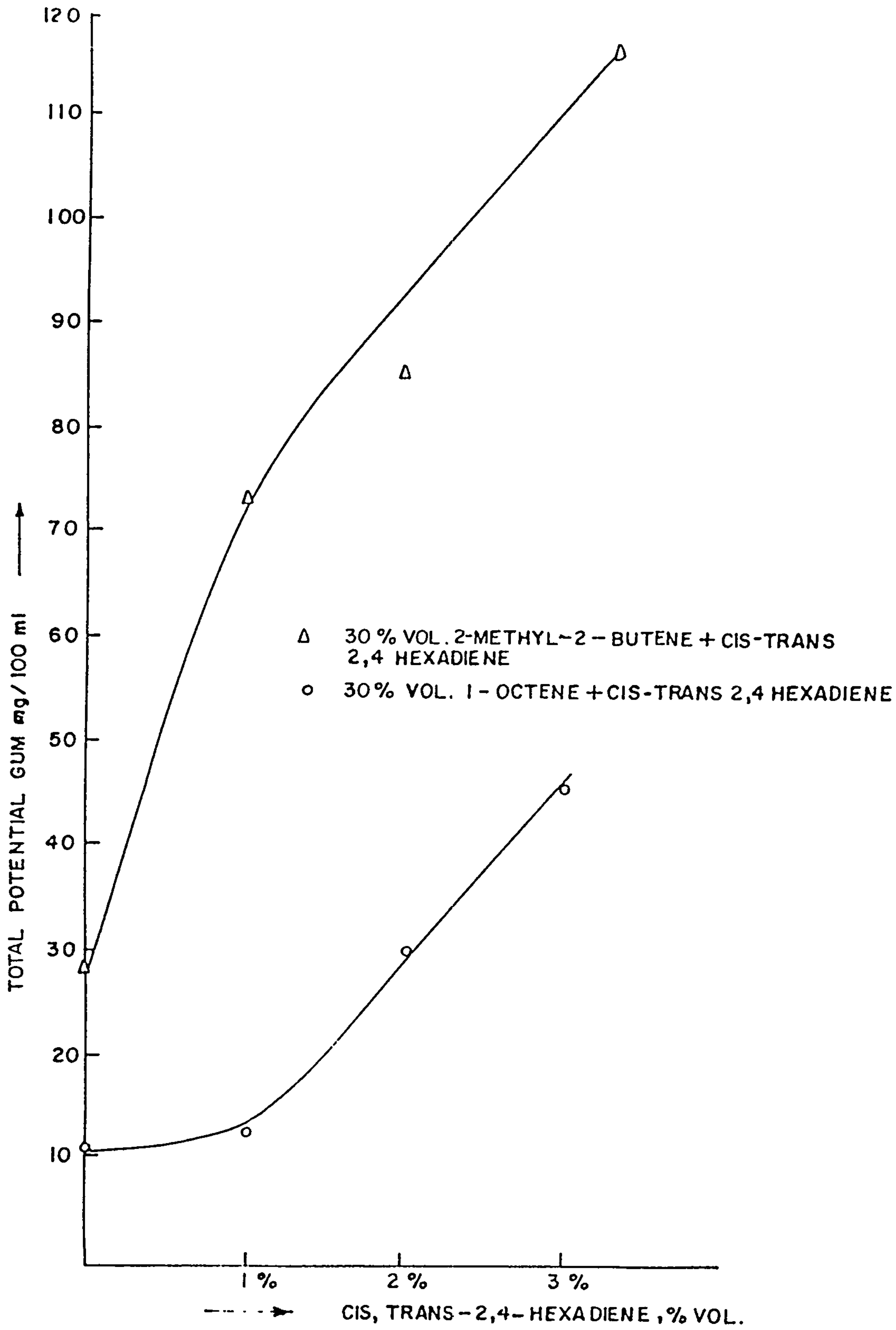

FIG. 8 : SYNERGISTIC EFFECT OF DIENES ON BRANCHED & STRAIGHT CHAIN OLEFINS : PERCENT DIENE IN STRAIGHT & BRANCHED OLEFINS VS PER OXIDE NUMBER

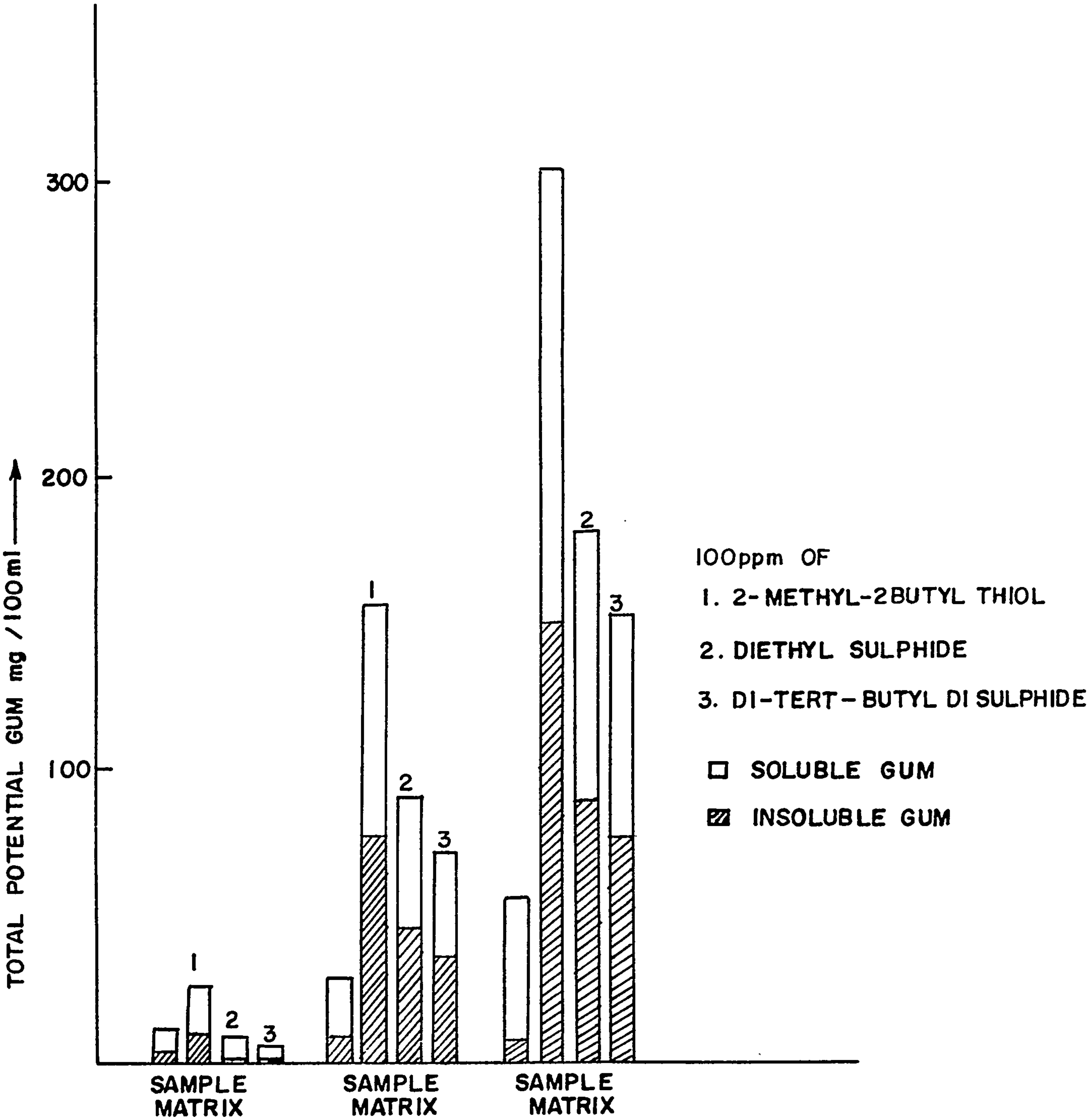

FIG. 9: SYNERGISTIC EFFECT OF SULPHUR COMPOUNDS & OLEFINS POTENTIAL GUM (ASTM D 873, 4 HRS. AGING)

TABLE 1

GASOLINE BLENDING COMPONENTS AND COMPOSITION, WT. %
REFINERIES WITH FCC

Sl. No.	COMPONENTS	BPCL	CRL	GUJARAT	HPCL (B)	HPCL (V)	MATHURA	MRL
1.	SR Naphtha	15-23	35	15-20	20	x	17-24	5-10
2.	VB Naphtha	-	-	2-4	-	-	3-6	0-5
3.	FCC Gasoline	60-80	65	45-52	80	x	70-80	80-90
4.	GAP R/S	-	-	8-10	-	-	-	-
5.	GOP R/S	-	-	15-18	-	-	-	-
6.	Reformate	-	-	1-2	-	-	-	-
7.	LAN	-	-	-	-	-	-	10(max)

x These components are blended in Gasoline

GAP RS : Gujarat Aromatic Project Return Stream

GOP RS : Gujarat Olefin Project Return Stream

LAN : Light Aromatic Naphtha.

TABLE - 2

GASOLINE BLENDING COMPONENTS AND COMPOSITION, WT. % OTHER REFINERIES WITH FCC

Sl. No.	Components	Barauni	Gauhati	AOD	BRPL*	HALDIA
1.	SR Naphtha	76	45	N.A.	-	1-8
2.	Heavy Naphtha	-	45	-	-	-
3.	Coker Gasoline	-	8	-	-	-
4.	LAN	24	2	-	-	-
5.	Reformate	-	-	-	-	89-93
6.	VB Naphtha	-	-	-	-	3-10

* No Gasoline Produce

LAN : Light Aromatic Extract

VB Naphtha : Visbreaking Naphtha

TABLE - 3

PHYSICO-CHEMICAL CHARACTERISTICS OF CRACKED NAPHTHA SAMPLES

Characteristics	FCC Naphtha-A	FCC Naphtha-B	VB Naphtha-A	VB Naphtha-B
Density, kg/ltr at 15° C	0.7143	0.7067	0.7273	0.7240
H^2S/Mercaptan Sulphur,ppm	ND/269.0	ND/0.8	227.0/3980.0	ND/3.3
Total Sulphur, ppm/%wt.*	674.4	328.0	0.80*	0.53*
Nitrogen Basic/ Total,ppm	4.3/15.8	0.8/7.3	2.9/9.6	1.9/10.7
Peroxide Number, ppm	4.8	5.0	1.0	2.7
Thiophenols,ppm	7.0	ND	32.0	ND
Copper,ppb	<10	<10	<10	<10
Dienes % wt.	2.0	1.6	0.9	1.0
Induction Period Minutes	104	22	39	108
Existant gum mg/100 ml	5.8	78.3	3.4	6.8
Total Potential gum mg/100 ml (ASTM D 873 4 Hrs.)	721.1	364.2	719.3	517.8

TABLE - 4

MASS SPECTROSCOPY ANALYSIS OF CRACKED NAPHTHAS

% Vol	FCC Naphtha (A)	FCC Naphtha (B)	VB Naphtha (A)	VB Naphtha (B)
Paraffins	26.2	32.2	42.9	46.1
Monocyclo-Paraffins	7.2	9.0	17.8	11.1
Dicyclo-Paraffins	0.4	0.1	0.0	0.9
Mono-Olefins	40.0	37.2	18.9	21.1
Cyclo-Olefins+ Diolefins+Acetylenes	14.1	15.0	11.0	13.8
Triolefins+ Cyclo-diolefins	1.0	0.2	2.2	1.0
Benzenes	11.1	6.3	7.2	6.0
Olefin Distribution,%Vol of total Olefin				
Mono-olefins	72.6	71.0	58.9	58.8
Cyclo-olefins+ Diolefins+ Acetylenes	25.6	28.6	34.3	38.8
Tri-olefins+ Cyclo-diolefins	1.8	0.4	6.8	2.8
Total				
Paraffins	33.8	41.3	60.7	58.1
Oleffins	55.1	52.4	32.1	35.9
Aromatics	11.1	6.3	7.2	6.0

TABLE - 5

NMR SPECTROSCOPY AND GLC ANALYSIS DATA OF CRACKED NAPHTHAS

% Vol	FCC Naphtha (A)	FCC Naphtha (B)	VB Naphtha (A)	VB Naphtha (B)
Ratio of Alpha to internal Olefins (NMR)	0.73	0.75	1.30	1.33
Analysis of Saturated Olefins (Separated By Column Chromatography) By GLC				
i-Paraffins	49.8	50.3	36.1	37.3
n-Paraffins	24.0	21.9	30.0	31.3
Naphthenes	24.3	27.7	30.1	22.2
Unknown +C9	1.9	0.1	2.8	9.2

5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam. The Netherlands
October 3-7. 1994

INTERCOMPATIBILITY OF RESIDUAL FUEL BLENDS

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ABSTRACT

It is a well known fact that two fuel oils. thermally stable by themselves, may produce sludge of asphaltenic nature when blended together. Settling out of asphaltenes from the fuel medium will result in strainer and burner plugging, causing serious operational difficulties in industrial and marine fuel systems.

It was the aim of the present study to establish criteria for the phenomenon of incompatibility. The parameters which influence thermal stability of the blend were assessed. and an attempt was made to predict possible separation of asphaltens from fuel oil mixtures.

Fuel oils originating from Brasil, France, Honk-Kong, Greece, U.S.A., Japan as well as locally (Israel) produced residual fuels were mixed. Thermal stability of the blend was determined by ASTM D-4740 method. In some cases, total sediment was measured by ASTM D-4870. Blends of fuels were stored at 50°C to assess the effect of elevated temperatures on thermal stability.

It was found that most of the blends were compatible though composed of fuels originating from different refineries. Density, Pour Point, Sulfur content and Xylene Number served as useful tools for predicting the thermal stability of residual fuel blends.

ACKNOWLEDGMENTS

The authors acknowledge the funding support of the Israel Fuel Corporations: Delek, Paz, Sonol, The Israel Refineries, The Israel Electric Corporation, Zim Shipping Company and Ministry of Absorption.

INTRODUCTION

Incompatibility is a tendency to form sediment after blending one residual fuel with another. This is believed to be one of the main causes for malfunctioning of utilities operated by residual fuels[1].

The phenomenon has been observed at late thirties[2-4]. Studies demonstrated that dry sludge, disintegrating from a blend of thermally stable fuel oils, is composed of insoluble material called asphaltene[5-9].

Almost every fuel batch is a blend, formed on its way from the producer's tank to the end user. Refineries blend residues to achieve a specified viscosity. Additional mixing occurs in tank farms. Residual fuel, reaching its final destination, is mixed with oil remaining in storage from the previous delivery, which in itself is a blend.

Incompatibility is manifested in field operation by:
a. loss of storage space caused by tank sludge formation
b. reduced efficiency of heat transfer from coils in storage tanks
c. filters clogging and plugging of transfer lines
d. pumps seizure
e. burners plugging
f. incomplete burning and soot formation.

Conventional residual fuel oil specifications and test methods were found to be inadequate to predict or prevent problems due to the incompatibility in blends. In some cases, tendency to form sediment can be foreseen by mixing the fuels in a laboratory. This solution is not practical because blend components are not always available in time.

In response to the need of improved means for predicting stability problems arising from storage and handling of residual fuel oils, Griffith and Siegmund[10] proposed the following equation:

1. $\mathrm{BMCI} - \mathrm{XE} = K$ For thermally stable product $7 \le K \le 14$

BMCI = Bureau of Mines Correlation Index[10].
XE = Xylene Number[10].

Griffith and Siegmund studied the stability of cracked residues mixed with various flux stocks. It was decided to check whether the mathematical formula suggested in their study is applicable to a blend of finished products.

OBJECTIVES

The objectives of the present study were:

1. To estimate whether the incompatibility problem is widespread locally .
2. To establish whether the Griffith and Siegmund criterion for compatibility is a workable assumption for blends of finished products.

MATERIAL AND METHODS

Fuel oil samples under study, were supplied by a local refinery, storage facilities, the Electrical Corporation and a shipping company.

Each sample was subjected to a number of tests summerized in Tables 1-3.

One to one mixtures were prepared from samples which were thermally stable. The blending was performed as per diagram 1.

This system allowed to mix every sample with every sample. The stability was determined 24 hours after preparation of the blends. Some of the samples were maintained at 50°C in order to follow the stability changes which occur with

time. The properties of the blend were calculated by suitable equations. The average boiling point was determined by use of correlations[11]. BMCI and Griffith constants were calculated as suggested by reference 10.

RESULTS AND DISCUSSION

The results are summerized in Tables 1-3 and Fig. 2-6.

105 blends have been prepared.

27 were incompatible.

Immediate flocculation of asphaltenes occured from every blend comprising fuel oil sample 1 (Table 1). Most blends comprising samples 3 and 5 disintegrated after few days storage in 50°C (Fig. 6).

Residual fuels 6-16 caused precipitation of sludge from some fuels and were not objectionable to others (Table 2).

Properties of fuel oils that were incompatible with their counterparts can be seen in Fig. 2-5. They were characterized by density under 0.9700 gr/cm^3, low sulfur content and high pour point. Fuels 3, 5, 6 and 9 with densities higher than 0.9780 gr/cm^3 had Xylene Numbers above 67 as a common feature. Asphaltene content could not serve as a useful tool for detection of residual fuels which carry a destructive potential (Fig. 5).

Fuel oil is a colloidal system in which macromolecules (asphaltenes) are in equilibrium with a dispersing medium (maltenes)[12]. A colloidal system is maintained in balance by two forces[13]:

1. a charge producing an electrostatic repulsion of macromolecules.
2. solubilizing efficiency of the medium.

In complex organic solutions precipitation of solute from solvent will be prevented if the difference between their solubility parameters will be under 3[14]. Mixing two fuel oils, considerably dissimilar in density and pour point, may change drastically the solubility parameter of the new dispersing medium causing precipitation of asphaltenes from the blend.

As indicated by Tables 1 and 2, all of the low density fuel oils were produced from low sulfur (LS) paraffinic crudes. Inoffensive fuel oils were rich in sulfur (HS) and aromatics (Table 3).

Since LS are stored separately from HS residual fuels, it was interesting to see whether blending of fuels with comparable densities and sulfur content can bring about precipitation of asphaltenes. Indeed, disintegration has been observed while blendind fuels 3:6; 5:12; 5:13. The deposition of sludge was time dependent. In all cases at least one of the unstable blend constituents had Xylene Number above 67.

BMCI is a measure of aromaticity of the dispersing medium. XE is a good estimate for predisposition of asphaltenes in residual fuels to form aggregates. The higher the BMCI the more aromatic is the dispersing medium. The lower XE the lesser is the asphaltenes tendency for association. In their paper, Griffith and Siegmund suggest that the BMCI of a blend is an average of its individual components. XE of a blend is calculated as indicated in reference 10. It is evident that the higher the difference between BMCI and XE the more stable will be the blend. Therefore, on structural considerations the use of Griffith and Siegmund mathematical formula for estimation of compatibility of blend constituents can be valid.

The Griffith constants were calculated for 105 blends. The results are demonstrated in Fig. 7. The analysis of the data reveals that Griffith constant is not a suitable estimate for a differentiation between thermally stable and unstable blends. Some incompatible mixtures had constants as low as 1. Others, which disintegrated immediately, had a constant as high as 23. Many compatible blends had constants in a vicinity of 7.

Looking at those results one must conclude that the behaviour of fuel oils in a blend is not governed solely by the character of a dispersing medium or insolubles tendency to aggregate. There are other factors not yet studied that should be taken into consideration.

CONCLUSIONS

1. The phenomenon of incompatibility exists.
2. Disintegration of asphaltenes from a blend can be immediate or time dependent.
3. Mixing of aromatic residual fuels with paraffinic counterparts can produce sludge.
4. Some fuel oils with compatible densities can form thermaly unstable blends as well.
5. In all blends which exhibited time dependent incompatibility, Xylene Number of at least one constituent was above 67.
6. Fuel oils with a low sulfur content were usually more offensive than their sulfur rich counterparts.
7. The quantity of asphaltenes was not an effective tool for discrimination of fuels with a damage potential.
8. The equation suggested by Griffith and Siegmund could not distinguish stable from potentially unstable blends.

