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Long Term Storage of Finished Gasolines
in large Salt Caverns

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Chairman, Ladies and Gentlemen

Strategic oil stocking requires large low cost storage facilities. Crude oil has been held in very large salt mines and/or artificially made salt caverns for many years, notably in Europe and the USA. Following crude oil, gasoils and refinery light feed stocks have been tried also. Military organisations tried jet fuel and early cases of underground aviation gasoline storage in steel tanks have been reported.

H I S T O R Y

- CRUDE AND DISTILLATE AND FEEDSTOCK PLENTIFUL
- ATTEMPTS STRATEGIC STOCKS (GASOLINE) VERY RARE IN CAVERNS
 - UNITED KINGDOM 1940 + DURING WW II IN BURIED TANKS
 - ABANDONED
 - SWEDEN UNTIL 1994 IN ROCK CAVERNS ON WATER TABLE
 - NOW BEING TERMINATED
 - GERMANY EBV "OFF SPEC" GASOLINE AT 3 SITES IN SALT EARLY 90'IES
 - NOW "RUNNING MATE" FOR SYNCRUDE
- GERMAN STRATEGIC PETROLEUM RESERVE : FINISHED GASOLINE IN SALT
 - HEIDE PROGRAMME 1985; RENEWAL 1993/94
 - BLEXEN PROGRAMME 1991/92

JWJK/cc-vd-5782

Motor gasolines have been stored in Swedish rock caverns on water table for twenty years or more, some is still there today but the programme is being phased out. In Germany naphtha/ off-specification gasolines were stored in salt caverns as syncrude blend stocks since the early eighties and large volumes are still being held today.

The real challenge started when in the "mid eighties" it was attempted to store finished premium 95 RON motor gasoline in salt caverns in Heide (North Germany) with the objective to recover the gasoline after 5 years or later and deliver it into the retail system without further processing. Now after almost 9 years, we still pump gasolines out of those caverns.

MANUFACTURING FOR CAVERN STORAGE

REFINING

- HYDROSKIMMING STOCKS PREFERRED BUT HARD TO GET
- CAT CRACK BLEND STOCKS AS LOW AS POSSIBLE
- ELIMINATE COKER-, CHEMICAL BY-PRODUCTS
- DO NOT H₂ - OVERTREAT (PRESERVE NATURAL INHIBITORS)

ADDITIVATION

- OXYGEN EX BRINE MAIN ISSUE - ANTIOXIDIZERS
- METALS IONIZED IN FUEL AND BLANK SURFACES - METAL DEACTIVATORS
- CORROSION COSTLY, NO AGEING PROMOTER - CORROSION INHIBITOR
- NO BIOCIDES (ENVIRONMENTAL)

JMJK/cc-70-5TR3

How could this be achieved? Normally modern gasolines - in spite of containing oxidation inhibitors - age in 18 to 24 months in Europe, in the USA due to the higher crack stock ratios sometimes in less than a year, even though "reformulated US gasolines" may be a little bit more stable in future.

The secret is of course hydroskimming and reforming naphthas only, if possible no cracked naphthas. For economic reasons this is impractical, thus reduce it to an absolute minimum. Coker and/or chemical by-products are not allowed and overtreatment of gasolines by e.g. hydrofining should be avoided, as this destroys natural ageing inhibitors like sulfur traces.

As special conditions exist in caverns careful additivition is necessary. Brine contains a fair amount of air when entering the cavern as seawater, thus antioxidants should be plentiful to catch the oxygen before it reacts with gasoline molecules. Salt contains metals like zinc and copper and iron - generally in minute quantities but enough to act catalytically, so does stainless steel which is used for sampling devices, thus metal deactivators should be added.

As corrosion reactions are suspected to promote ageing, also corrosion inhibitors are advisable. So far no microbial activity has been found in German caverns, thus biocides would not be needed, they would also contaminate the brine and may pose at discharge of brine an environmental hazard. This is the set of precautions, as we understand them today.

WHAT PRESERVED THE HEIDE GASOLINE ?

- LOW ON CRACKED STOCKS IN BLEND (< 17%)
- REFINERY: FED DIRECTLY INTO CAVERN
 - * CRACKER: SEVERITY MODEST, UNUSUAL TYPE: "THERMOFOR" CATALYTIC CRACKER
 - OLEFIN CONTENT LOW: < 20 WT% IN BLEND
 - * NATURAL PROTECTIVE COMPONENTS IN VIRGIN NAPHTHA - DISULFIDES FROM MEROX
 - * ADDITIVES - BUT LOW RATE - AS ANTIOXIDIZERS (HYTEC 4733)
- SMALL TEMPERATURE GRADIENT PREVENTS CONVECTION/MIX FLOW
- SALT DOES NOT CONTAIN CATALYTIC METALS
- BRINE LOW ON OXYGEN, A GUESS ONLY