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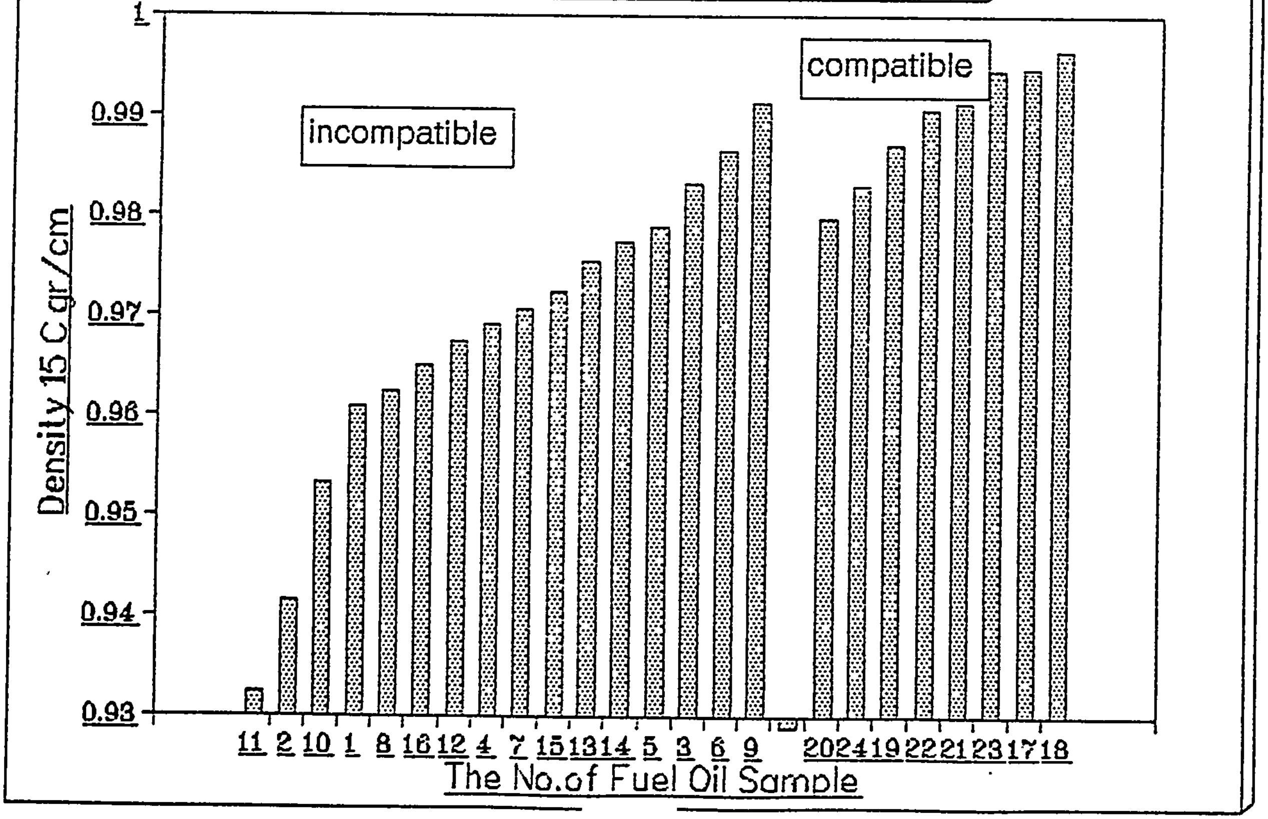
FIG. 1: The Blending Matrix

	1	2	3	4	5	6	7	8	9	10
1	////									
2	////	////								
3	////	////	////							
4	////	////	////	////						
5	////	////	////	////	////					
6	////	////	////	////	////	////				
7	////	////	////	////	////	////	////			
8	////	////	////	////	////	////	////	////		
9	////	////	////	////	////	////	////	////	////	
10	////	////	////	////	////	////	////	////	////	////

FIG.2:Density of Fuel Oils
Compatible & Incompatible Blends



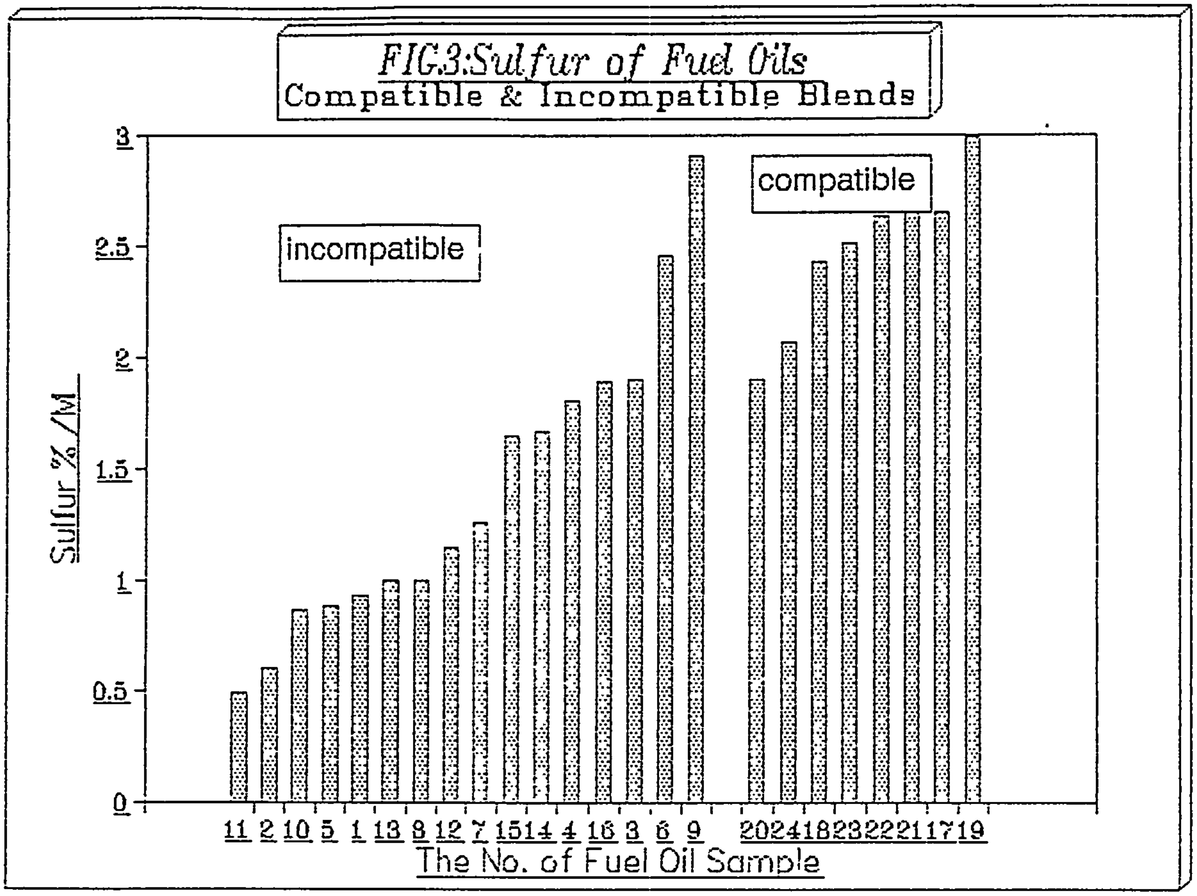


FIG.3:Sulfur of Fuel Oils
Compatible & Incompatible Blends

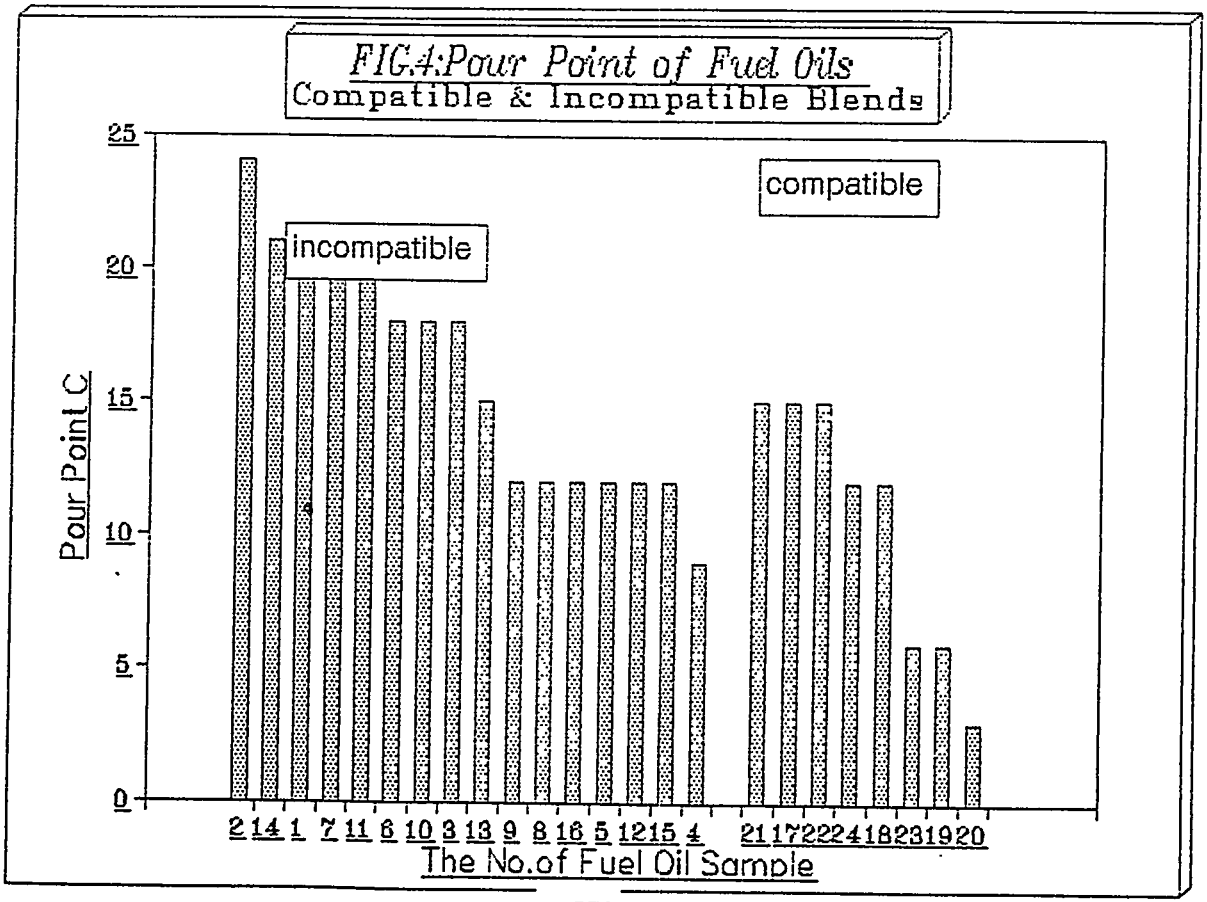


FIG.4:Pour Point of Fuel Oils
Compatible & Incompatible Blends

FIG.5: Asphaltenes Content of Fuel Oils

Compatible & Incompatible Blends

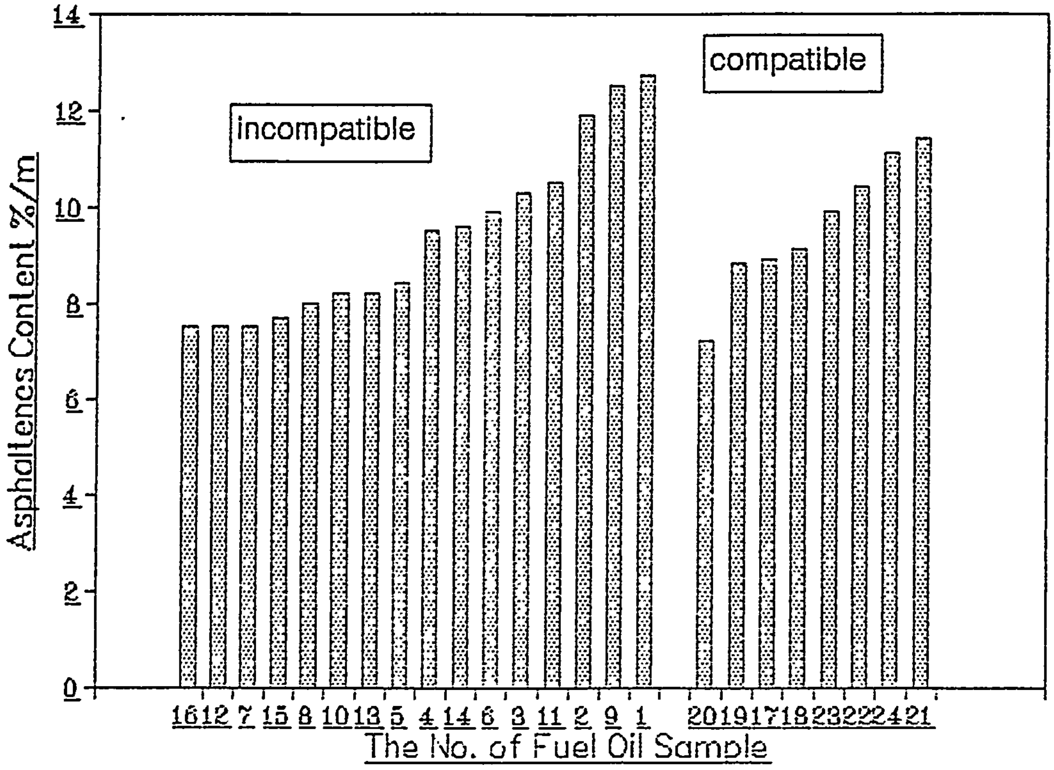
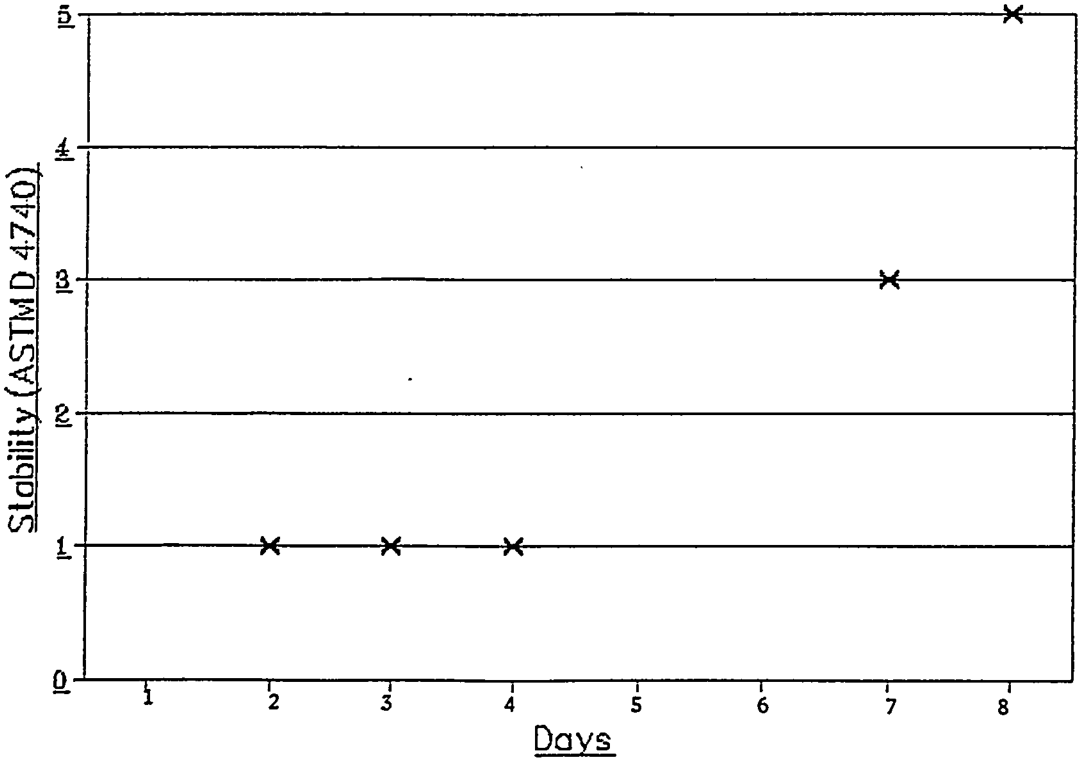


FIG.6: Variation of Stability with Time

Blend of Fuel Oils No.5 & 6



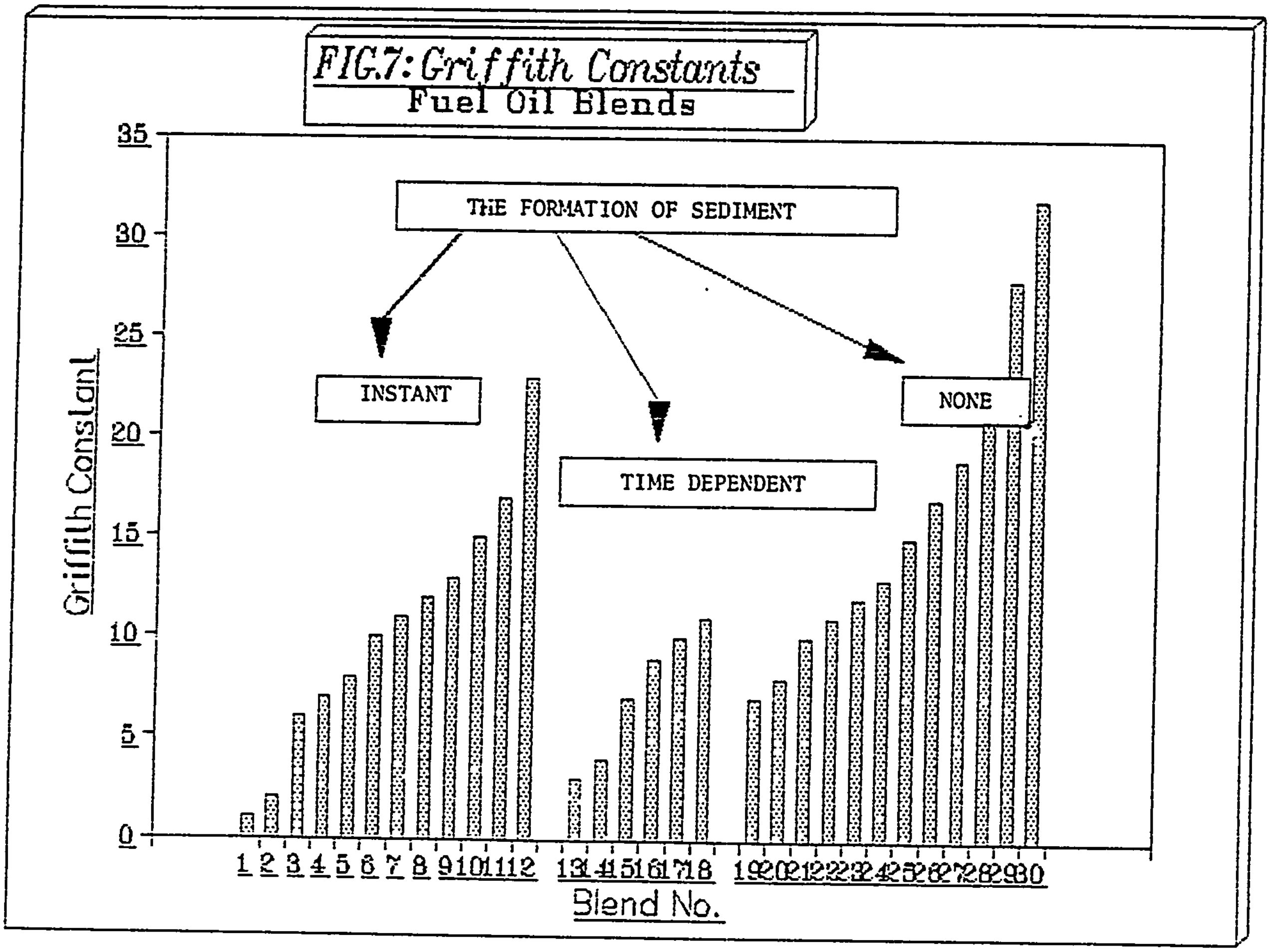


FIG.7: Griffith Constants
Fuel Oil Blends

Table 1: Properties of fuel oils that formed unstable blends

PROPERTY	Always	In most cases			
	1	2	3	4	5
1. Density, 15°C, gr/cm^3	0.9607	0.9414	0.9832	0.9690	0.9789
2. Pour Point, °C	+21	+24	+18	+9	+12
3. Viscosity, 50°C, cst	347.4	567.0	317.9	393.5	164.6
4. Asphaltene content, % m	12.7	11.9	10.3	9.5	8.4
5. Sulfur content, % m	0.93	0.60	1.90	1.80	0.88
6. BMCI	62	53	73	66	71
7. Xylene number	67	37	72	62	72
8. Griffith Constant	-5	16	1	4	-1

Table 2: Properties of fuel oils that formed unstable blends in less than 30% of cases

PROPERTY	6	7	8	9
1. Density, 15°C, gr/cm^3	0.9864	0.9705	0.9624	0.9911
2. Pour Point, °C	+18	+21	+12	+12
3. Viscosity, 50°C, cst	414.7	497	375.1	493.9
4. Asphaltene content, % m	9.9	7.5	8.0	12.5
5. Sulfur content, % m	2.45	1.26	0.99	2.9
6. BMCI	75	67	63	77
7. Xylene number	67	47	37	70
8. Griffith Constant	8	20	26	7

PROPERTY	10	11	12	13
1. Density, 15°C, gr/cm^3	0.9533	0.9323	0.9673	0.9754
2. Pour Point, °C	+18	+21	+12	+15
3. Viscosity, 50°C, cst	275.1	573.2	373.6	431.2
4. Asphaltene content, % m	8.2	10.5	7.5	8.2
5. Sulfur content, % m	0.87	0.49	1.14	0.99
6. BMCI	59	49	66	69
7. Xylene number	42	25	52	52
8. Griffith Constant	16	24	14	17

Table 2: Properties of fuel oils that formed unstable blends in less than 30% of cases

PROPERTY	14	15	16
1. Density, 15°C, gr/cm^3	0.9774	0.9723	0.9650
2. Pour Point, °C	+21	+12	+12
3. Viscosity, 50°C, cst	456.1	184.6	172.1
4. Asphaltene content, % m	9.6	7.7	7.5
5. Sulfur content, % m	1.66	1.65	1.89
6. BMCI	70	68	64
7. Xylene number	52	52	52
8. Griffith Constant	18	16	12

Table 3: Properties of fuel oils that always formed stable blends

PROPERTY	17	18	19	20	21	22	23	24
1. Density, 15°C, gr/cm^3	0.9946	0.9965	0.9869	0.9797	0.9912	0.9904	0.9943	0.9830
2. Pour Point, °C	+15	+12	+6	+3	+15	+15	+6	+12
3. Viscosity, 50°C, cst	425.7	492.7	398.5	171.9	422.2	400.0	367.2	483.8
4. Asphaltene content, % m	8.9	9.1	8.78	7.2	11.4	10.4	9.9	11.1
5. Sulfur content, % m	2.65	2.43	2.98	1.9	2.65	2.63	2.51	2.06
6. BMCI	78	79	75	71	77	76	78	73
7. Xylene number	55	57	57	47	62	62	62	57
8. Griffith Constant	23	22	18	24	15	14	16	16

5th International Conference on
Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7, 1994

COMPATIBILITY AND STABILITY OF RESIDUAL FUELS

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"Much of the heavy viscous so-called "bunker" fuel oil of the present day contains residual products from cracking operations. This material varies widely in character with the nature of the crude oil from which it is derived and the method and degree of cracking to which it has been submitted. Cracked residues are not always completely soluble in petroleum distillates or uncracked residues, thus complicating the problem of preparing merchantable blends. They usually contain solid or semisolid particles which are not objectionable if dispersed, but which sometimes agglomerate in the form of troublesome sludges or deposits if the fuels are subjected to unfavorable conditions of storage and use. The solubility problem at one time was most serious, when it was frequently necessary to blend cracked residues with paraffinic gas oils. Difficulties of this particular kind are less frequent today, since the oil industry is plentifully supplied with cracked distillates for blending purposes. However, the solubility problem in lesser degrees still exists, even though it may not be recognized as such. The problem of minimizing the precipitation of residues and sludges is still frequently troublesome, and even the best informed technologists are not always able to predict whether or not a given oil will cause difficulty."

While I fully concur with these words and concepts, I must admit I did not write them. They were published in 1938, in a paper which described the Exxon Sediment by Hot Filtration (SHF) Test.

There are a number of other papers, published about 50 years ago which describe procedures for predicting whether two fuel components will be compatible, i.e., will produce a stable fuel when blended. The actual concepts of fuel composition, stability and compatibility of which I speak today are relatively unchanged from these very early papers. Among the most thorough and influential papers on the subject in my opinion, were those published by Shell and Exxon.

Throughout out this paper we will use the terms stability and compatibility, which we define as:

Stability - A stable fuel is one which contains a minimum amount of sediment when produced. On storage sediment level and other properties, such as viscosity do not change significantly over time. Sediment level is currently most widely measured by the IP 375 and/or IP 390 Sediment Test. Stable fuels have sediment levels of ≤ 0.1 % wt.. This test is actually a measure of fuel cleanliness.

Compatibility - Refers to the condition of a blend of two fuel components. Two fuels, each with low sediment content are compatible if the sediment of the resultant blend is low. If on the other hand the sediment level of the blend is significantly higher than the individual components, (>> 0.1%) the fuels are incompatible. The blended fuel itself would be described as unstable.

We believe these definitions are generally accepted in the industry.

Residual fuels are extremely complex products both physically and chemically. The most widely held view of composition is one in which very large asphaltene molecules are colloidally dispersed in an oil phase (maltenes). The asphaltene molecules have a tendency to agglomerate, and this propensity is a function of the oil phase composition. In stable fuels the oil phase prevents the asphaltene micelles from agglomerating and precipating as sludge. This is related to the oil phase aromaticity and solvency. In order to be stable the oil continuous phase of a fuel must have a minimum level of aromaticity to keep the asphaltenes in suspension. The asphaltenes themselves vary in the amount of aromaticity required to prevent their agglomeration. This requirement is related to the origin of the asphaltenes. It is again well documented that asphaltenes in thermally cracked or visbroken residues have a higher aromaticity requirement than the asphaltenes from a straight run residue. As we have seen it was known as far back as 1938 that diluents such as cat cracked gas oil, are excellent cutter stocks for the production of "stable" residual fuels.

In an Exxon Research paper by M. G. Griffith and C. W. Siegmund the available solubility of the "solvent" portion of fuel oil is defined by BMCI (Bureau of Minis Correlation Index) and the required aromaticity or "solubility" of the asphaltene portion is measured by "Toluene Equivalence" (TE). Shell refers to these parameters as Peptizing Power (Po) and Flocculation Tendency (FT) respectively. While the terminology in these papers is different the fundamental concepts and experimental methods are in fact very similar. Although these papers and their respective test methods have been available for years, they do not appear to have been widely used. We believe this is due to the experimental difficulty involved in the measurement of these parameters.

We have succeeded in greatly simplifying the procedure to calculate BMCI and determine TE.

The attached figure is a plot of a family of curves which relates BMCI to fuel viscosity and density. We are indebted to Mr. R. H. Thornton of Exxon Co. International for making this chart available to us. We have developed a simple algorithm which enables the calculation of BMCI from parameters routinely reported in a fuel analysis, namely CCAI and viscosity in centistokes at 50 ° C.

$$\text{BMCI} = (0.5074 - 0.0101 \log V_{50})\,\text{CCAI} + 15.36 \log V_{50} - 374.08$$

where V_{50} = kinematic viscosity at 50° C (CST)

Toluene Equivalence (TE) is the minimum percentage of toluene, in a toluene/heptane blend that will just keep the asphaltenes of a fuel in "solution". As originally described by Siegmund and Griffith, the determination of TE required a series of ten individual blends of the fuel with toluene/heptane mixtures varying form 0% toluene to 100% toluene (at 10% intervals) and 1 g fuel, followed by a spot test on the blend. The whole procedure is then repeated again with five individual blends of 1g fuel and Toluene/Heptane mixtures at 2% intervals in the critical ten percentile range for final evaluation of T.E.

This requires, multiple sample weighings and multiple solvent blends. A TE by this procedure requires approximately 2 -3 hours. The Shell experimental procedure, we believe, is even more time consuming. The latter also requires multiple blends and microscopic examination of the test solution to determine end point.

We have succeeded in converting the TE analysis described in the Griffith and Siegmund paper to a titration method. In brief the determination is conducted as follows:

(1) Weigh 1 gm ± 0.1 g fuel into a 100 ml beaker. The fuel weight is not very critical to the success of the procedure.

(2) Completely dissolve the fuel sample in 10 ml of toluene The 10 ml is dispensed with an automatic buret, with 0.1 ml accuracy. It is also convenient to use a magnetic stirrer for this and subsequent solvent additions.

(3) While stirring add 5 ml increments of heptane. The 5 ml is dispensed with a second automatic buret.

(4) After each increment of heptane, place a drop of the solution on absorbent filter paper and examine the spot. Because the sample is already in solution, the mixing is very rapid and the test drop can be withdrawn within seconds of the heptane additions.

(5) Toluene Equivalence (TE) is the point between a uniform spot and a spot with a dirty inside ring. This is the same type spot as seen in the ASTM Spot Test. In this method the % toluene is 100% initially (i.e., 100 TE), and is progressively reduced to 67TE, 50TE, 40TE, 33TE, 29TE......

This procedure is actually a bracketing method. We have generally found bracketing, according to this procedure, adequate for most purposes. However, if greater accuracy is desired, the procedure can be repeated using smaller increments of heptane (e.g., 2 ml). This incremental addition gives brackets as follows, 83TE, 71TE, 63TE, 55TE, 50TE, 45TE.........

Griffith and Siegmund concluded that for fuels to be stable BMCI must exceed TE by a minimum of 7 to 15, i.e., BMCI/TE >1. In re evaluating their work, the BMCI/TE ratios for stable fuels are > 1.1 - 1.2. We have confirmed this in our own research. It is interesting to note that Shell, in their research, concluded that stable fuels must have a Po/FT > 1. It is implicit in both these approaches that the higher this ratio, the more stable the fuel (and the greater its "stability reserve").

Early in the development of this procedure we wondered if this was like a normal acid/base titration?. That is can we back titrate to the same end point. We confirmed that once the end point is reached, i.e., asphaltenes are precipitated, it is very difficult to reverse, even when large excesses of toluene are added. In other words once asphaltenes are agglomerated and precipitated it is extremely difficult to reverse the process. Other researchers have reached the same conclusion.

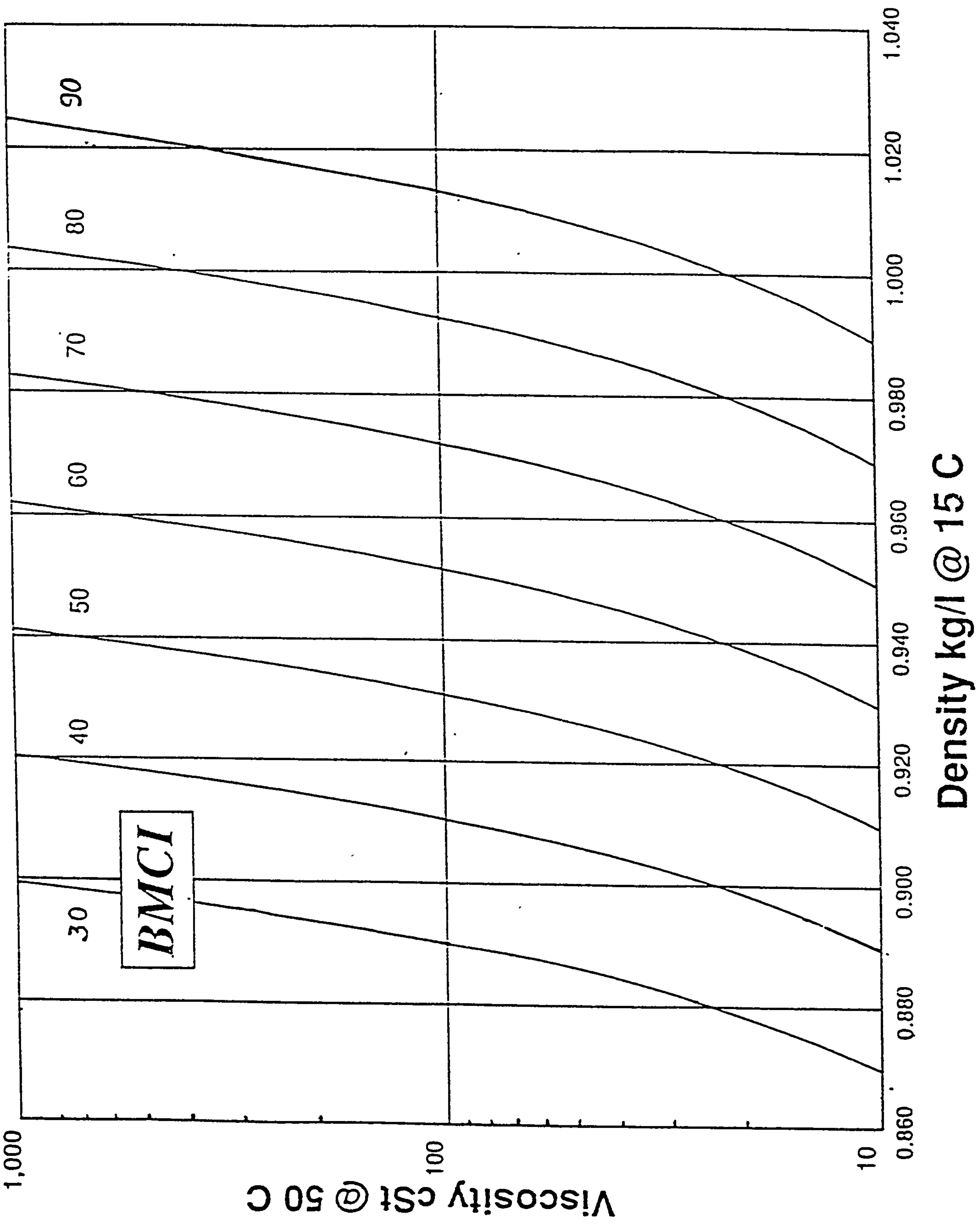
In our evaluation of fuels for compatibility we have observed that residual fuels with TE's of ≥ 40 are more prone to incompatibility. For such fuels, the selection of diluent is critical. A poor choice of diluent can lead to incompatibility. On the other hand, fuels with TE's < 33 are relatively insensitive to the selection of diluent. In other words, if the aromaticity requirement of the asphaltene is low, even relatively paraffinic type diluents are not likely to produce an unstable blend.

Examination of the BMCI chart which we showed earlier indicates that residual fuels have relatively high BMCI's. (65 - 85). We have also found fuels with TE > 50 to be rare. In other words, when dealing with heavy fuels the BMCI's of the blend components are >65 and the TE of these components is almost always <50. This leads to the conclusion that the likelihood of incompatibility when mixing two residual fuels is rare. Shell researchers reached the same conclusions over 40 years ago. We draw this to your attention not to advocate mixing of fuels. We believe the common practice of minimizing the mixing of fuels is prudent However, our experience confirms that when residual fuels are mixed they are generally compatible.

The likelihood of incompatibility when mixing an MDO with an IFO is significantly greater. While this BMCI chart does not cover the total MDO area we have calculated that MDO's have a BMCI of 25 - 45 as determined from the figure. (We have not yet determined an algorithm for fuels with viscosity < 100 cSt @ 50 °C). Incompatibility is most likely to occur when a residual fuel with a high TE (generally ≥ 40) and relatively low BMCI is mixed with an MDO which has a low BMCI (< 35).

An implication of these considerations is that the order of mixing can be very important. The low BMCI diluent (MDO) should ideally be added to the high BMCI and high TE component (Residual Fuel) while vigorously mixing. This procure minimizes the possibility of high localized concentrations of the low BMCI fuel which can cause instability. As we indicated earlier, once precipitated the aspahaltenes are not likely to go into solution. The reverse addition, that is the addition of the component with high TE and high BMCI (the residual fuel) to the low BMCI diluent (MDO) creates a situation in which some fuel is in the presence of a large excess of a significantly poorer (i.e., low BMCI) solvent. This is the most critical case for instability. However, if the residual fuels TE is low enough (< 33) the probability of incompatibility is significantly reduced.

We have found these concepts and procedures to be valuable in our evaluation of fuels and fuel components. These concepts have also been used to develop a variety of other tests. We will expand on these findings in subsequent papers.



Exxon/ihl/9-90

$$BMCI = (0.5074 - 0.0101 \log V_{50})\ CCAI + 15.36 \log V_{50} - 374.08$$

where V_{50} = kinematic viscosity at 50° C (cSt)

TOLUENE EQUIVALENCE TEST

DNVPS TITRATION METHOD

1. Weigh 1 gm (± 0.1) fuel into 100 ml beaker and dissolve in 10 ml (± 0.1) Toluene

2. Withdraw drop for SPOT test

3. Add 5 ml Heptane, while stirring

4. Withdraw drop for SPOT test

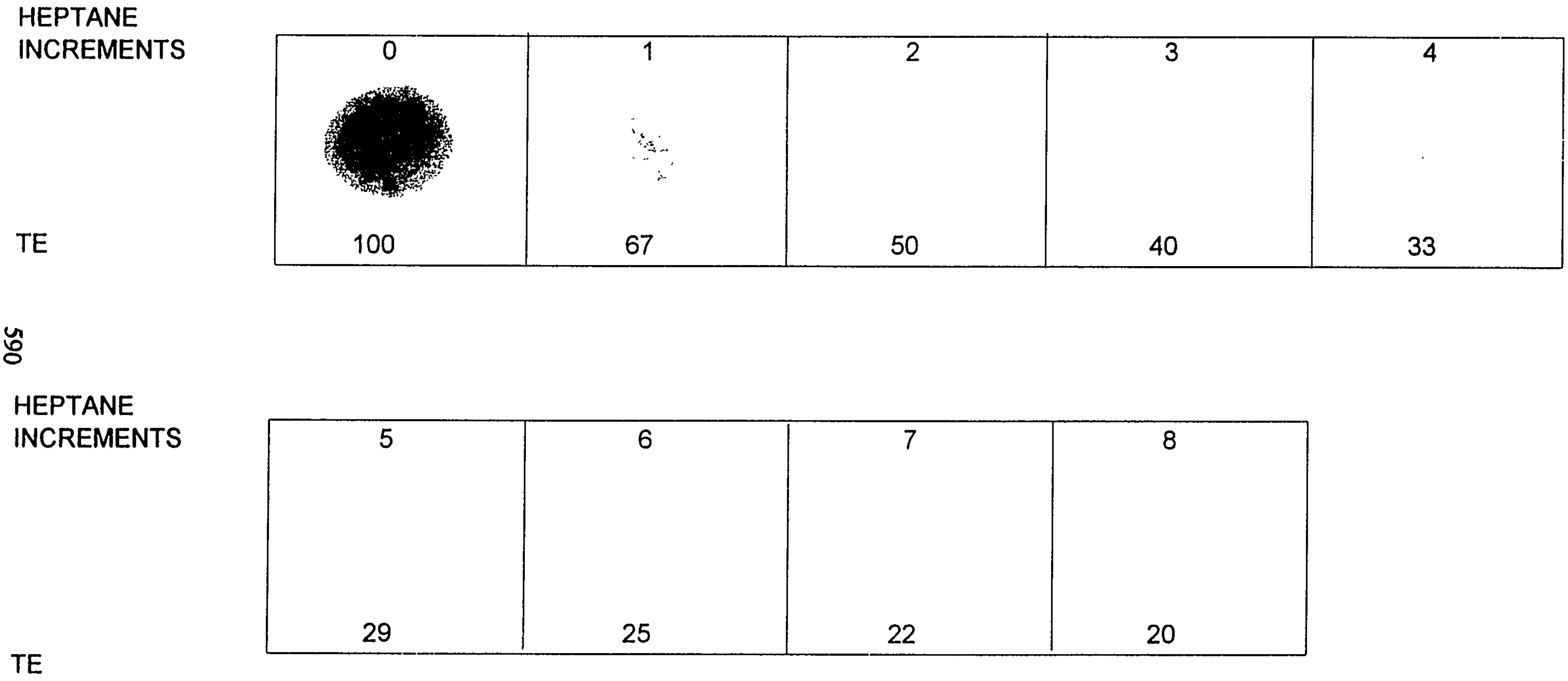
5. Repeat 3 & 4 until distinct inside ring obtained

Toluene Equivalence (TE) is bracketed between clean/dirty SPOT

TOLUENE EQUIVALENTS TEST

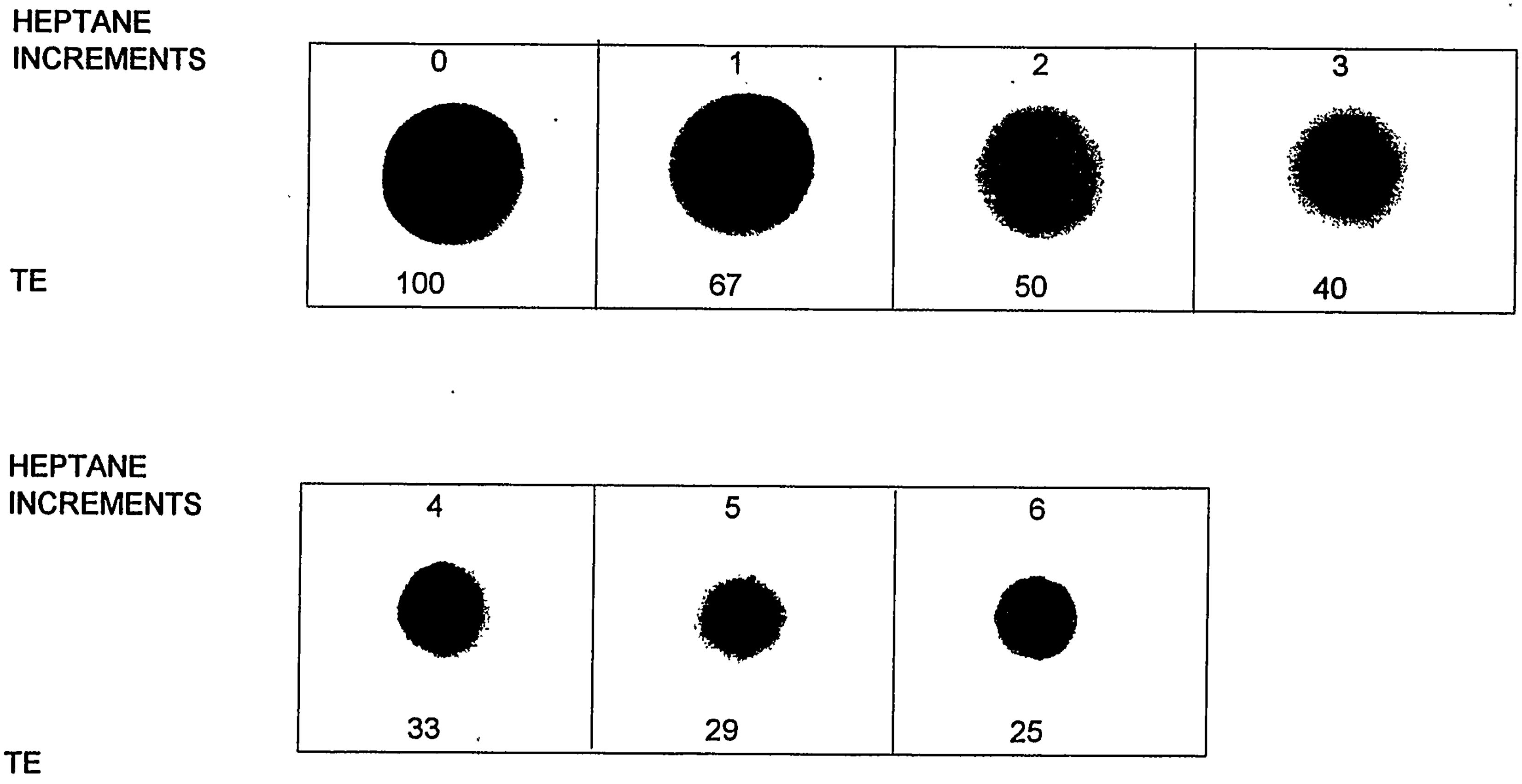
TYPICAL SPOTS

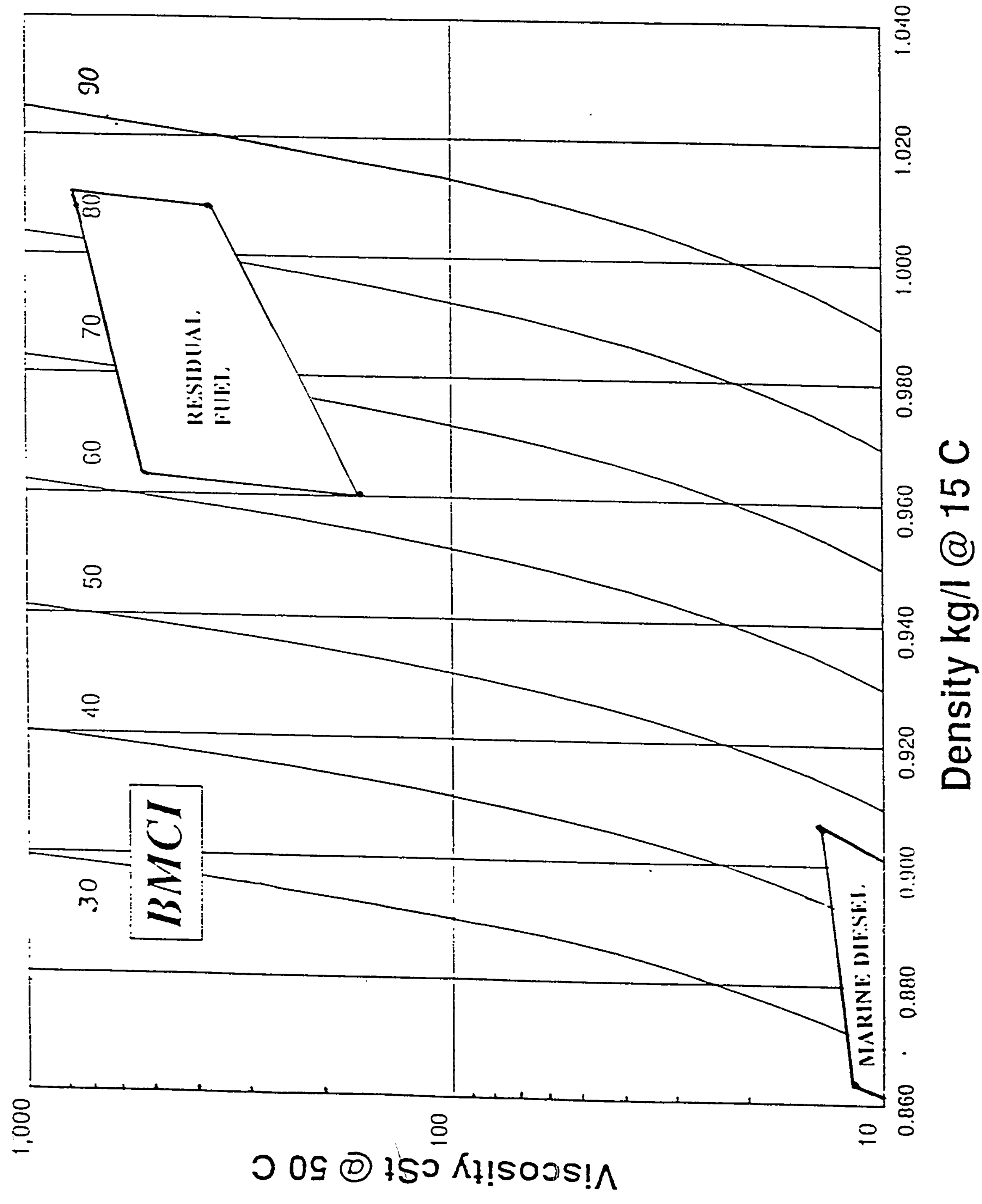
TE ≅ 24



TOLUENE EQUIVALENTS TEST
TYPICAL SPOTS

TE≅ 45




BMCI
RESIDUAL FUEL
MARINE DIESEL
30
40
50
60
70
80
90
Viscosity cSt @ 50 C
1,000
100
10
Density kg/l @ 15 C
0.860
0.880
0.900
0.920
0.940
0.960
0.980
1.000
1.020
1.040

5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7, 1994

THE U.S. DEPARTMENT OF ENERGY'S OIL PROCESSING PROGRAM

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INTRODUCTION

The U.S. Department of Energy's (DOE) Office of Gas and Petroleum Technology (OGPT) has been engaged in a strategic planing activity in response to the changing needs of the oil and gas industry and DOE's expanding role to address these needs. The Oil Processing sub-program is an important element of the OGPT program and is the topic of this paper. The major components of the Oil Processing Strategic Plan are described including the Mission, Situation Analysis, Vision of the Future, Strategic Goals, Strategic Barriers, and Objectives and Strategies.