BUT: HEIDE STILL CONSIDERED RISKY IN EARLY '90IES
RESULT SOME SURPRISE AND A BIT OF LUCK

JWJK/CC-90-5785

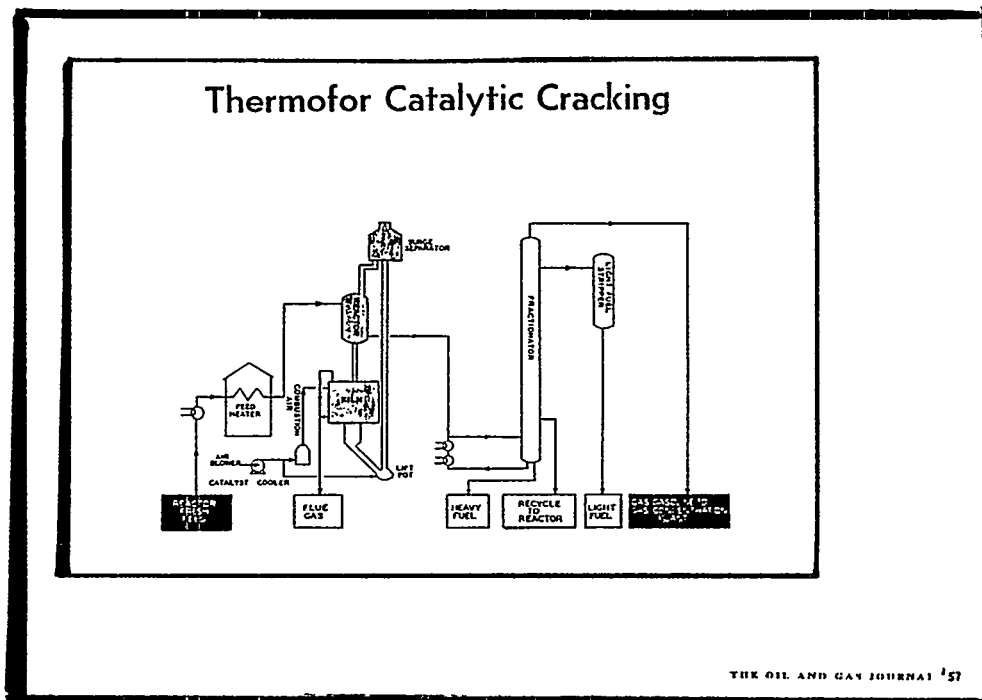
But what preserved the Heide gasoline for so long as some of its stock is now 9 years old. Some of the protective measures were planned, others may have been windfalls.

Indeed the crack stock content was kept low at 17% and the gasoline was fed directly into the caverns as the Heide refinery more or less stands on top of it.

The cracker run at modest severity is of a type known for manufacturing stable products. It is an old Thermoform process. There were disulfides from a MEROX unit sweetening the virgin naphtha portion and acting as natural inhibitors to ageing. The Heide refinery has no disulfide extraction unit normally used to increase lead susceptibility in the pre-lead-free area.

The additive addition was low, only the crack naphtha was slightly inhibited.

The cavern conditions were also optimal. As they are relatively shallow (not very deep into the ground) overall temperature is around 40 °C and there is hardly a temperature gradient, thus convection does not occur. The salt is rather pure with hardly any catalytic metals and we suspect that the brine was low on oxygen to start with. Still we were worried about those caverns, thus at least one may have been emptied prematurely and possibly would have been good for 3-5 more years.



Allow me to spend a few more words on the "friendly" cracker unit. It is a discontinued unit of mobil (socony vacuum) airlift type, of which less than a handful have survived in Europe. Its characteristics were: very high feed flexibility from total crude over low-asphaltene-residues to gas oils, and due to the moving-solid-bed-technique low catalyst deactivation;

CHARACTERISTICS OF THERMOFOR(*)

- o MODERATE CRACKING TEMPERATURES
- o REACTION PRODUCTS RICH IN ISOMERS, LOW ON AROMATICS
- o EXCELLENT ROAD OCTANE No. vs. RON, MON GOOD
- o EXCEPTIONAL STABILITY OF PRODUCTS, BEATS FCC
- o GOOD CETANE NUMBER OF DISTILLATES
- o CAN FEED FROM TOTAL CRUDE TO RESIDUES (LOW ASPHALTENES)
- o LOW CATALYST DEACTIVATION RATE. MOVING SOLIDS - BED TECHNIQUE

→ DEA OPERATES UNIT TODAY ON HEAVY GASOILS (VACUUM), WITH MODERN SELECTIVE CATALYSTS AT HIGHER THAN DESIGN SEVERITY

(*) SOCONY VAC. AIRLIPT TCC

product qualities in "its days" were exceptional as the naphthas are rich in isomers and low in aromatics and thus Road Octane Number and Motor Octane are quite good. It is said that its middle distillates show less of the low cetane number problems compared to normal FCC's and stability of all products is superior.