MISSION

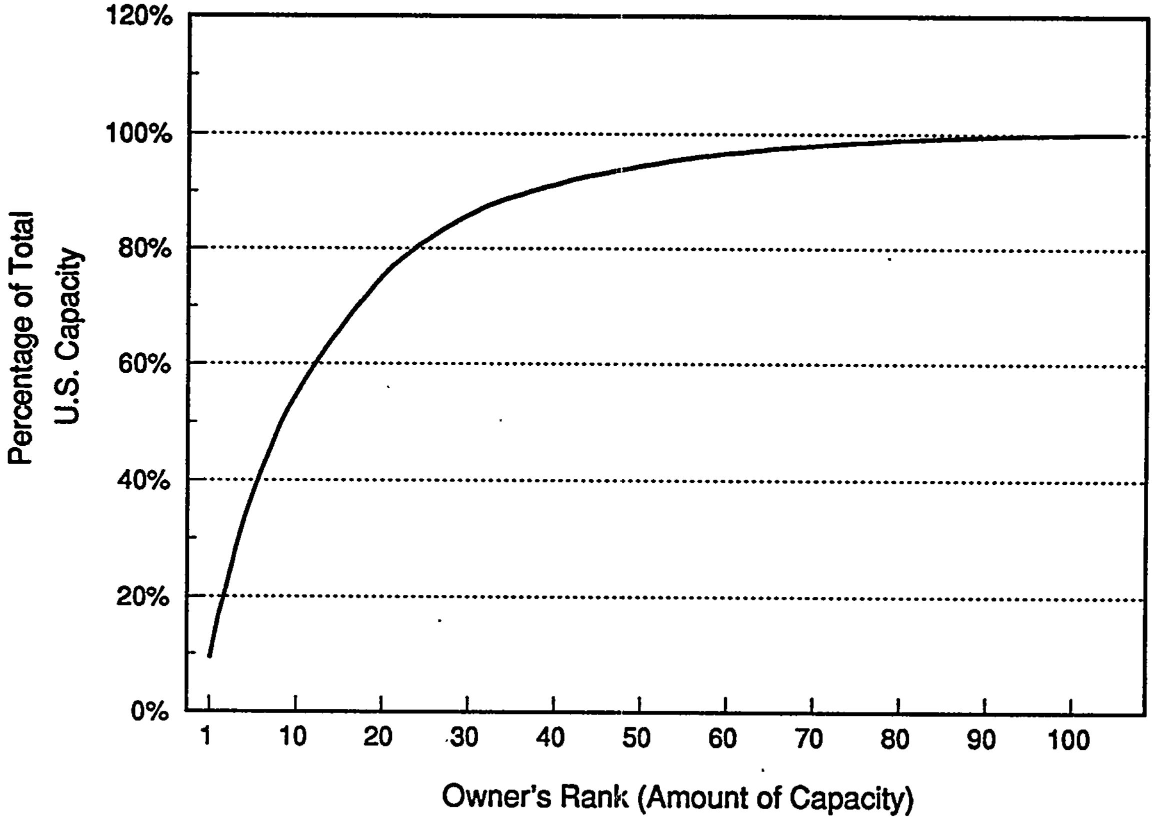
The mission of the Oil Processing Program is to maintain a viable domestic refining industry by stimulating the maximum yield of environmentally acceptable transportation fuels and other high-value products while minimizing the output of low-value products and waste streams.

SITUATION ANALYSIS

Global integration and high dependence on technology characterize the refining industry. Because refined products move freely among countries and refinery and process technology R&D is international in character, technological advances become available worldwide relatively quickly.

The 192 refineries in the U.S. account for 21 percent of the total world-wide distillation capacity.[1] Seventy percent of this domestic capacity (which is among the most sophisticated in the world) is owned by twenty companies, as shown in Figure 1. Among the top ten refinery capacity owners in the United States, four are foreign owned enterprises. Countries represented include the Netherlands, Great Britain, Saudi Arabia, Venezuela, and Mexico.

Figure 1
Concentration of Refinery Ownership
in the United States



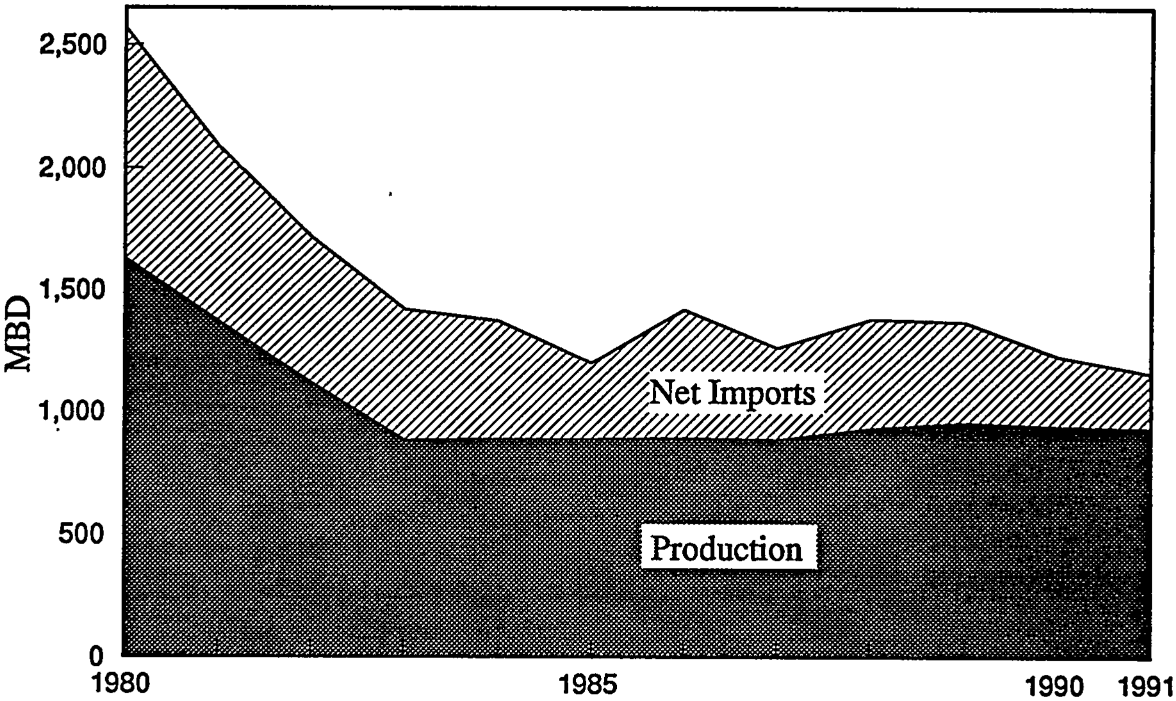
Sources: DOE/EIA 1991 Petroleum Supply Annual, Oil & Gas Journal

Over the last twenty years, three general trends have become apparent:

(i) **Demand has shifted to light, high-value products, particularly transportation fuels.**

Demand for light, high-value products (e.g. gasoline, jet fuel, and petrochemical feedstocks) is expected to continue to increase over time relative to heavy, low-value products. Demand for residual fuel oil, the main heavy product, is rapidly declining in the U.S. as cost competitive and "environmentally friendly" natural gas displaces it. The floor demand level of residual fuel oil is composed primarily of bunker fuels, utility peaking, and industrial use in low-demand, isolated areas which have no economically competitive alternative and/or less environmental restrictions on its combustion. Figures 2 and 3 show the decline both in supply of and demand for residual fuel oil within the U.S. Demand is expected to decline further as natural gas pipelines are on its combustion. Figures 2 and 3 show the decline both in supply of and demand for residual fuel oil within the U.S. Demand is expected to decline further as natural gas pipelines are extended on the East Coast and as natural gas continues to replace residual fuel oil in the utility sector.

Figure 2
U.S. Residual Fuel Balance - Supply

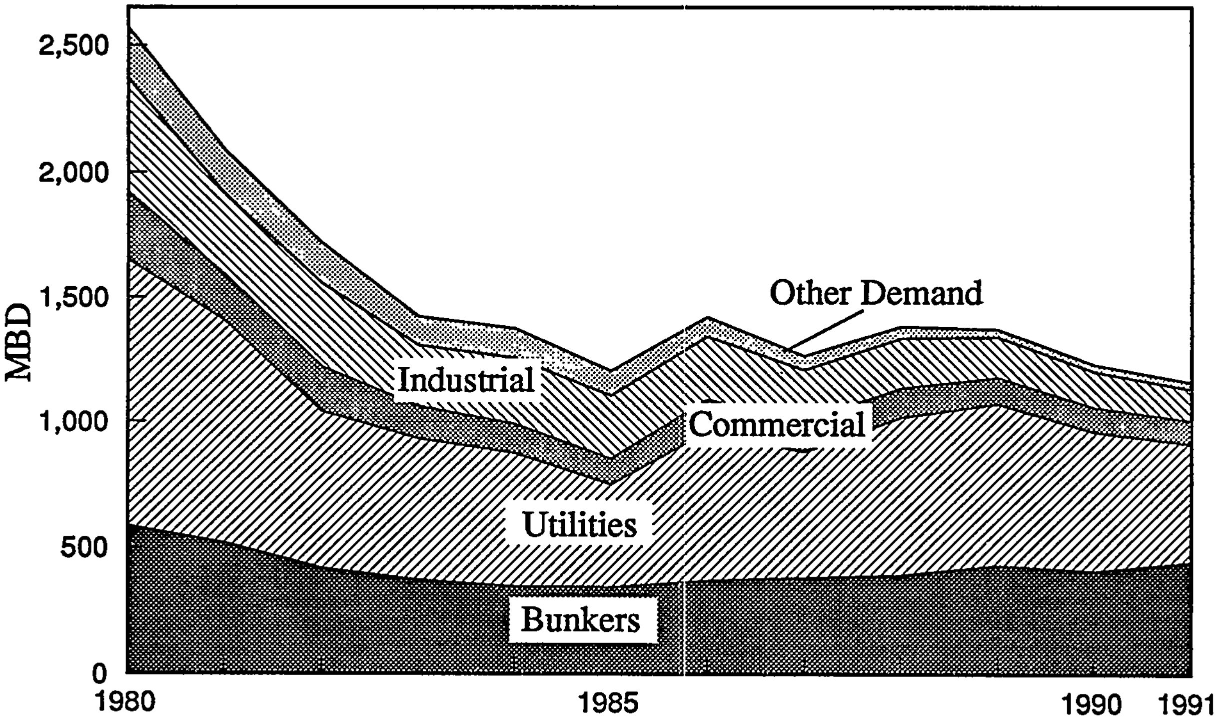


Source: DOE/EIA; Petroleum Supply Annual (1980-1991).

(ii) Crude oil feedstocks to U.S. refineries, both domestic and imported, have become heavier and higher in sulfur content.

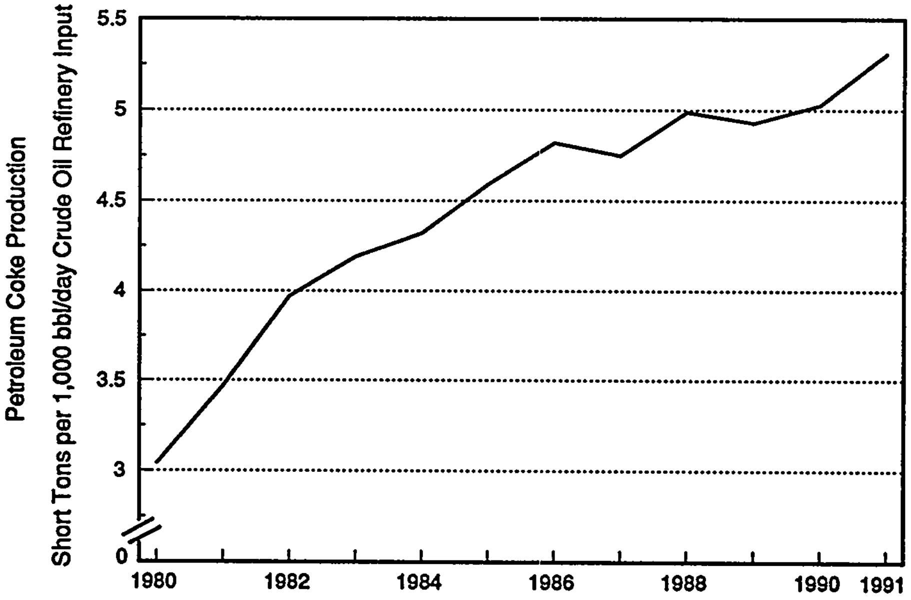
Heavy, high sulfur crude oils are more contaminated with metals, carbonaceous residues, and asphaltenes, thus they result in higher yields of residual fuel oil, other low-value products, and a higher volume of waste streams. Present technologies to upgrade resid include hydrocracking, catalytic cracking, and coking; but as the feeds get ever heavier, the trend is toward additional residual upgrading. In the U.S. coking is the most commonly used technology. Figure 4 shows the trend in U.S. petroleum coke production.

Figure 3
U.S. Residual Fuel Oil Balance - Demand



Source: DOE/EIA; Petroleum Supply Annual (1980-1983); Petroleum Marketing Monthly (1984), Fuel and Kerosine Sales (1985-1991).

Figure 4
U.S. Petroleum Coke Production

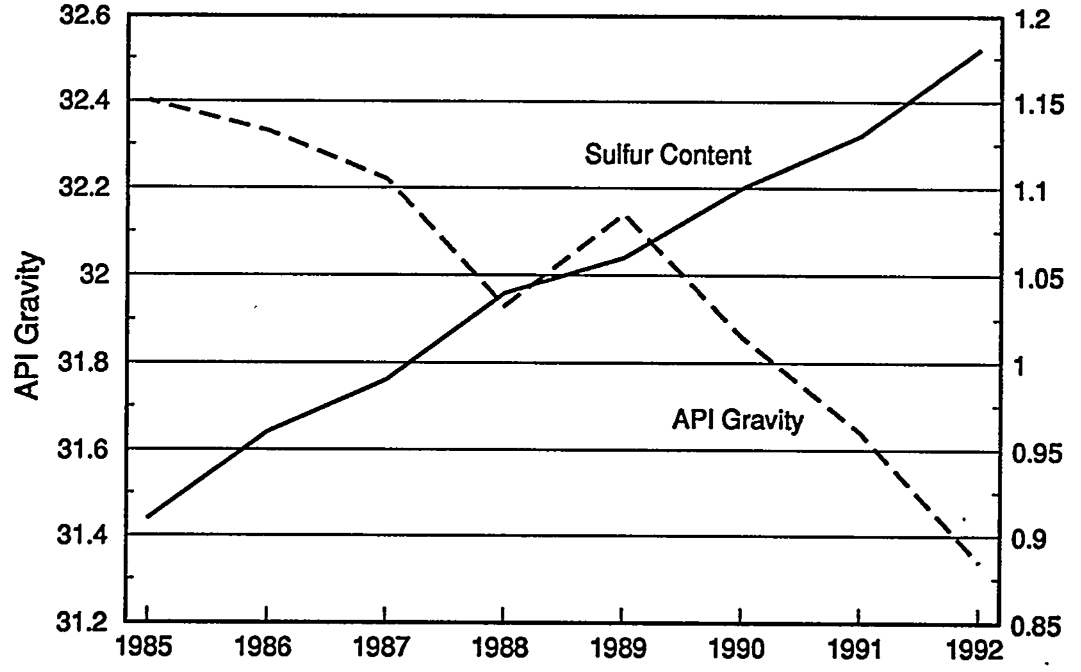


Source: DOE/EIA Petroleum Supply Annual (1980-1991)

Of the coke produced, roughly 50% is anode or electrode grade coke, with the rest being low-value, high sulfur, high metals fuel coke. Much -- 84 percent -- of the low grade coke is exported since its use as a fuel in the U.S. is constrained by environmental laws regulating combustion emissions.

The trend towards heavier and higher sulfur crude oils in U.S. refinery feedstocks (as shown in Figure 5) is expected to continue. The increase in crude oil prices since the early 1970s has made the domestic and foreign production of heavy crude oils economic and widely available and the U.S. has significant heavy crude oil reserves.

Figure 5
API Gravity and Sulfur Content of Crude
Oil Used by U.S. Refiners



* 1985 and 1992 are an average of the monthly data which may differ from EIA's weighted average.

Sources: DOE/EIA Petroleum Supply Annual, and Petroleum Supply Monthly

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The major domestic sources of heavy crude oil are California, North Slope Alaska, the Gulf Coast, and the Rockies. Of the current 500,000 b/d of domestic heavy oil production, 99% is from California. The potential for large scale production from all sources exists, but the market for domestic heavy crude is not robust. The volumes and costs of these resources are discussed in more detail in the preceding chapters.

The crude oils imported into the U.S. are also becoming heavier on average. Canadian crude oils, on which the Northern Tier and some Midwestern refiners depend, are steadily becoming heavier. In addition, the Canadian producers and pipeline companies are examining the possibility of moving their heavier crude oils further south. Both Venezuela and Mexico are major producers of heavy crude oil and the U.S. refineries that they own or jointly own are expected to process increasing volumes of these heavy crude oils.

(iii) Environmental regulations have imposed additional costs on refineries as well as restrictions on modifications and expansions.

Environmental constraints, whether in the form of government regulations or public opposition to expansions, comprise an ever increasing burden on U.S. refiners. While this trend is occurring in Europe and the Far East as well, the present U.S. regulatory approach of command-and-control, end-of-pipe treatment may in fact work against innovative approaches and cost-effective technologies and make regulatory compliance in the U.S. particularly costly. This contributes to the reduced competitiveness of U.S. refiners in the global market, raising concerns of the general viability of the domestic industry and the probability of an increasing rate of refined product imports. Refineries generate hydrocarbon and combustion emissions to the atmosphere plus contaminated aqueous and solid wastes. In total, U.S. refineries generate over two and a half million tons per year of aqueous and hazardous wastes and emissions from "losses."[2] Waste disposal is becoming more costly and more restrictive. Depending on new amendments to the Clean Water Act and the Resource, Conservation and Recovery Act, both of which are awaiting re-authorization, some waste disposal systems may be prohibited. This will require new technologies for waste disposal or changes in technologies to minimize waste generation, or a combination of both.

VISION

New upgrading/processing technologies will be available by the year 2000. Deeper, more efficient, and more cost-effective processing of each barrel of crude oil refined will result in increased yields of high-value light products with fewer low-value and environmentally adverse products produced. These new technologies will produce fewer emissions and waste streams.

The regulatory burden on U.S. refiners will be reduced while improving environmental protection. Accurate scientific data will be used by regulators to produce cost-effective, risk-based regulations. The regulatory environment will stabilize, with constructive dialogue between industry and the various levels of government regulators.

The domestic refining industry will be competitive in the global market. New technology, particularly environmental technologies, will be exported as environmental regulations and product specification requirements spread to the rest of the world. The U.S. will thus continue to be a major player in the international processing technology market. In addition, the development of cost-competitive new technologies will help the U.S. industry to maintain its refining share in the U.S. market relative to refined product imports.

STRATEGIC GOALS

The program has three strategic goals:

Goal 1: To increase the yield of environmentally acceptable, cost-competitive, high-value transportation fuels and petrochemical feedstocks from each barrel of crude oil refined while reducing low-value products and residuum.

Goal 2: To develop environmental data and technologies and encourage the development of rational, science- and risk-based regulations on refinery and downstream operations by the regulators.

Goal 3: To communicate with all "clients" to understand their needs and plan activities to address them, consistent with national goals.

STRATEGIC BARRIERS AND OBJECTIVES

Several barriers must be overcome in order to achieve these strategic goals. These barriers fall into two broad categories: processing technology constraints and environmental regulatory data and implementation concerns.

Processing Technology Constraints

Development of processing technology proceeds in two steps: knowledge of the fundamental chemistry and thermodynamics of the feedstocks and process reactions is required as a basis for optimal processing technology development; then laboratory and pilot plant scale versions of the new technology must be developed, tested, and evaluated to facilitate translation into full scale engineering designs and construction.

Lack of Chemical and Thermodynamic Knowledge: Substantial work has been done over the last half century in compiling thermochemical and thermophysical databases on the range of compounds found in light crude oils. The research has focused on the properties of the gasoline fraction and on the major sulfur-containing components. This data has been used to design processes that produce the required products with a very high degree of efficiency and cost-effectiveness.