COMPARISON TYPICAL TCC vs. FCC NAPHTHAS (DEA)

| | FCC KARLSRUHE 08.1990 | TCC HEIDE 13.08.1990 |
|--|-----------------------------|----------------------------|
| ANTIOXIDANTS | POSITIV | POSITIV |
| ROZ | 92.0 | 92.1 |
| MOZ | 82.4 | 82.1 |
| FBP (OC) | 204 | 210 |
| AROMATES (VOL %) | 31.5 | 20.6 |
| OLEFINES (VOL %) | 21.2 | 24.7 |
| BROMINE No. (g BR ₂ /100g) | 37.9 | 45.3 |
| EXISTENT GUM (mg/100ml) | 4/2 | 3/1 |
| POTENTIAL GUM (mg/100ml) (4h, 100°C, 7 BAR O ₂) | 4.9/4.1 | 3.6/3.0 |
| INDUCTION PERIOD (MINUTES) (100°C, 7 BAR O ₂) | 660 | 975 |
| NITROGEN ppm | 50 | 60 |
| PHENOL ppm | 29.2 | 36.5 |
| SULFUR ppm | 365 | 265 |

TCC MARGINALLY MORE STABLE

Today the owner DEA-Mineraloel AG operates the unit on vacuum gasoil similar to normal FCC feedstock. A comparison of the TCC and FCC cat naphthas (the latter from an industry refinery at Karlsruhe, where DEA is a partner) show a strong similarity but a 25-30% better stability of TCC naphtha (induction period, potential gum, low aromatics) in spite of marginally higher olefin, nitrogen and phenol contents.

TYPICAL CAVERN GASOLINE BLENDS

HEIDE CAVERN H 104A

BLEND RANGES OF BATCHES

| | <u>VOL %</u> |
|---------------------------|--------------|
| C4 | 2 - 5 |
| STRAIGHT RUN NAPHTHA | 13 - 15 |
| LIGHT REFORMATE (*) | 10 - 13 |
| HEAVY REFORMATE (*) | 6 - 10 |
| TOTAL (UNSPILT) REFORMATE | 44 - 54 |
| CAT CRACKER (LCN) | 10 - 17 |

CAVERN GASOLINE RETAILED ON SPEC 1992
AFTER 7 YEARS OF STORAGE

BATCHES MANUFACTURED AT HEIDE REFINERY 1985

(*) PLATFORMER (UOP)

The blend of the cavern gasoline batches produced by DEA consisted of Butane 10-17% TCC cracker naphthas and UOP reformates (with higher yield of light reformat than normally obtained from a UOP reformer); important is the 13-15% MEROX-treated straight run naphtha, whose disulfides shielded the fuel. The latter unfortunately today is not possible any more as the octane balance of the refinery requires total-reforming of all virgin naphthas.

EXPERIENCED Q U A L I T Y C H A N G E S A F T E R C A V E R N S T O R A G E

- FINDINGS FROM H 104A AND H 112 (HEIDE) -

- MAIN BODY OF GASOLINE : NO SIGNIFICANT CHANGES
- BOTTOM SECTION (8 m ABOVE BRINE LEVEL)
 - STRONG TOTAL AROMATICS LOSS INTO BRINE
 - BENZENE CONTENT REDUCED, OCTANE LOSS
 - INCREASE OF FINAL BOILING POINT BEYOND SPECIFICATION (ACCUMULATION OF HEAVY POLYMERES/GUM)
 - MINOR DENSITY INCREASE
 - INCREASE OF OLEFIN CONTENT COMPARED TO MAIN OIL BODY (SO FAR UNEXPLAINED)
 - CHEMICAL REACTION AREA NOT INTERFACE BUT BOTTOM SECTION > 3 m ABOVE BRINE LEVEL
 - HYDROCARBON CONCENTRATION IN BRINE INCREASES WITH CAVERN DEPTH, CERTAINLY NOT MAX AT INTERFACE

NOTE: BUT EVEN THE BOTTOM SECTION WAS USABLE AS RETAIL STOCK AFTER BLENDING WITH FRESH REFINERY GASOLINE AT HEIDE REFINERY

JMJK/CC-VU-5786

In spite of most of the cavern volumes being useable directly without blending or reprocessing, we experienced some changes in the quality of the product near the oil/brine interface, which are worth discussing. These changes were more pronounced in the cavern emptied after 7 years than the one which was turned over after 9 years.

We saw a strong loss of aromatics into the brine, of which part was benzene. Consequently the octane level fell significantly by about 2 points.

Obviously some gum/polymers must have been formed and sank to the bottom so that the final boiling point increased well above the specification limit - and a minor gravity increase occurred.