Significantly less work has been done for heavier crude oils and residua. In comparison to the light crude oils, there are many more compounds in heavy fractions and the chemistry is much more complex. The heavier crude oils contain more polycyclic aromatics and sulfur-, oxygen-, and nitrogen-containing compounds, and less hydrogen than do light crude oils. There is insufficient basic chemical and thermodynamic data on the hydrocarbon fractions and other constituents of residua and heavy crude oils. Hence, processing crude oils containing increasing levels of oxygen, sulfur, and nitrogen using current technology produces fuels with a tendency towards poor performance and storage and thermal instability.

Technological Constraints: Although there are established technologies for dealing with heavy crude oils and residua, they have substantial technological and cost problems. The technologies are:

☐ **Coking**, a severe form of thermal cracking, is the most economical method and produces low-value, environmentally adverse products: delayed coking results in large volumes of high-sulfur, high-metals, environmentally damaging coke; flexicoking results in a low-BTU gas that can only be used as a refinery feedstock, distillate oils, and a residue of ash. In addition, the use of coking results in yield losses. Coking processes produce a lighter gasoil stream by rejecting carbon to a petroleum coke byproduct. Associated with this shift in the hydrogen to carbon ratio is a significant reduction in liquid yield. Although it might be argued that coking is not the technology of the future, due to its low liquid yield and environmentally adverse by-products, substantial investments have been made and are being made in this technology in the U.S.

☐ **Hydro-cracking**, which embodies cracking over a catalyst combined with hydrogen addition and sulfur and metals removal, produces a lighter, less contaminated product. Volume yields are thus higher than for coking. However, the technologies for hydrogen processing of heavy streams are typically among the most expensive in a modern refinery. Once all available hydrogen from reformers is fully utilized, the manufacturing of additional hydrogen feedstock becomes very expensive. All the component parts of hydrogen processing contribute to the cost: feedstock, hardware, and catalyst. Hydrogen processing, such as hydro-cracking, is performed at high temperatures and pressures. Due to improved catalysts, temperatures and pressures are somewhat less than when the technologies were first developed, but hardware is still extremely expensive. Because of the changes in composition as one moves from light to heavier crude oils process-design correlations will have to be modified or new ones developed that can be demonstrated at the pilot scale.

☐ **Fluid catalytic cracking (FCC)**, which is a catalytic process but which also leads to a measure of carbon rejection. Technological advances have been such that FCC units are now routinely used to upgrade the whole low-sulfur, low-metals residua from conventional crude oils, or poor quality residua from heavy crude oils that have been subjected to desulfurization and demetalization.

Overall, the growing use of heavier crude oils which tend to be asphaltic, are causing processing problems particularly in the FCC units with increased carbon deposits on catalysts, and poisoning of the catalysts by the heavy metals also typically found in these crude oils. Various forms of solvent-based asphalt extraction have been developed, as have additives to the FCC units such as sulfur scavengers, but the problems and the high costs resulting from these problems still remain.

The following objectives have been established to overcome these barriers:

<u>Objective</u>: To develop sufficient understanding of the chemical and thermodynamic properties of heavy oil fractions and residua constituents to enable industry to develop cost-effective processing technology or to effectively upgrade existing technologies.

<u>Objective</u>: To develop fundamental molecular knowledge of coke precursors in heavy crude oil feeds and residua to improve the technology or to optimize its configuration so that wastes and impurities are minimized, resulting in a higher-value, more environmentally attractive product.

<u>Objective</u>: To increase understanding of the chemistry and thermodynamics of adding hydrogen to the feedstocks so that the full use can be made of heavy crude oils and residua to make transportation fuels and other light products with the ultimate aim of reducing costs.

<u>Objective</u>: To identify where the critical R&D impasse lies in developing new and novel technologies. To evaluate new and promising technologies and to co-fund or fund those with the greatest apparent cost-effectiveness in lab tests, possibly up through the pilot scale.

Environmental Concerns

The increasing costs of environmental regulations have contributed towards the closure of a number of refineries within the U.S. and threaten the continued viability of others. Apart from the costs of emission controls and waste disposal there are the costs entailed by long permitting processes and by public opposition to refinery expansions and upgrading.

Recent studies have shown that much of the emissions regulatory structure applicable to refineries is not based on objective measurement data taken at individual refineries, but is based on outdated studies, poor understanding of refinery operations and configurations, or generic assumptions about the pollution reducing impact of specific waste treatment equipment and is exacerbated by the general atmosphere of conflict between regulators, environmentalists, and industry.

An example is the Amoco refinery at Yorktown, Virginia,[3] where EPA regulations required substantial investment to control benzene emissions from the waste water treatment facilities. Actual emission measurements showed low levels of benzene emissions from the waste water site, but very high levels from the loading dock, a location that EPA had ignored in its regulations. This type of regulatory miscalculation can result in substantial costs to an individual refinery with little environmental benefit.

Regulations governing refinery waste disposal are also becoming more stringent and some traditional forms of disposal are being forbidden. The trend is to eliminate land farming as a waste disposal means. For some catalysts, there is currently no readily available alternative disposal method. New technologies, such as solvent extraction, are emerging, but they are expensive. Other technologies such as incineration and pyrolysis have limited application due to permitting constraints and public opposition.

There is also a lack of cost-effective instruments sophisticated enough to measure the ever increasing number of regulated chemicals, and to reflect the complexity of the refinery streams and the emission shifts at different points as different refinery streams co-mingle and/or separate. The distribution of emission types from these streams can also shift as the molecular make-up of the specific crude oil feedstock changes and can also be very different from refinery to refinery. In conjunction with this generally accepted methodologies for aggregate measurement of all potential refinery pollution, whether air emissions, solid wastes, or water discharges, have not always been developed.

There are a number of institutional barriers to effective environmental regulation that need to be overcome. A major problem with developing new technologies to meet new regulatory requirements is the different time frame between R&D outcomes and regulatory requirements. R&D for new and innovative technologies and definitive data about cost and efficiency is typically long-term. Regulatory requirements, whether statutory or otherwise, tend to operate in the short-term.

The following objectives have been established to overcome these barriers:

<u>Objective</u>: To improve understanding of refinery emissions and waste streams at various point sources in the refinery to provide a basis for developing the scientific data necessary for generating risk-based regulations.

<u>Objective</u>: To develop sufficient understanding of the optimal configuration and functioning of new processing technologies to consume less catalysts, generate less pollution, and generate fewer overall wastes.

<u>Objective</u>: To develop sophisticated, cost-effective devices to measure refinery waste stream components.

<u>Objective</u>: To facilitate better communication and co-operation between federal, state, and local regulators, the refining industry and other players, such as environmental groups.

STRATEGIES

The Oil Processing area consists of a number of strategies to achieve the three strategic goals and objectives.

Goal: <u>To increase the yield of environmentally acceptable, cost-competitive, high-value transportation fuels and petrochemical feedstocks from each barrel of crude oil refined while reducing low-value products and residuum</u>.

Strategy 4.1: Develop cost effective and environmentally acceptable residua and heavy oil upgrading and processing technologies. To implement this strategy DOE will undertake the following strategic elements:

☐ Continue to develop fundamental chemical and thermodynamic knowledge of heavy crude oils and residua. The fundamental chemistry will be investigated for asphaltenes, porphorines, sulfur removal, and organometallics compounds. Advance concepts of functional group chemistry will be developed. Hydrocarbon fractions and various other constituents will be characterized for residua and various heavy crude oils. Thermodynamic measurements and correlations in residua and heavy crude oils will be developed:

  - As a basis for predicting chemical processes, their temperature pressure range, and their likely yields;

  - To ascertain the stabilities of the reaction intermediates and whether reactions are possible and reversible under specific conditions; and

  - To calculate the heat and material balances.

☐ Develop basic thermodynamic data for hydrogen processing. Understanding of the thermodynamics of hydrogen addition to processes will be increased. Laboratory testing and measurement will be used to determine the optimum chemical reaction sequences and the optimum reaction conditions, temperatures, and pressures necessary to obtain a desired conversion.

☐ Working with industrial partners, undertake RD&D for promising new upgrading/processing technologies and for improvements to existing technologies. The basic chemistry and thermodynamic properties of existing technologies, such as coking, will be investigated in an effort to improve efficiencies, reduce wastes, and lower the costs. Investigate the need to modify or redevelop the process-design correlations derived from light crude oil data. changed. Fundamental thermodynamic investigations will be undertaken of selected key compounds to develop predictive models for developing new correlations to represent the process stream.

Goal: To develop environmental data and technologies and encourage the development of rational, science- and risk-based regulations on refineries by the regulators, and to bring industry and regulators together.

Strategy 4.2: Conduct environmental R&D and outreach programs. To implement this strategy DOE will undertake the following strategic elements:

☐ Conduct studies to define major classes of refineries by installed processing equipment, specific configuration, and likely emission distributions; prioritize these classes by capacity, likelihood of improving emissions, and impact of regulations.

☐ Collect and document basic emission data at proto-typical refineries from each major class (taken in priority order) through co-operative agreements with the industry.

☐ Develop advanced measurement instrumentation for collecting complex emission data, particularly newly regulated air toxins.

☐ Jointly support RD&D on innovative approaches and technologies for waste minimization and treatment.

☐ Work with industry, federal, state, and local regulators, and environmentalists to improve information and data availability for regulatory development, and to improve relations between all parties.

Goal: To communicate with all clients to understand their need and plan activities to address them, consistent with national goals.

To achieve this goal DOE has three strategies which are also discussed in greater detail in Chapter VI. Technology Transfer.

Strategy 4.3: Conduct analysis and evaluations to both focus and prioritize the processing mission. To implement this strategy DOE will undertake the following strategic elements.

☐ Define the direction, the priorities and the activities for the program. Undertake scoping studies and surveys of industry to identify critical R&D needs in processing technology. Based on these studies and surveys prioritize the R&D areas critical to the achievement of the program's goals, and use this prioritization to evaluate R&D requests.

☐ Evaluate the extent to which the Plan is being implemented and to which the program objectives are being achieved.

☐ Provide analytical information to the Program's planning functions and analytical products to public and private decision makers.

☐ Assure that the program runs efficiently and that the clients are satisfied with quality products.

Strategy 4.4: Transfer processing and related environmental technologies aggressively. Under this strategy DOE will undertake the following strategic elements:

☐ Continue traditional DOE technology transfer functions by publishing fundamental research and presenting it at scientific/industrial conferences.

☐ Support technology transfer consortia and other co-operative efforts. Firms developing new technologies with the help of the National Laboratories will be encouraged to license the technologies as soon as possible.

☐ Conduct lab or pilot scale demonstrations of appropriate emerging technologies.

☐ Improve understanding of domestic clients, needs, and technology transfer. Contact refiners directly to facilitate the distribution of information.

Strategy 4.5: Ensure compliance of the program with DOE's environmental, safety and health standards.

OGPT has begun to implement this program through its Bartlesville Project Office (BPO). The strategic plan will be reviewed each year and revised as appropriate.

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5th International Conference on
Stability and Handling of LiquidFuels
Rotterdam, the Netherlands
Ocotober 4-7, 1994

Mechanisms for ageing of Middle Distillates manufactured from Crude Oils.

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Abstract

European middle distillate marketers and manufacturers have recently seen a surprising increase of ageing phenomena, mainly in the new eastern provinces of Germany after installation of new home heating oil units. Some of these phenomena remain unexplained, so that the "Committee Product Application-Fuels" of the DGMK (German Society for Petroleum and Coal Science and Technology) agreed to foster a research study with respect to ageing of middle distillates manufactured from mineral oils. As step I a literature search was authorized, as it was felt that since over 50 years of work had been done on the subject without culminating in an overall deterioration and degradation theory yet. The available literature from international sources is massive. 320 papers/books have been reviewed and it is hoped that the most important publications have been covered. A step II may follow in future looking into the verification of the most promising theories via laboratory testing and possibly providing better methodology to predict the most common ageing through its parameters - and finally recommending prevention methods. What has been found by the search is a majority of papers dealing with the results of ageing processes taken from real life cases and trying to resimulate them in the laboratory while reducing the reaction time. Relatively few papers try to explain chemical/physical reaction mechanisms on which an ageing theory could be built. Differentiation into chemical, physical and biological causes becomes necessary. An obvious problem with testing distillates and presented by many papers is the isolation of a blend component often found harmful for a finished product, from the rest of the fuel components, thus omitting preventative forces or activating/accellerating agents from the findings. Many tests with Light Cat Cycle Oil (LCO) are typical examples. This isolation can explain the many contradictive findings in literature, which this paper will document in detail. The most promising theory requires a set of conditions/chemicals to be met/present to kick off the ageing process and progress it until one of the components is consumed. On their own many of the "danger chemicals" may not be harmful at all, unless they are being matched by theirs corresponding mates. The paper will provide details on these "danger chemicals" found in literature. Finally the most promising reaction kinetic models found in the literature will be critically reviewed.

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Introduction

Up to the mid-40ies of this century there were no problems with storage stability of gasoils. Until then the demand could easily be met from gasoil fractions of processed crude oils. Difficulties with these so called "Straight-Run-Gasoils" were mainly encountered through involuntary comingling, poor distillative fractionation, and high sulfur content - mainly hydrogen sulfide and mercaptanes.

At the end of WW II the volume demand for gasoils increased drastically as a result of converting whole ship fleets to diesel or gasturbine engines, applying diesel powering to railroads, and the increasing usage of gasoils for home heating; straight-run gasoils could not cover this demand any more. As a result the gasoil fractions from crack processes, which so far had been added to industrial fuel oil, had to be included into the middle distillate (gasoil) pool. Difficulties appeared mainly with those gasoils which had been stored over some time. Gasoils (home heating oils) were stored for long periods in end-user tanks over the summer and surplus refinery gasoils were stored seasonally at the manufacturing sites and/or bulk plants in preparation for the prime winter heating season.

Major volumes were also stored as strategic reserves by the military.

In both cases two major new ageing phenomena appeared during storage: darkening and shedding of sediments. The latter resulted in filtration difficulties causing handling and operational disruptions [1].

The main culprits were soon identified as the thermally cracked gasoils and mainly by the military research was started to find the exact causes and any means to prevent the difficulties.

Instability of Gasoils and its consequences

Stability of gasoils can be defined as follows:

Stability means the immunity against changes in operational performance characteristics during storage (storage stability) and not to form deposits on hot surfaces in engines, which may inhibit the operation and heat exchange (thermal stability).

Figure 1 shows in simplified summary form the trigger, causes and consequences, which occur with instable gasoils. Ageing processes leading to organic sediments, which occur mainly during long term storage of instable gasoils, are being researched by this study.

Since those problems occured and still occur mainly during strategic long term storage for military defense and civil crisis management, initially mainly research institutions of the military looked into these ageing phenomena [e.g. 2 - 8].

Reasons für sedimentaion

Inorganic sediments like ironoxydes, ironsulfides, sand etc. can be eliminated or at least kept at very low level through proper housekeeping measures; especially the regular water withdrawal from tanks, by which corrosion and H_2S formation leading to ironsulfides and caused by SRB = Sulfate-Reducing-Bacteria can be kept at a low level.

Concerning organic sediments one has to differentiate between different types. There is slime and emulsion formation at the interface between tank bottom water and oil caused by bacteria and further biomass growth possibly by fungi. Precondition of such slime/biomass - which can cause substantial filtration problems of the fuel - is the availability of water. In above ground fixed roof tanks water can migrate into the tank bottom even when "dry" product is charged by the breathing to the open atmosphere; floating roof tanks often leak around the tank walls at the roof seals. Generally dewatering will avoid biological slime and sediments: in extreme cases biozides can be used to destroy the microbial population.

Further sediment formation can be caused by blending of incompatible gasoils, means: fall-outs can happen, when gasoils of very different types (e.g. paraffinic with highly aromatic ones) are mixed together purposely or accidentally; this can even happen if fresh gasoils are filled on top of non withdrawable tank bottoms. These phenomena happen more often with industrial heavy fuel oils and crude oils, though they are by no means rare with diesel and light heating oils in long term storage, shedding mainly waxes.

Sedimentation not controllable by good housekeeping and/or precaution rules against incompatibility mixing are most certainly based on reactive gasoil components.

Since many years it is known that instable gasoils forming sediments, shed fall-outs with compared to the main oil body lower carbon and hydrogen contents, while nitrogen sulfur and oxygen are increased (see table 1).

This points to heterocyclics, which are available in gasoil as traces only, which may decisively and overproportionally participate in the ageing process. The low content of hydrogen allows the conclusion, that the sediments are highly unsaturated (aromatic). This fits also to the postulated increase of instability starting with paraffinic and naphthenic hydrocarbons (stable) over alkylaromatics, polycyclic aromatics up to the olefines and diolefines (very instable).

The values of oxygen are only explainable, if one assumes that oxygen from the air is being introduced into the sediment molecules, since the oxygen content of gasoils manufactured from crude oil via distillation or thermal cracking is very low - in contrast to untreated gasoils from tar sands or synthesized from coal. This shows, that oxygen is important for the ageing process and not only for the triggering of the reaction.

Ageing without molecular oxygen does generally not take place in a temperature range up to 50°C.

Contradictive results, e.g. ageing in a nitrogen atmoshere, most certainly have ignored the oxygen dissolved in the gasoil, since for the in the ppm range already damaging sediment formation oxygen in the microgram range would be sufficient.

Of the nitrogen containing heterocyclics the nonbasics are reactive substances, especially in case of alkyl-substitution in alpha position. Herewith a sequence of declining reactivity from pyroles over indoles to carbazoles is being reported. Many publications have dealt with the effect of pyrroles, most of them however obtained from oil containing shale oil. It was discovered, that pyrroles do not require any reaction partners to form sediments - possibly with the exception of oxygen. Those sediments cannot be dissolved in gum solvent in contrast to those formed by ageing of gasoils, which points to a basically different structure. Furthermore there were no pyrroles found in gasoils created from natural crude oils. Basic N-heterocyclics are generally labelled as non-reactive and thus not harmful. There are however contradictory reports in the literature (see table 2). All agree however, that the total amount of nitrogen is no measure alone for the stability of gasoils, it is important to identify the type of nitrogen compound.

The role of sulfur compounds with respect to gasoil stability is so far unexplained. Besides the inhibitor role of some compounds very strong reactions of others are known (Fathoni et al) [9]. Thiophenol in hydrogenated gasoils has been found to be an inhibitor of the hydroperoxide reaction, on the other hand it has a profound influence on the sedimentation of crack gasoils and its blends with straight-run gasoils. Since it has been found that organic sulfonic acids have a strong influence on sedimentation, it is assumed that this is caused by the oxidation of thiophenoles and other thioles to sulfonic acids.
There is an indication, that the first step towards ageing is based on acid catalysation and furthermore - as shown later - a base/acid reaction strongly influences sedimentation. Thus also organic acids or oxygen containing hydrocarbons like phenols, which can be oxidized in the process of ageing to acids, are to be considered as reactive components in unstable gasoils (see table 2). Also the condensation from phenols to di, tri- and tetrameres is considered to be an ageing process (Hazelett [7.10]).

Metals, which can be introduced into the gasoils during manufacturing, storage, transport and end-use are suspected to act catalytically already in trace concentrations only (PPB), whereof copper is reported to be more acitve than iron or aluminium.

As already mentioned earlier, gasoils from thermal/catalytic processing of heavy crude oil compounds are especially vulnerable to ageing (coker > thermal cracker > fluid cat cracker). Gasoils from steam cracking (incl. quench oils), oil from shale oil deposits, tar sands and coal hydrogenation are so unstable, that even the blending of very small percentages into the gasoil is impossible. They definetely have to be treated prior to use - generally by hydrogenation. On the other hand gasoils from hydrocracking and those having undergone other forms of strong hydrogenation have become vulnerable to hydroperoxid formation and subsequent chain reactions. Stable are generally only those gasoils obtained directly from crude oils by simple pipestill distillation.

Ageing Tests

Already in the 1950ies attempts were made to simulate the experienced ageing by field test and in laboratories. During the first "Symposium on Stability of Distillate Fuel" in 1958 Mac Donald and Jones [11] presented 32 different tests and appropriate comments. They ranged from long term tests using large volumes in land and marine tanks, barrels, cans and glass containers at ambient temperature to 0.05 liter samples exposed to high temperatures up to 200°C and short exposure time of 90 minutes.

Subsequently in the following years more test methods were reported, whose results were hardly comparable due to differing test conditions and configurations. Widely differing results and interpretations were offered for the ageing mechanisms.

With time, standardization organizations like ASTM and IP developed ageing methods specially geared to gasoils (ASTM D 2274, 4625, 5304; IP 378).

Aside from those there are many other test methods, which were mainly created by manufacturers of gasoils and additive producers. Also methods used to judge gasolines and jet fuels were adapted to gasoils. The results show, that even with good repeatability the comparability remained poor, which means different laboratories rule differently on identical samples with respect to storage stability.

Since manufactures as well as consumers have a strong interest in getting reliable indications on storage stability in a short time, short term tests were created an forced into use. The shortening of the time factor is supposed to be compensated by higher test temperatures and additional supply of oxygen required to trigger ageing reactions. It was shown however, that these "quick tests" do not always correlate well, sometimes due to a frequently prolonged induction period prior to the start of sedimentation, that means ageing is starting after quick test is completed (often found with ASTM D 2274), or because at higher temperatures other reactions take place than at ambient temperatures.

Only ageing at 110°F resulted in relatively proper matches with long term tests. The long test period of 12 weeks however is prohibitiv for operational applications. Therefore other methods have to be found, which allow predictions on the stability of gasoil batches at short notice. First attempts can be seen by the fieldtests of Solly [12, 13] and Marshman [14] and in the laboratory test methods of Marshman [15, 16].

Ageing Mechanisms

During the long period of investigation many attempts were made to explain the ageing phenomena of gasoil. In a very simplified tabulation by Taylor et al. [17] (see figure 2) the long known conditions are presented.

The first all embracing description of an ageing mechanism was presented by Sauer et al. [18]; reactive hydrocarbons, sulfur and nitrogen heterocyclics with branches are oxidized and via the formation of hydroperoxid, hemiacetales and esterification high molecular weight compounds can be formed, which in further chemical reactions result in chromophores and sediments.

Schrepfer et al. [19, 20] hold 3 reactions responsible for gum (sediment) formation.

1) Acid/Base-Reactions
2) Oxidative gum formation from olefines
3) Esterification

Hazelett et al. [7, 10] found out, that with low sulfur gasoils from Bass Straight crude an oxidative coupling of phenols can occur, however at elevated temperatures (65° and 80°C), going hand in hand with an increase of molecular weight, polarity and a solubility reduction leading ultimately to sedimentation. However the absolute sediment volume remains low and is barely above the test methods detection capabiltiy.

Stirling et al. [21] postulate as first step of ageing a equilibrium reaction using oxygen as catalyst, by which out of two different components SOP (Soluble Organic Polymers) are formed.

$$A + B \xleftrightarrow{O_2} SOP$$

These SOP act then in a second step catalytically for further reactions with other compounds of gasoils resulting in sedimentation.

$$C + D \xrightarrow{SOP} Sediment$$

In spite of a large test programme it was impossible to find a convincing explanation for the ageing reactions, possibly due to some misinterpretations of the results.

Wechter et al. [22 -24] thought they could isolate in LCO (Light Crack Gasoil) and blends of straight run (SR) and LCO so called soluble macromolecular oxidatively reactive species (SMORS) with the help of a methanol extraction. The quantities directly are proportional related to the capacity of a gasoil to form sediments. Later [25] it was shown, that these SMORS do not occur in "fresh" gasoils, thus they are themselves products of the ageing process, which are however still soluble in gasoils. MS-Tests (Malhotra et al. [26] show that indolylphenalenes are the main components of SMORS.

Por [27] has shown recently in an all embracing study several ageing mechanisms:

Polymerisation of unsaturated hydrocarbons
Condensation
Oxidation

All these reactions are explained by free radical reactions. Since sedimentation of gasoils does not occur in the absence of oxygen, the first two reaction types are possibly insignificant, at least for the ageing at low temperatures and under exclusion of daylight. The free peroxid radical chain oxidation

Initation $I_2 \longrightarrow 2\, I\bullet$

Propagation $R\bullet + 0_2 \longrightarrow R00\bullet$
$R00\bullet + RH \longrightarrow R00H + R\bullet$

Termination $2R00\bullet \longrightarrow$ inert products

is being labelled by many authors as the basis-reaction, which is mainly responsible for the ageing process. This may well be true for the gasoline and kerosene sector, for the gasoil/middle distillate sector this reaction appears improbable, because antioxidants effective in light products are ineffective in gasoils. Neither the tocopheroles (Vitamin E) - considered to be the most powerful radical catcher - is according to Beaver et al. [28] effective - nor do the hindered phenoles or other amino substances the job, though long known to be effective in gasolines and kerosenes. The latter may even foster ageing in gasoils. Exception are trialkylamines, which as strong base increase the induction time, that means delay the start of sedimentation, because they neutralize the organic acids required for sediment fall-outs.

But since the oxygen influence is overall recognized another form of reaction must be the culprit. Beaver [29] thinks that in the so called "Electron Transfer Induced Oxidation (ETIO)" he has found the key. Herein electron rich organic compounds act as electron donator and oxygen as electron acceptor, and after further very fast reactions hydroperoxid is formed. This ETIO cannot be influenced by the at present known antioxidants. Beaver however is optimistic that also against this reaction a cure can be found [30].
At the end of the 1980ies Pedley et al. [31 - 41] have shown based on field tests and ageing at 110°F, in conjunction with many analytical test methods (GC-MS, MS, TLC, LC, HPLC, IR etc.), that the ageing of gasoils with LCO components progress in two steps. The first step resulting in the formation of chromophores and consequently color darkening consists of a reaction of phenalenes and non-basic nitrogen compounds, like alkylindoles and to a minor extent alkylcarbazoles under the influence of oxygen and organic acids as catalysts. These products - mono, bis, tris - indolylphenalenes/nones - are still gasoil soluble. At a second step under the influence of (powerful) organic acids a salt formation results with the consequence, that reaction products become insoluble in gasoil and fall out. This reaction in simplified form is shown in figure 3.

The hypothesis has been paralleled by the synthetic production of indolylphenalenes and the identity with the obtained sediments compared to the naturally occuring ones has been proven.

Bernasconi et al. [42 - 46] have confirmed these reactions in further research. They were able to prove in LCO phenalenylradicals, which occur as relatively stable intermediate products from the oxidation reaction and which may also be responsible for the ageing reaction which cannot be suppressed by the known antioxidants.

This theory is supported by the fact, that in all tested LCO's or blends with LCO either phenalenes (fresh) or phenalenones (aged) have been found. A direct dependency of the sediment formation from phenalenes and phenalenones content has been published by Marshman [41].

The theory can explain the existence of SMORS only for aged gasoils containing LCO, which were identified by Malhotra [26] as mono, bis and trisindolylphenalenes. Also the SOP found in high boiling fractions as well as the strongly sedimentation promoting distillation residue of LCO (Bernasconi et al [47] can be explained by the indolylphenalenes boiling at higher temperatures as gasoil.

The theory of Pedley et al: "4 different components (oxygen, reactive olefinic hydrocarbons, non-basic nitrogenheterocyclics and organic acids) have to be present at the same time to allow sedimentation" can explain many so far not understandable results of the past, e.g. incompatibility, induction period, influence of strong bases.

Because up to 20 % polar bi-, poly- and heterocyclic aromatics can be adsorbed at the sediments, the partly incompatible results of element analysis and conclusion thereof can be explained.

It appears, that the reaction mechanism by Pedley allows an allround conclusive explanation of sedimentation ageing of gasoils; various authors want to view this however not as the only possible one.

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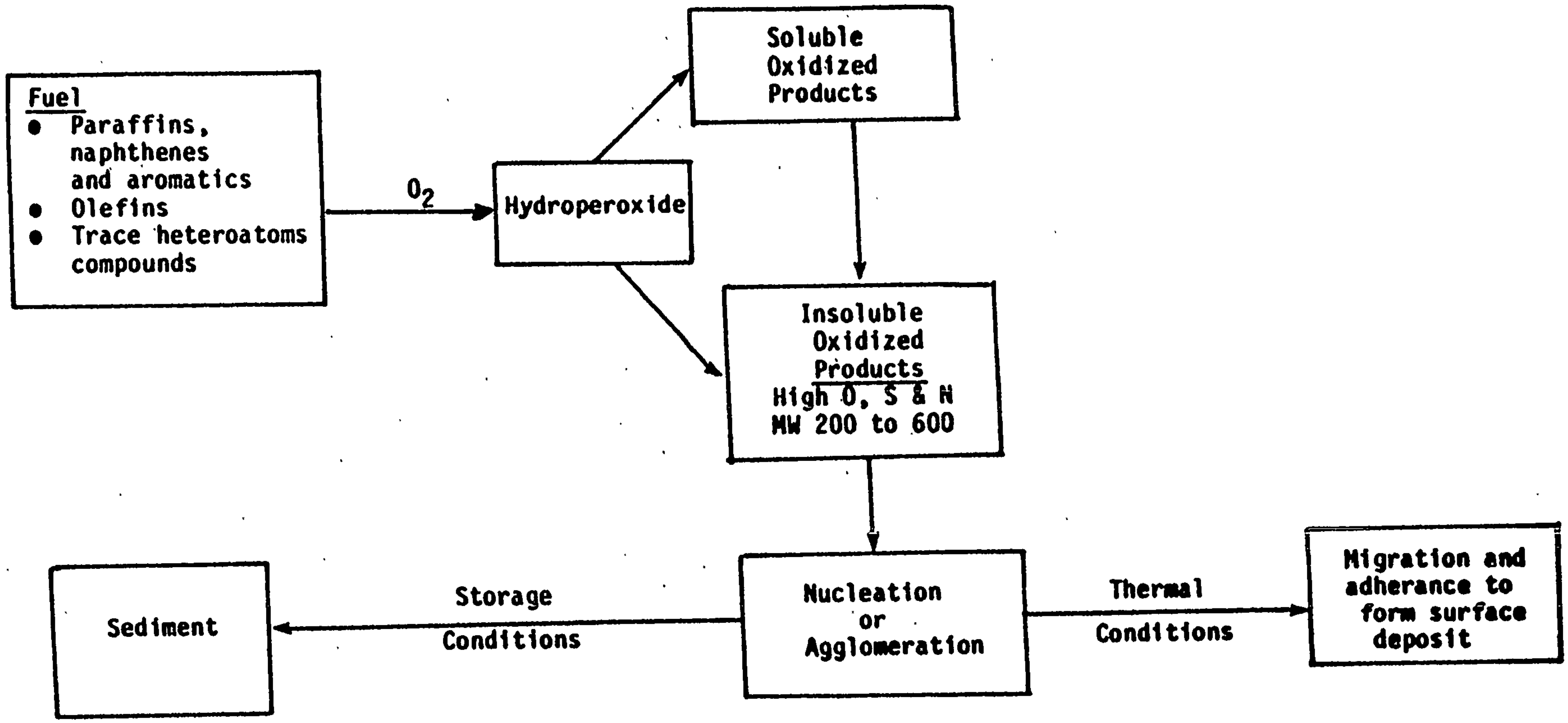
(IN-)STABILITY OF GASOIL

Type	Storage stability						Thermal Stability	
	Colour formation	Sediment				aggressive Substances	Sediment	Desposition on hot Surfaces
		org. Sediments			anorg. Sediments			
		caused by gasoil	extraneous					
			Microorganism.	Incompatibility				
Consequences	none, but customers prefer lightly coloured products		Poor Filtrability, filterplugging			Damage of elastomeric of tubingmaterials, gaskets in motors	Poor filtration, filterplugging	Poor heat exchange injectorfouling, - coking
Reasons	instab. HC	instab. HC	Microorganisms like Bacteria, Fungi + H_2O	different HC composition	Rust, sand other solids, H_2O	Formation of hydroperoxides	accelerated ageing at higher temperatures.	Polymerisation, cracking
Reaction	Oxidation of instab. HC first step to sediment-formation	Olefinic, aromatic, heterocyclic HC and organ. acids in O_2-atmosphere → deepening of colour → soluble gum → insol. gum → sediment	free water in GO + Microorganisms → coherent mats at the oil waterface	paraffinic and highly aromatic/ asphaltenic gasoils are sometimes incompatible.Seldom with GO, more often Fuel Oil	Corrosion of tanks, Pipelines, transfer utilities, H_2S-formed by sulfat-reducing bacteria → iron-sulfide	Oxidation of HC in hydrogenated GO or GO with low heterocyclic components	soluble gum + high temperatur → sedimentformation	soluble Gum → deposition; RC00HI → RCOO $^{\bullet}$-radials + instab. HC →polymerisation; therm. instab. HC, e.g. olefines → cracking → coke deposition
Possiblities of prevention	Hydrogenation of GO, nothing else	Sufficent hydrogenation, otherwise only limited possiblities, e.g. basic tert. amines can reduce oil sediment formation with some gasoils	keep GO dry; addition of biocides	avoid mixing of extreme GO, especially in transport	Good house Keeping	Addition of anti-oxidants, e.g. hindered phenols	Hydrogenation, other possibilites limited	Hydrogenation of instab. HC, addition of antioxidants with hydrogen. fuels, e.g. Jet, GO with max. 50 ppm S

Figure 1

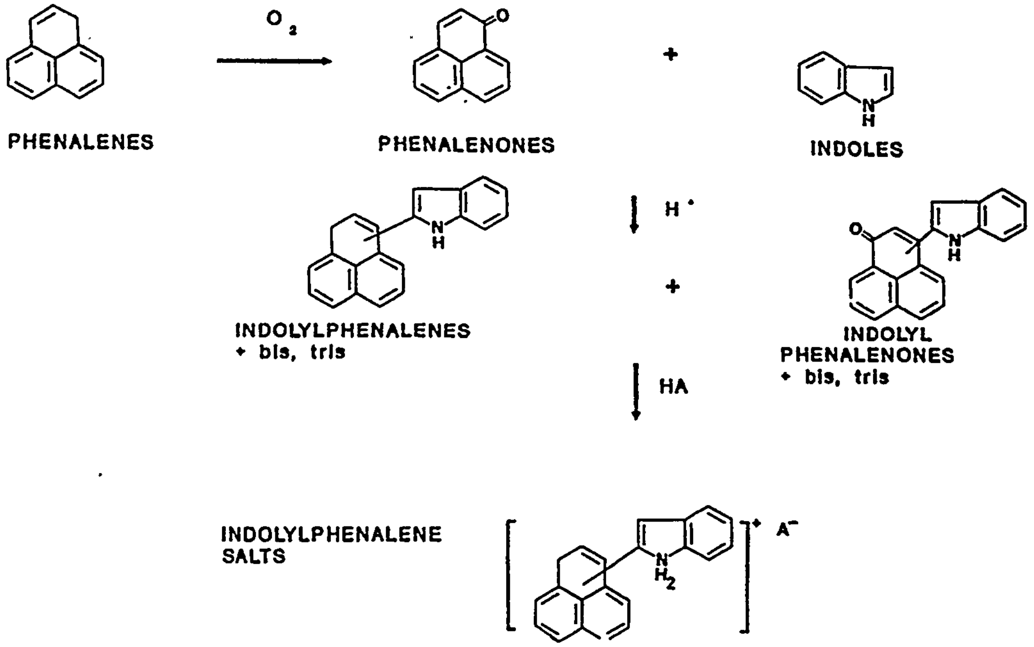
Fuel Stability Coupled Chemical and Physical Process



Source: Taylor et al

Figure 2

REACTION MECHANISM FOR SEDIMENT FORMATION



Source: Marshman

Figure 3

NON - HYDROCARBON ELEMENTS MAJOR CAUSE OF PROBLEMS

	GASOIL % (WT)	SEDIMENTS % (WT)
CARBON	~ 85	70 - 80
HYDROGEN	13 - 14	6 - 7.5
NITROGEN	< 0,08	1.5 - 3.5
SULFUR	0.1 - 1	1 - 6
OXYGEN	< 0.05	7 - 15

Table 1

Effect of Phenols on Fuel Stability

Phenol-Type	Reference	Result	Remarks
Phenols	Offenhauer et al [60]	not reactive	Exception: 1.-Naphthol
	Nixon [1]	reactive	more than other O-containing HC's FCC-SR Mix
	Hazelett et al [7, 10]	reactive	
	Fookes et al [52, 53]	reactive	in Austr.Shale Oil
Phenols, polyaromatic	Bhan et al [61]	reactive	
Phenols, monoaromatic	Bhan et al [61]	weak reactive	
1-Naphthole	Offenhauer et al [60]	reactive	

Effect of Nitrogen Compounds on Fuel Stability

Nitrogen Compound	Reference	Result	Remarks
Pyrrole	Thompson et al [48]	reactive	SR+FCC Mix, 43 °C
Alkylpyrroles	Thompson et al [48]	reactive	SR+FCC Mix, 43 °C
	Hazelett et al [49]	reactive	in Shale Oil (D1), 80°C
	Cooney et al [50, 51]	reactive	in Shale Oil (D1), 43°C
	Fookes et al [53, 53]	reactive	most reactive Compounds in crude Shale Oil
	Frankenfeld et al [54]	reactive	SR-F, JP, n-C10, amb., 43 °C, 65 °C
Di-M-Pyrrole	Frankenfeld et al [54]	very reactive	Oligomerisation of DMP only
	Conney et al [50, 51]	very reactive	in Shale Oil (D1,D11) 43°C-120°C
	Loeffler et al [55]	very reactive	H-Coal Liq., Jet, DF, 50°C
	Mushrush et al [56]	very reactive	in Shale Oil (D11),43-80°C
Tri-M-Pyrrole	Frankenfeld et al [54]	reactive	SR-DF,JP, n-C10, 43°C, 66°C
Alkylindoles	Thompson et al [45]	reactive	SR+FCCMix, 43°C
	Offenhauer et al [57]	very reactive	FCC, 43°C
	Cooney et al [50, 51]	reactive	in Shale Oil (D1,D11)
	Hazelett et al [49]	reactive	in Shale Oil (D1), 80°C
	Hiley et al [31-37]	reactive	DF, amb., 43°C
	Dorbon et al [42, 45]	reactive	FCC/FCC-SR Mix, 43°C, 120 °C
2-M-Indole	Jones et al [58]	not reactive	Shale Jet, 80 °C
	Beraneck et al [59]	very reactive	FCC-SR Mix, 95°C
	Tort et al [43, 44]	reactive	
	Frankenfeld et al [54]	weak reactive	SR-DF, IP, n-C10

Table 2/1

Nitrogen Compound	Reference	Result	Remarks
3-M-Indole	Cooney et al [62]	reactive	Shale Oil (D11), 80°C
	Beraneck et al [59]	not reactive	FCC-SR Mix, 95°C
7-M-Indole	Jones et al [58]	weak reactive	Shale Jet, 80°C
2,5-D-M-Indole	Jones et al [58]	not reactive	Shale Jet, 80°C
Alkylcarbazoles ,	Dorbon et al [42, 45]	not reactive	FCC-SR Mix, 43°C, 120°C
Tetrahydrocarbazole	Veloski et al [63]	reactive	
N-ethyl-carbazole	Thomposon et al [45]	not reactive	FCC-Sr Mix, 43°C
Dodecahydrocarbazole	Cooney et al [50, 51]	very reactive	Shale Oil (D1), 43 °C
	Beal et al [64]	very reactive	Shale Oil (D1,D11), 43°C, 80°C
	Mushrush et al [56]	very reactive	Shale Oil (D1,D11), 43°C, 80°C
Quinolines	Cooney et al [50]	not/weak reactive	Shale Oil (D1), 43°C
Quinoline	Thomposon et al [45]	not reactive	SR-FCC-Mix 43°C
	Offenhauer et al [57]	not reactive	FCC, 43°C
	Frankenfeld et al [54]	not reactive	
ISO-Quinoline	Thompson et al [45]	weak reactive	
Di-M-Quinoline	Loeffler et al [55]	weak reactive	
	Beal et al [64]	not reactive	Shale Oil (D1,D11), 43°C, 80°C
	Mushrush et al [56]	not reactive	Shale Oil (D11), 43°C, 80°C
2-M-Quinoline	Frankenfeld et al [54]	not reactive	
Aniline	Dorbon et al [42, 45]	not reactive	
Di-ethyl-Aniline	Hazelett et al [49]	not reactive	FCC-SR Mix
Pyridine	Offenhauer et al [57]	not reactive	
Alkylpyridines	Cooney et al [50, 51]	weak reactive	in Shale Oil
	Musrush et al [56]	weak reactive	in Shale Oil
2-M-Pyridine	Beal et al [65]	not reactive	in Shale Oil
	Mushrush et al [56]	not reactive	in Shale Oil
2,6-Di-M-Pyridine	Hazelett et al [49]	not reactive	in Shale Oil
2,4,6-Tri-M-Pyridin	Hazelett et al [49]	not reactive	in Shale Oil
2-Amino-Pyridin	Thompson et al [45]	weak reactive	
Phenylendiamines	Hazelett et al [46]	very reactive	DF, FCC-SR Mix
	Schrepfer et al [20]	not reactive	Antioxidant!?
Tri-alkyl-Amines	Hazelett et al [66]	not reactive	prevent sediment by neutral acids
2-ethyl-Hexylamine	Hazelett et al [49]	not reactive	weak sediment prevention
Benzylamin	Hazelett et al [49]	not reactive	weak sediment prevention

Table 2/2

5TH INTERNATIONAL CONFERENCE
ON STABILITY AND HANDLING OF LIQUID FUELS
Rotterdam, the Netherlands
October 3-7, 1994

EVALUATION OF COMMERCIAL STABILITY ADDITIVES IN MIDDLE DISTILLATE FUELS

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ABSTRACT

Ten commercial distillate stability additives were evaluated to determine their effect on the stability and chemistry of two distillate fuels. The two fuels were light catalytic cycle oil (LCCO) and a diesel fuel blend containing 15% of the same LCCO. Additives were evaluated for their ability to improve stability as measured by three test procedures. Also, their effect on fuel composition was measured. All additives were essentially sulfur-free nitrogen-containing compounds. Most of the nitrogen in each additive was basic nitrogen. Additive effectiveness did not correlate with total or basic nitrogen content. Additives that were blends of stabilizer, dispersant, and metal deactivator did not show a clear performance improvement when compared to additives of a simpler composition. The most cost-effective additive in improving stability was N,N-dimethylcyclohexylamine, with only one other additive giving comparable performance. One additive decreased stability. All additives were found to inhibit the formation of SMORS, species reputed to be sediment precursors. Also, all additives promoted increased levels of phenalenones that were formed in aged LCCO. The effect on SMORS and phenalenones are consistent with current theories of distillate instability chemistry.

INTRODUCTION

The problem of diesel fuel storage instability has been recognized for many years.[1] When diesel fuel is composed of straight run distillate, stability is generally good. However, when cracked stocks are incorporated into the fuel, storage stability can be adversely affected.[2] Poor diesel fuel storage stability is characterized by increased levels of insolubles (sediment) and darkened color. The insolubles can cause plugging problems in fuel filters and injectors.[3] Although darker color is not a real problem in and of itself, it is often associated with increased fuel insolubles, and is therefore unacceptable to many diesel fuel users.[2,4]

The chemistry of diesel fuel instability is complex. Certain unsaturated hydrocarbons have been shown to be more susceptible to instability.[5,6] Likewise, certain nitrogen and sulfur-containing compounds have been implicated as causes of diesel fuel instability.[1,7,8] Sulfonic acids have been shown to strongly promote sediment formation.[9] Although sulfonic acids are not usually present in freshly refined diesel fuel, it has been hypothesized that other sulfur-containing species are oxidized to produce the sulfonic acids.[10] Five years ago, J. F. Pedley proposed a mechanism that unified much of the previous observations concerning the various contributions of diesel fuel compounds to instability.[11] Although the Pedley mechanism cannot account for all diesel fuel instability,[12-13] it remains a useful advance in the understanding of distillate chemistry.

Refiners have used additives for many years to control diesel fuel storage instability. However, traditional antioxidants do not improve the storage stability of diesel fuels. Hindered phenols have little or no effect; aryl amines are detrimental, significantly increasing sediment formation.[14] Diesel fuel stability-enhancing additives are generally basic nitrogen-containing materials.[15] Historically, a common such additive has been N,N-dimethylcyclohexylamine. The effectiveness of this additive as reported in the literature is given in Table I. It has been proposed that stability additives work by neutralizing acidic species that would otherwise catalyze and/or directly participate in sediment-forming reactions.[16] While basic nitrogen additives have shown varying success in reducing sediment formation, they have been less effective in preventing color formation.[17,18] One group of researchers showed that when diesel fuels containing cracked stocks used tertiary amine additives, alkyl indole levels decreased less than when no additive was used. However, even when indole levels did not decrease, a significant amount of sediment still formed. This was viewed as evidence that mechanisms other than the one proposed by Pedley occur, and that basic nitrogen compounds are not effective at halting those other mechanisms.[18]

Dispersants have also been used to improve the stability-related performance of diesel fuels. Dispersants not containing basic amine groups do not inhibit the chemical reactions causing sediment formation, but inhibit sediment nucleation.[18] The use of dispersants to improve diesel fuel storage stability has been controversial. Several studies have shown that dispersants can actually increase measured sediment and/or decrease fuel filterability.[7,19] However, these adverse affects may be avoided and beneficial results achieved when the correct dispersant for a given fuel is used at a sufficient concentration.[20] Apparently, when dispersants are incorrectly used, sediment can be suspended in the fuel without being sufficiently dispersed to prevent filter plugging.[7] It has also been observed in several studies that dispersants can prevent otherwise adherent, gum-like instability products from depositing on test containers or fuel tank walls. These adherent materials can then adversely affect filter plugging.[19,20] The incremental effectiveness of dispersants is further complicated by the fact that many of these additives contain basic nitrogen groups as part of the moieties responsible for their dispersant properties.[21-27] Therefore, a clear separation of sediment dispersion and sediment inhibition can be difficult. Also, dispersants can aggravate water emulsion problems.[14,28]

Metal deactivator additives (MDA) have also been used in combination with basic nitrogen-containing stabilizers and dispersants to improve the storage stability properties of diesel fuels.[14] The MDA most commonly used in fuels is N,N′-disalicylidene-1,2-propane diamine. The usefulness of these additives is unclear, especially where trace metal contamination of the fuel is negligible.[17,28]

Often, combinations of basic nitrogen-containing stabilizers, dispersants, and metal deactivators are used. Prior studies have not provided a clear picture of the effectiveness of such combined additives. Several studies found best performance when a combination of tertiary amine stabilizer and metal deactivator was used.[14,17] A later study found that tertiary amines when used alone were most effective.[28] Another group of researchers found that dispersant/MDA combinations were more effective in reducing sediment formation than tertiary amine/MDA combinations.[18] However, the dispersants used contained nitrogen and may have also acted as true stabilizers.

The objective of the work documented herein was to evaluate a relatively large set of commercial stability additives using refinery-fresh diesel fuel.

EXPERIMENTAL

Additives

Ten commercial distillate stability additives were evaluated in a non-hydrotreated LCCO and in a diesel fuel blend containing 15%(vol) of the same LCCO. Additives and their concentrations were selected by the additive vendors after we discussed our planned tests with them. Two of the additives were also evaluated at twice the recommended concentrations, based on our prior experience with those additives. Comparative information on the additives is given in Table II.

The type of additive most commonly recommended was a blend of stabilizer, dispersant, and metal deactivator. Only one additive, Additive E, included a corrosion inhibitor, a dimer acid obtained by Diels-Alder condensation of unsaturated fatty acids.

Additive E was evaluated only in the 15% LCCO blend since it was not available when the LCCO samples were taken.

Additive F was N,N-dimethylcyclohexylamine. This additive was chosen since it has been a common distillate stabilizer additive for more than 30 years. Because of this long history of usage, Additive F was used to normalize cost considerations for all additives.

Fuel Samples

Stability additives were added to fresh hot LCCO using the following procedure. Each additive was added to an empty, labeled, one-gallon can in an amount sufficient to give the desired concentration when the can was three-quarters full. The cans were then taken to the refinery catalytic cracking unit and filled three-quarters full at the hot LCCO rundown. Each can was vigorously shaken upon filling to ensure complete mixing of the additive in the hot LCCO. A one-gallon can without any additive was also filled with LCCO as a control.

In addition to the additive-treated LCCO samples, an additive-free diesel fuel blend was made in the laboratory using the following composition:

Hydrotreated No. 2 Distillate	42.5 %(vol)
Straight Run No. 2 Distillate	25.5 %(vol)
Straight Run No. 1 Distillate	17.0 %(vol)
LCCO (Additive-Free)	15.0 %(vol)

The individual blend components were obtained fresh at the respective refinery units at the same time as the LCCO. Portions of the diesel fuel blend were additized with the various additives several days later, using the concentrations given in Table II. A portion of the diesel fuel without additives was also retained as a control.

Tests

The additives were analyzed for total nitrogen, basic nitrogen, and total sulfur. Test procedures were the same as those used to analyze the LCCO samples.

The following analytical tests were run on the LCCO samples:

1. Total Nitrogen by chemiluminescence (ASTM D4629, modified)
2. Basic Nitrogen (ASTM D2896)
3. Total Sulfur by X-Ray Fluorescence (ASTM D2622)
4. Neutralization Number (ASTM D974)
5. SMORS
6. Phenalenone analysis

The modification to the ASTM D4629 total nitrogen procedure was that the fuel sample was delivered to the combustion tube by a platinum boat rather than by standard syringe injection. SMORS (Soluble Macromolecular Oxidatively Reactive Species) are believed to be sediment precursors,[29, 30] and the procedure used for measuring them has been previously documented.[31] Phenalenones are also implicated as participating in distillate fuel storage instability.[11,32] The analytical method used to measure them was based on a previously documented procedure.[33]

The LCCO samples were also evaluated for initial ASTM D1500 color and ASTM D4625 storage stability (13 weeks, 110°F). Stability tests were run in duplicate. After D4625 tests were completed, the aged, filtered LCCO samples were re-evaluated by the analytical tests listed above.

The following tests were run on the 15% LCCO diesel fuel blend samples:

1. Initial ASTM D1500 Color
2. ASTM D4625 (13 weeks, 110°F)
3. ASTM D2274 (16 hours, 210°F)
4. Nalco Pad (90 minutes, 300°F)

The ASTM procedures are well documented and will not be described further here. All D4625 tests were run in duplicate. All other tests were performed in single runs.

The Nalco Pad Test is a well established distillate fuel stability test procedure, also known as the EMD-Diesel Fuel Stability Test, the Union Pacific Diesel Blotter Test, and the Santa Fe Blotter Test. The procedure involves: heating a 50 ml. sample at 300°F for 90 minutes; allowing the fuel to cool to room temperature; filtering it through a Whatman No. 1 filter paper; rinsing the filter with n-heptane until all remaining fuel is removed; allowing the filter to air dry; and visually rating the filter against a set of numbered standard filters. The Nalco Pad Test is a common U. S. pipeline specification test for fungible No. 2 distillate fuel stability,[34-36] although it is well known that such tests do not correlate well with real storage stability.[4]

RESULTS AND DISCUSSION

Detailed results are given in Tables II-VI. Graphical presentations of the most important points are given in Figures 1-16. A discussion of these points is given in the following three sections.

LCCO Samples: Additive Effectiveness

1. The most effective additives, independent of cost, in reducing ASTM D4625 aged sediment were Additives B, C, D, F, H, and J (Figure 1).

2. The most effective additives, independent of cost, in reducing ASTM D4625 aged color were Additives D, F, G, and H (Figure 2). Additives were not nearly as effective in reducing aged color as they were in reducing aged sediment.

3. The most cost-effective additives were F and H. The least cost-effective additives were Additives A, J, and I (Figure 3).

4. Increasing the dosage of Additives F and H to twice the recommended level had little or no additional benefit (Figures 1-2).

5. Additives containing stabilizer, dispersant, and metal deactivator showed no clear improvement over additives of a simpler composition. No additive clearly outperformed the long-used Additive F (N,N-dimethylcyclohexylamine).

LCCO Samples: Additive Chemistry

1. All the stability additives evaluated were sulfur-free, nitrogen-containing compounds. Most the nitrogen in each stability additive was basic nitrogen (Figure 4). Of the four additives containing a dispersant, two (Additives C, D) utilized a dispersant in which all its nitrogen was basic.

2. There was not a strong correlation ($r = 0.60$) between the basic nitrogen of the additives or additive-treated LCCO and ASTM D4625 aged sediment reduction (Figure 5). This indicates that basic nitrogen content as measured by ASTM D2896 is not the only parameter influencing an additive's ability to affect ASTM D4625 aged sediment. A

comparison of Additives F, H, and I provides a good example of the poor correlation between basic nitrogen content and stability enhancement.

3. All stability additives inhibited the formation of SMORS in LCCO. This was somewhat evident in the initial SMORS values; it was especially evident in the SMORS measured after aging the LCCO samples under ASTM D4625 conditions (Figure 6). Actually, both sets of data reflected aged LCCO samples, since the "initial" SMORS values were measured after three months storage at 40°F. This result is especially significant since it supports several theories about diesel fuel instability chemistry. Stability additives have been purported to work by reacting with acidic species, thereby preventing acid-catalyzed reactions such as condensation reactions of multi-ring aromatics (phenalenones) with alkyl indoles.[11, 16] These condensation products are believed to be fuel-soluble sediment precursors and, as already mentioned, are candidates for SMORS. The inhibition of SMORS formation by stability additives is consistent with both notions.

4. There was not a strong quantitative correlation ($r = 0.44$) between aged SMORS and ASTM D4625 aged sediment (Figure 7). Test method precision may have been part of the reason, but other factors were probably also important. For instance, one of the most effective additives for preventing SMORS formation, Additive I, actually promoted sediment formation. Obviously, the inhibiting effect of additives on SMORS formation is only one aspect by which sediment formation is restricted. Also, SMORS may not be the only intermediate that leads to sediment and color bodies. In the case of Additive I, the additive itself may be introducing a new reaction pathway. It is interesting to note the singularly high total and basic nitrogen levels in Additive I. There was a strong correlation ($r = 0.83$) between aged SMORS and ASTM D4625 aged color (Figure 8), supporting the idea that SMORS directly contribute to aged color.

5. All stability additives promoted an increase in the level of phenalenones in aged LCCO. This was somewhat evident in the initial phenalenone values; it was especially evident in the phenalenones measured after aging the LCCO samples under ASTM D4625 conditions

(Figure 9). Actually, both sets of data reflected aged LCCO samples, since the "initial" phenalenone values were measured after one month storage at 40°F. The significance and reasoning behind this trend are similar to that discussed concerning SMORS in item 3, above. Phenalenones are known to form by the facile oxidation of phenalenes. Stability additives do not inhibit this oxidation reaction, but they are reputed to inhibit the further reaction of the phenalenones with alkyl indoles. It has previously been shown that alkyl indoles decrease less in diesel fuels that have stability additives.[18] The observed effect of stability additives on aged phenalenones in LCCO is consistent with this proposed mechanism.

6. There was not a strong quantitative correlation between aged phenalenones and ASTM D4625 aged sediment ($r = -0.33$) or aged color ($r = -0.52$) (Figures 10-11). The expected inverse relationship between aged phenalenones and aged sediment or color was not very apparent. Test method precision may have been partially responsible. The relative standard deviation of the phenalenone analysis method is believed to be about 5%.[37] The relatively small difference between the aged color and sediment values for many of the LCCO samples must also be considered. However, there are probably other reasons why a quantitative relationship between aged phenalenones and stability would not exist. Other reaction pathways that are not impeded by the stability additives may be available to phenalenones. Also, it has been shown that other multi-ring aromatics besides phenalenones can react with alkyl indoles to form sediment-like species.[38] Therefore, even a complete blocking of the reaction of phenalenones may not entirely prevent the formation of sediment or color bodies.

Diesel Fuel Samples: Additive Effectiveness

1. ASTM D4625 results were very good for the additive-free diesel fuel blend, leaving no room for significant improvement by any of the additives evaluated (Figures 12-13). Apparently, the 15%(vol) LCCO in the diesel fuel blend was not sufficient to cause

instability as measured by ASTM D4625. Additive I caused a decrease in stability, similar to its effect in pure LCCO.

2. Only a moderate level of ASTM D2274 instability was measured for the additive-free diesel fuel blend. The most effective additives by this test were Additives F, G, H, and J; Additive I was the least effective (Figures 14-15). The ASTM D2274 results are interesting since they are not what are typically expected. Usually, D2274 results underestimate aged sediment when compared with the more reliable D4625.[39-40] The opposite was observed in these diesel fuel samples.

3. Significant Nalco Pad instability was induced by the 15%(vol) LCCO content of the additive-free diesel fuel blend. This illustrates the already known fact that poor Nalco Pad test results are possible even when D4625 stability is good. All stability additives improved Nalco Pad ratings to an acceptable level of 7 or less[34-36] (Figure 16). The most effective additives, independent of cost, were Additives C, D, G, and H. The most cost-effective additive was Additive H.

4. Increasing the dosage of Additives F and H to twice the recommended levels had little or no additional benefit in improving ASTM D2274 or Nalco Pad test results (Figure 14-16). For Additive H, increasing the dosage decreased effectiveness.

CONCLUSIONS

All diesel fuel stability additives evaluated were sulfur-free, nitrogen-containing materials where most of the nitrogen was basic. However, additive effectiveness in LCCO did not correlate well with basic nitrogen content of the additive. Although blends of stabilizer, dispersant, and metal deactivator were commonly recommended by additive suppliers, the most effective additive for reducing sediment formation was the simple and long-used stabilizer N,N-dimethylcyclohexylamine. Only one other additive gave comparable performance. One additive decreased diesel fuel storage stability, and no additive was very effective in inhibiting color body formation.

Although most additives were tested at only one concentration in a given fuel (the concentration recommended by the additive suppliers), the superior cost-effectiveness of the two best additives is probably real. Doubling the concentration of those two additives did not improve fuel stability. Diesel fuel thermal stability was significantly improved by all stability additives, even by the additive that decreased storage stability. This underscores the caution needed when using such highly stressed tests to evaluate the storage stability-improving performance of diesel fuel stability additives.

All additives inhibited SMORS formation and promoted increased levels of phenalenones in aged LCCO. Both of these observations directionally agree with the Pedley mechanism and the acid-base theory of how storage stability additives work. However, the additives's ability to inhibit SMORS and promote increased phenalenone levels did not strongly correlate with their ability to improve overall storage stability. There are several implications from this. First, diesel fuel stability additive effectiveness is not just a manifestation of simple acid-base chemistry. Other properties may be at work. It is well known that tertiary amines can decompose hydrogen peroxide, forming tertiary amine oxides.[41] N,N-dimethylcyclohexylamine has been shown to decrease hydroperoxide levels in jet fuel at elevated temperatures.[42] However, it has not yet been shown that tertiary amines decompose hydroperoxides formed in diesel fuel aged at ambient temperatures. In some cases, an additive may actually contribute to fuel storage instability by enhancing or introducing harmful reaction pathways. Second, the Pedley mechanism, if correct, is likely not the only significant pathway by which diesel fuel instability is propagated. If new diesel fuel stability additives with "quantum leap" improvements in effectiveness are to be developed, improved understanding of these other mechanisms must be achieved.

ACKNOWLEDGMENTS

The contributions of the following people are gratefully acknowledged: Steve Sibo for obtaining the test fuels from the refinery; Susan Taskila for blending and testing the fuels.

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Figure 1

Effect of Additives on LCCO ASTM D4625 Stability

Sediment Values

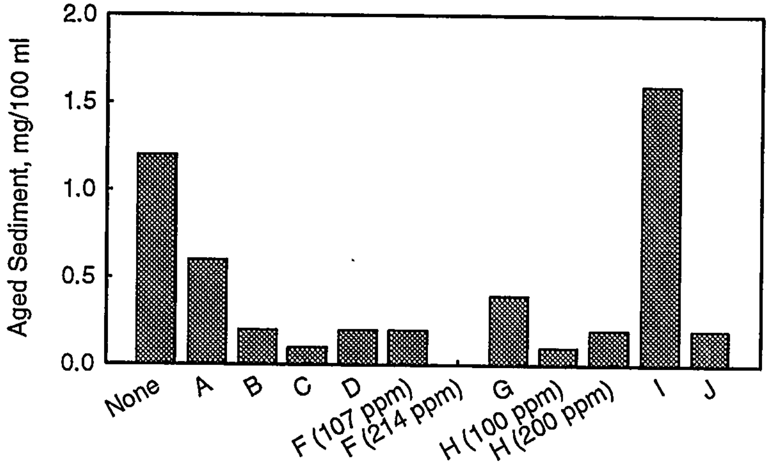


Figure 2

Effect of Additives on LCCO ASTM D4625 Stability

Color Values

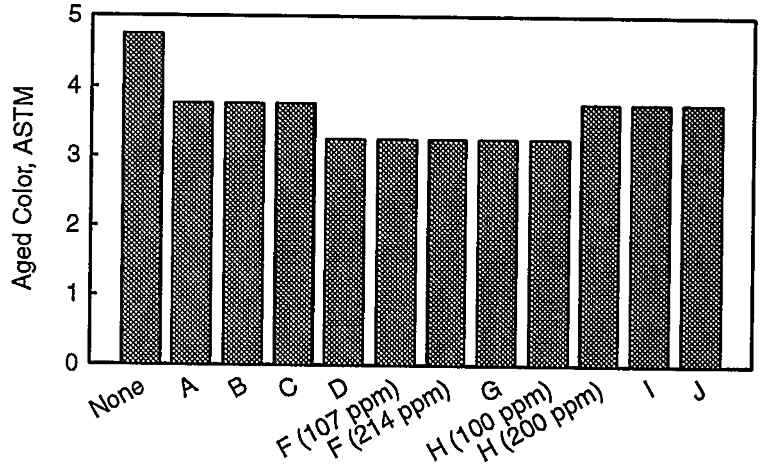
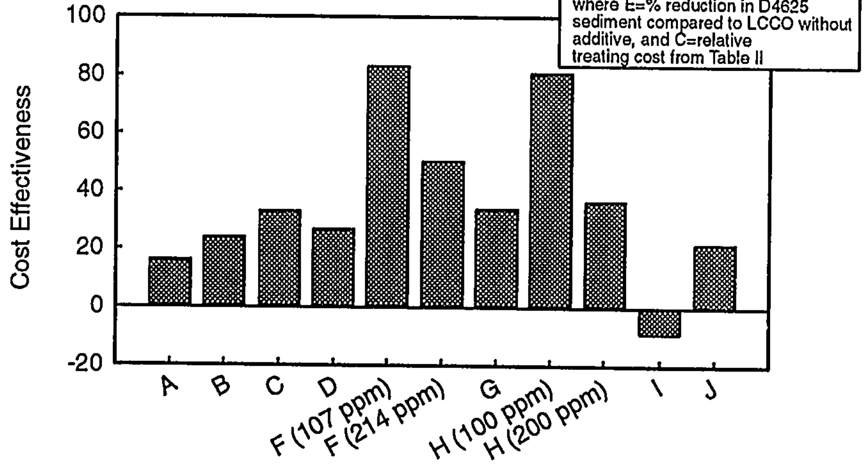


Figure 3

Cost-Effectiveness of Additives at Reducing ASTM D4625 Sediment in LCCO



Cost-Effectiveness is (E/C)(100) where E=% reduction in D4625 sediment compared to LCCO without additive, and C=relative treating cost from Table II

Figure 4

Nitrogen Content of Stability Additives

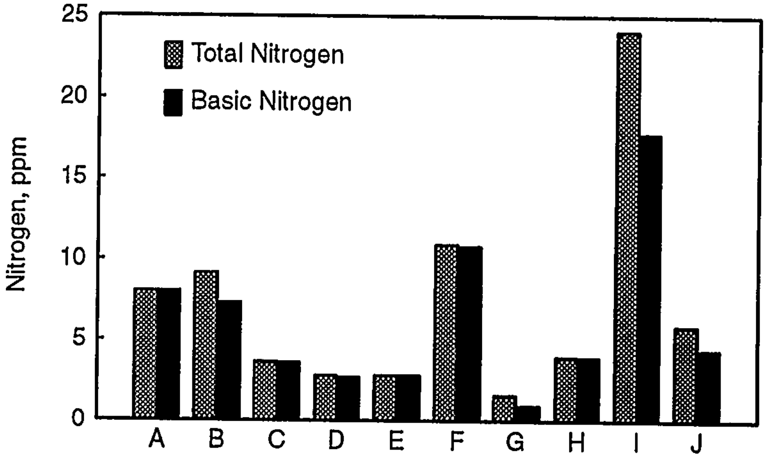


Figure 5

Relationship Between Basic Nitrogen and ASTM D4625 Sediment Values in LCCO

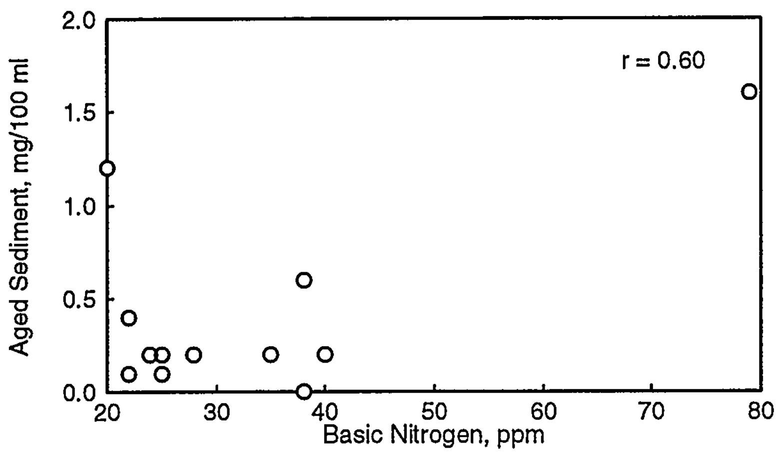


Figure 6

Effect of Additives on LCCO SMORS Content

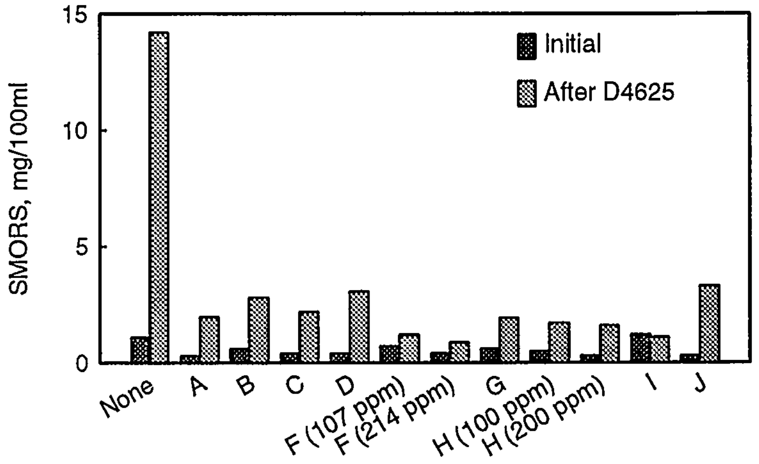


Figure 7

Relationship Between Sediment and SMORS After ASTM D4625 in LCCO

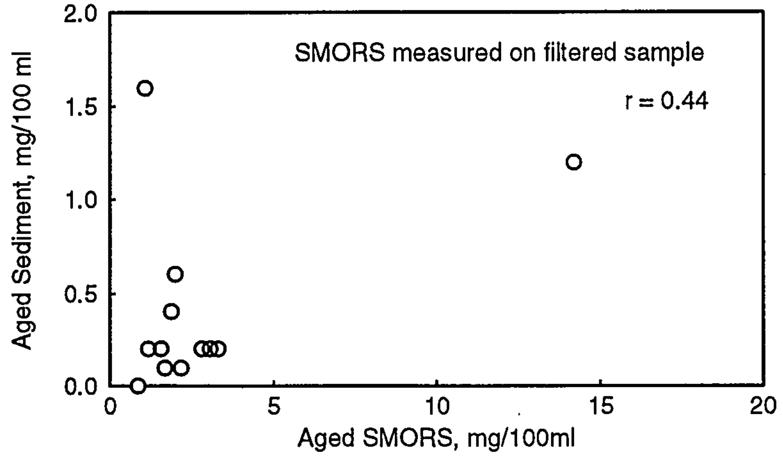


Figure 8

Relationship Between Color and SMORS After ASTM D4625 in LCCO

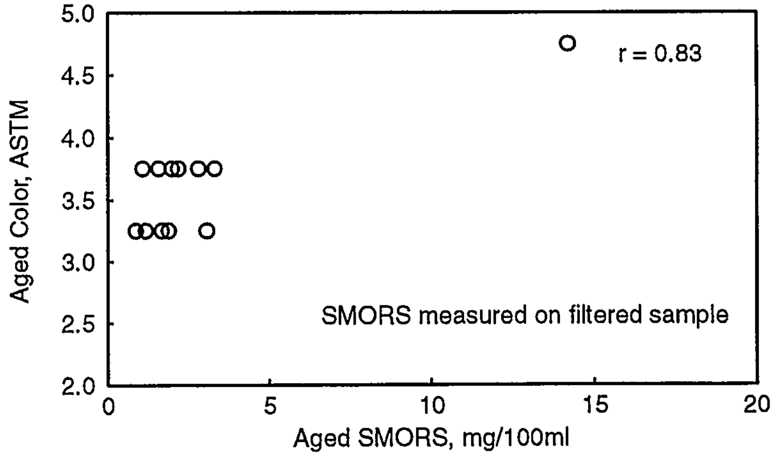


Figure 9

Effect of Additives on LCCO Phenalenones Content

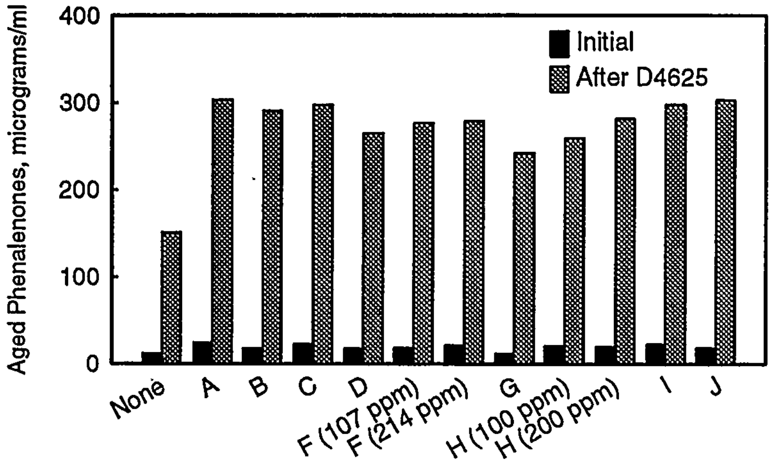


Figure 10

Relationship Between Sediment and Phenalenone Content in LCCO After ASTM D4625

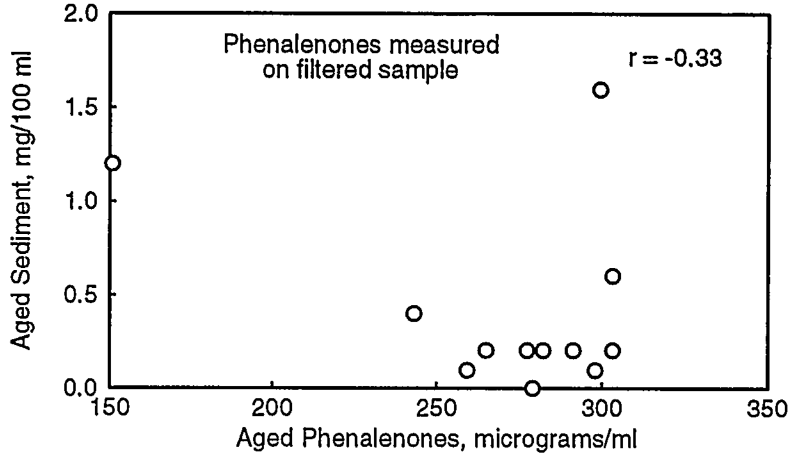


Figure 11

Relationship Between Color and Phenalenone Content in LCCO After ASTM D4625

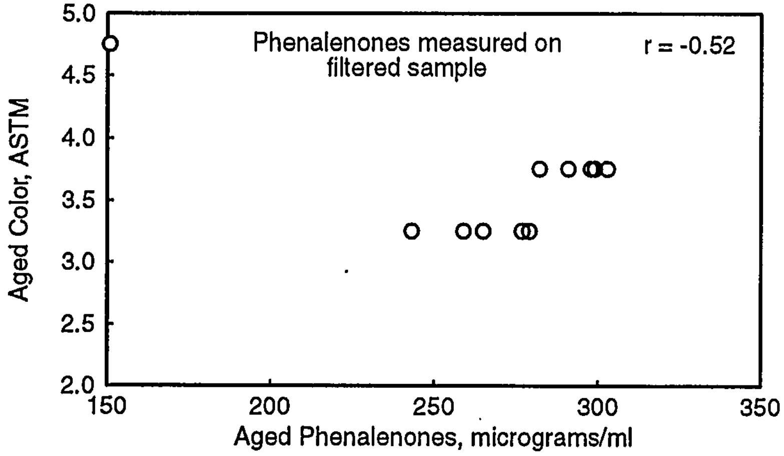


Figure 12

Effect of Additives on ASTM D4625 Stability in Diesel Fuel Blends

Sediment Values

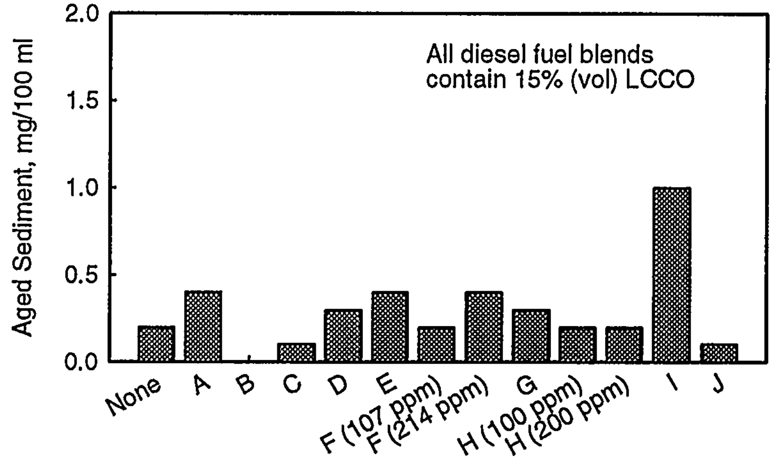


Figure 13

Effect of Additives on ASTM D4625 Stability in Diesel Fuel Blends

Color Values

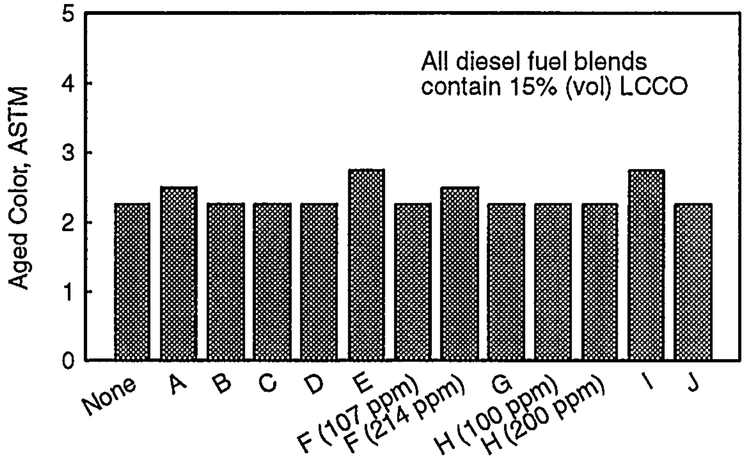


Figure 14

Effect of Additives on ASTM D2274 Stability of Diesel Fuel Blends

Sediment Values

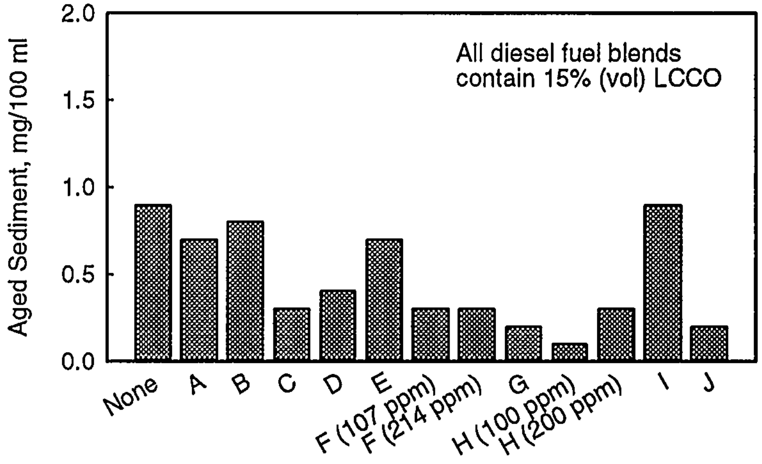


Figure 15

Effect of Additives on ASTM D2274 Stability of Diesel Fuel Blends

Color Values

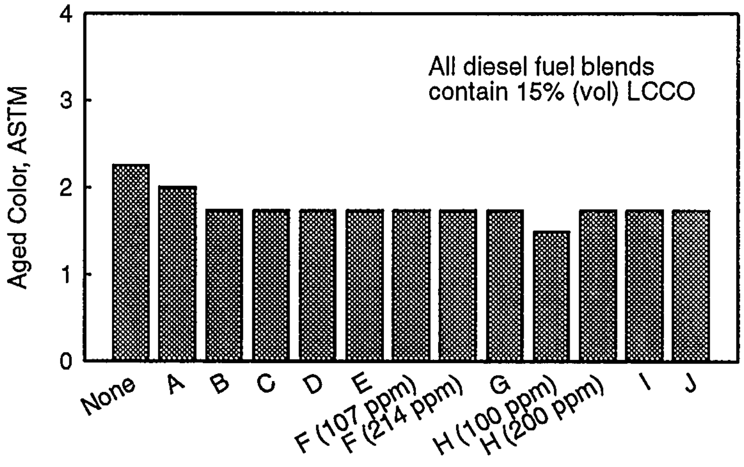


Figure 16

Effect of Additives on Nalco Pad Stability of Diesel Fuel Blends

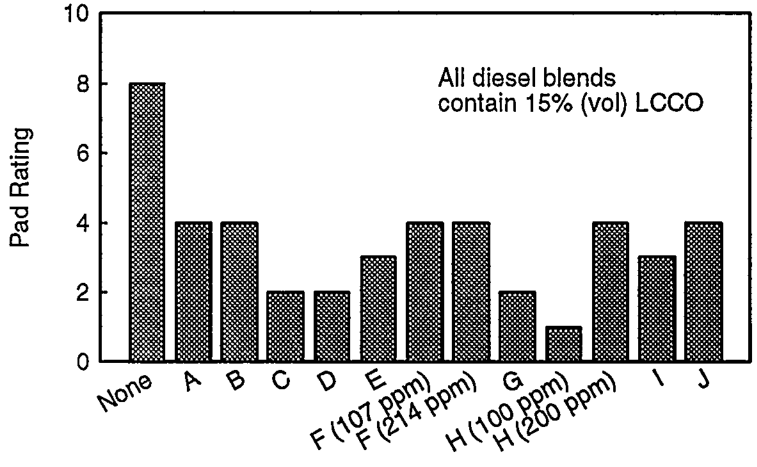


TABLE I

DIESEL FUEL STABILITY ADDITIVE EFFECTIVENESS: N,N-DIMETHYLCYCLOHEXYLAMINE

Source	Test Method Used	Concentration, ppm	Sediment Reduction %	Color Improvement(1)
US 3,490,882	212°F, 16 hr, 100 psig O_2	33	66	7.0-->5.0
US 3,490,882	210°F, 16 hr	33	96	--
US 3,701,641	180°F, 8 days, 5 l/hr air	3.3	53(2)	4.5-->3.5(2)
US 3,701,641	180°F, 8 days, 5 l/hr air.	9.8	40(2)	4.5-->3.5(2)
US 4,040,799	110°F, 4 wks	60	21	--
US 4,867,754	300°F, 90 minutes	100	--	2.8-->2.4
Amoco(3)	110°F, 13 wks	18-58	58	3.5-->3.8
Solly et al.(4)	110°F, 15 months	24	40	--

(1) Improvement is A-->B where A is aged color (ASTM D1500) without additive and B is aged color with additive.
(2) Amount of improvement over an equal concentration of a tetra-amine oligomer.
(3) Unpublished data.
(4) Reference 19.

TABLE II

DISTILLATE STABILITY ADDITIVE INFORMATION

					Dosage, ppm(2)		
Additive Name	Additive Description(1)	Tot. N %(Wt)	Basic N % (Wt)	Tot. S ppm	In LCCO(3)	In FO2(4)	Treating Cost(5)
A	S+S+M	8.0	8.0	26	300	45	311
B	S+D+M	9.1	7.3	31	300	45	345
C	S+D+M	3.7	3.6	32	220	33	281
D	S+D+M	2.8	2.7	78	220	33	302
E	S+C	2.8	2.8	235	57	8.5	29
F	S	10.9	10.8	22	107	16	100
G	S+D+M	1.6	1.0	28	220	33	195
H	S+M	4.0	3.9	324	100	15	114
I	S	24.1	17.8	41	360	54	371
J	S	5.9	4.4	196	367	55	370

(1) S = stabilizer; D = dispersant; C = corrosion inhibitor; M = metal deactivator.
(2) Obtained as recommendations from additive suppliers.
(3) Assumes all additive added to the LCCO.
(4) Assumes 15%(vol) LCCO in diesel fuel.
(5) Treating cost is relative to a normalized value of 100 for Additive F.

TABLE III

EFFECT OF STABILITY ADDITIVES ON LCCO: GENERAL COMPOSITION DATA

Additive Name	None	A	B	C	D	F	G	H	I	J
Dosage, ppm(wt)	--	300	300	220	220	107/214	220	100/200	360	367
Initial Properties(1)										
Total Nitrogen, ppm(wt)	168	186	186	170	169	176/187	170	169/172	219	183
Basic Nitrogen, ppm(wt)	20	38	40	25	24	28/38	22	22/25	79	35
Total Sulfur, %(wt)	0.162	0.162	0.161	0.160	0.160	0.162/0.160	0.161	0.168/0.161	0.159	0.159
Neutralization Number	0.00	0.01	0.01	0.01	0.01	0.01/0.01	0.01	0.00/0.01	0.02	0.01
SMORS, mg/100 ml(2)	1.1	0.3	0.6	0.4	0.4	0.7/0.4	0.6	0.5/0.3	1.2	0.3
Properties After ASTM D4625(3):										
Total Nitrogen, ppm(wt)	172	193	191	178	176	182/191	176	176/178	224	188
Basic Nitrogen, ppm(wt)	21	34	36	25	21	28/36	21	22/26	60	30
Total Sulfur, %(wt)	0.155	0.160	0.159	0.160	0.157	0.158/0.159	0.159	0.159/0.155	0.162	0.159
Neutralization Number	0.01	0.01	0.01	0.01	0.01	0.01/0.01	0.02	0.01/0.02	0.02	0.02
SMORS, mg/100 ml	14.2	2.0	2.8	2.2	3.1	1.2/0.9	1.9	1.7/1.6	1.1	3.3

(1) Further details of the test methods used can be found in the EXPERIMENTAL section.
(2) Measured after three months' storage at 40°F.
(3) ASTM D4625 stability test results can be found in Table V.

TABLE IV

EFFECT OF STABILITY ADDITIVES ON LCCO: PHENALENONE ANALYSIS DATA(4)

Additive Name	None	A	B	C	D	F	G	H	I	J
Dosage, ppm(wt)	--	300	300	220	220	107/214	220	100/200	360	367
Initial Phenalenones, μg/ml(1)										
Phenalenone	5.7	10.8	7.9	9.8	7.8	8.4/9.5	5.6	9.4/8.8	10.9	8.6
8-Me Phenalenone	2.3	4.6	3.3	4.6	3.4	3.7/3.7	2.2	4.2/4.3	4.8	3.8
5-Me Phenalenone	1.8	4.3	2.9	3.9	2.9	3.1/3.4	2.0	3.6/3.4	3.9	3.4
6-Me Phenalenone	0.6	2.1	1.1	1.5	0.8	1.0/1.7	0.7	0.9/1.0	1.0	0.7
7-Me Phenalenone	0.4	1.0	0.9	1.1	1.0	0.9/1.2	0.6	0.6/1.1	1.0	0.7
3+4-Me Phenalenone	0.9	1.6	1.5	1.9	1.5	1.5/1.6	1.0	2.0/1.5	1.6	1.8
Total Phenalenones(2)	11.7	24.4	17.6	22.8	17.4	18.6/21.1	12.1	20.7/20.1	23.2	19.0
Phenalenones after ASTM D4625(3)										
Phenalenone	83.2	148	144	146	132	137/164	116	135/167	188	152
8-Me Phenalenone	35.0	69.3	64.8	67.4	62.9	61.0/62.0	54.3	60.9/63.0	73.2	70.3
5-Me Phenalenone	15.8	33.3	29.7	31.6	30.2	25.7/ND(5)	27.2	23.9/ND(5)	ND(5)	29.0
6-Me Phenalenone	7.5	19.8	20.1	20.4	14.1	20.7/19.9	18.0	14.0/19.9	15.9	19.4
7-Me Phenalenone	4.3	14.5	14.2	14.3	10.0	14.1/14.2	11.8	9.9/13.9	11.0	14.2
3+4-Me Phenalenone	5.5	18.5	18.3	18.1	15.7	18.6/18.5	15.6	15.0/18.3	10.9	18.2
Total Phenalenones(2)	151	303	291	298	265	277/279	243	259/282	299	303

(1) Measured after one month storage at 40°F.
(2) Sum of phenalenone and the various measured methyl phenalenone isomers.
(3) ASTM D4625 stability test results can be found in Table V.
(4) Further details of the test method used can be found in the EXPERIMENTAL section.
(5) Not detected.

TABLE V

EFFECT OF STABILITY ADDITIVES ON LCCO: ASTM D4625 STABILITY DATA

Additive Name	None	A	B	C	D	F	G	H	I	J
Dosage, ppm(wt)	--	300	300	220	220	107/214	220	100/200	360	367
Initial Color(1)	2.5	<3.0	<3.0	<3.0	<3.0	<3.0/2.5	2.5	<3.0/<3.0	<3.0	2.5
ASTM D4625										
Aged Sediment, mg/100 ml										
Rep 1	1.3	0.6	0.2	0.1	0.2	0.1/0/0.0	0.3	0.2/0.2	1.7	0.3
Rep 2	1.0	0.6	0.2	0.1	0.1	0.3/0.1	0.4	0.0/0.2	1.6	0.2
Average	1.2	0.6	0.2	0.1	0.2	0.2/0.0	0.4	0.1/0.2	1.6	0.2
Aged Color(1)										
Rep 1	<5.0	<4.0	<4.0	<4.0	<3.5	<3.5/<3.5	<3.5	<3.5/<4.0	<4.0	<4.0
Rep 2	<5.0	<4.0	<4.0	<4.0	<3.5	<3.5/<3.5	<3.5	<3.5/<4.0	<4.0	<4.0

(1) ASTM D1500

TABLE VI

EFFECT OF STABILITY ADDITIVES ON DIESEL FUEL BLEND STABILITY

Additive Name	None	A	B	C	D	E	F	G	H	I	J
Dosage, ppm(wt)	--	45	45	33	33	8.5	16/32	33	15/30	54	55
Initial Color(1)	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5/<1.5	<1.5	<1.5/<1.5	<1.5	<1.5
ASTM D4625											
Aged Sediment, mg/100 ml											
Rep 1	0.2	0.3	0.1	0.1	0.4	0.4	0.3/0.4	0.2	0.1/0.1	1.0	0.1
Rep 2	0.3	0.4	0.0	0.1	0.2	0.4	0.2/0.3	0.4	0.2/0.2	1.1	0.1
Average	0.2	0.4	0.0	0.1	0.3	0.4	0.2/0.4	0.3	0.2/0.2	1.0	0.1
Aged Color(1)											
Rep 1	<2.5	2.5	<2.5	<2.5	<2.5	<3.0	<2.5/2.5	<2.5	<2.5/<2.5	<3.0	<2.5
Rep 2	<2.5	2.5	<2.5	<2.5	<2.5	<3.0	<2.5/2.5	<2.5	<2.5/<2.5	<3.0	<2.5
D2274											
Aged Sediment, mg/100 ml	0.9	0.7	0.8	0.3	0.4	0.7	0.3/0.3	0.2	0.1/0.3	0.9	0.2
Aged Color(1)	<2.5	2.0	<2.0	<2.0	<2.0	<2.0	<2.0/<2.0	<2.0	1.5/<2.0	<2.0	<2.0
Nalco Pad Stability											
PAD Rating	8	4	4	2	2	3	4/4	2	1/4	3	4
Aged Color(1)	<4.0	<2.5	<2.5	<3.0	<3.0	<3.0	<2.5/<2.5	<3.0	<2.0/<3.0	<2.5	<3.0

(1) ASTM D1500.