It remains unexplained, why an increase of olefines content over the average of the main oil body occurred in a zone 5-8 m above brine level, while obviously near the interface those olefines had reacted to gum to a level well below average. Another unexplained finding was that the hydrocarbon content at the oil/brine interface is lower than at 2-3 meters below the interface. Theories are invited.

In spite of all those findings (see attachment A for detailed data) in the last few meters of the oil, all bottom cavern product in the end was blended down with fresh product from the refinery to marketable premium gasoline.

CAN WE REDUCE THE RISKS IN NEW STOCKS ?

- TAYLORMADE SPECIFICATIONS TO MODERN GASOLINES
- INCREASE PROTECTIVE SHIELD OF ADDITIVES
- USE OF "FRESH" CAVERNS IF POSSIBLE

BECAUSE: - GASOLINE TAKEN FROM VARIOUS MARKET SOURCES
RATHER THAN ONE REFINERY ONLY

- SEVERITY OF CRACKERS INCREASE AND FEEDSTOCKS HEAVIER
- NATURAL INHIBITORS REMOVED BY OCTANE DEMAND
IN LEAD FREE ENVIRONMENT

As we go from 1985/86 to 1994, or with the first refill to 1992, what will we do/have we done differently? As we can not expect to get gasoline from one "sympathetic" refinery only for our cavern storage in future, we had to issue a special cavern specification based on the EN 228, the new European Union spec. As a matter of fact we have used this spec for the 1 million m³ fill of Blexen caverns near Bremerhaven. These caverns cover Germany's additional IEA/EU obligations for the new Eastern territories. The caverns were filled 1992.

We substantially increased the protective shield of additives, e.g. the gasoline contains now among others 80 ppm antioxidants.

Learning from some bad experience in the past we will use new (fresh) caverns in future or only those, which contained acceptable gasoline without major signs of deterioration, since spoilage by aged product is taken as a serious problem at EBV.

These measures are significantly tougher than those in force at Heide, but when we take from various market sources, we must expect high severity cracker naphthas in the blend and the super hydrogen treating processes will almost certainly have removed all natural ageing inhibitors from the fuel.

How much tougher did we then make EN 228?

R.B.V. SPECIFICATION : GASOLINE FOR SALT CAVERN STORAGE

BASE : EN 228

- o EXCLUSIONS: ALCOHOLS; ETHERS; COKER-, PYROLYSIS-NAPHTHAS
ALKADIENES, CYCLODIENES, ALL CONJUGATED DIENES,
ORGANIC HALOGENES
- o UNSATURATES: BROMINE NUMBER 40 g /Br₂/100g
OLEFIN CONTENT MAX 20 wt%
DIENE NUMBER < 0,5 J₂/100g
- o OXIDATION STABILITY: POT. GUM (4 h/100°C/7bar O₂) AFTER nC₇ WASH MAX 2 mg/100ml
EXISTENT GUM (AFTER WASHING nC₇): MAX 1.5 mg/100ml
INDUCTION PERIOD: MIN 480 MINUTES
- o MICROBIAL: MAX 500 UNITS/LITER
- o ADDITIVES: OXIDATIONINHIBITOR: MIN 80 ppm HALCO 5316
METALDEACTIVATOR AND CORROSIONINHIBITOR COMPULSORY

JMJK/cc-VU-5789

Due to solubility-in-brine problems we have to exclude all alcohols and ethers (including MTBE); chemical naphthas - mainly pyrolysis naphthas from "ethylene crackers" - had to be banned and anything containing any form of double unsaturated hydrocarbons (DIENES). Organic halogenes are excluded on legal/health grounds, even as additives.

A rather high olefin content of 20 wt% (40 Bromine No) is tolerated on the basis of strong additivation but Diene No should be very low eliminating practically all hyperreactive chemicals.

In line with this, gum values and induction period times are tightened over EN 228, a second prediction oxidation test (potential gum) has been added.

Antioxidizer additives have been specified at a substantial level and metal deactivator and corrosion inhibitor additives are required.

For the first time in Europe a microbial specification of 500 units per liter has been introduced, which is liberal for gasoline because we are confident (but not entirely sure) that microbes - if present - will not multiply in our high salinity environment.

We are convinced that these precautions will allow us to store gasoline 8 to 10 years. We have installed special devices to inspect the product and brine at various cavern horizons. Routine inspection is every 6 months to avoid surprises.

Reformulated gasolines and environmental specification changes (like max benzene content 1%) are to be expected over the next 10 years. Arrangements have to be made to prevent that the gasoline has to be exchanged prematurely before its designed storage life is over.

Thank you for your attention.

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Laborbefunde: Cavern horizons, lab. analysis

o H 112 Nov 1992
o H 104A 19.8.1992

Analysenzertifikate.

Paid for analysis work requested by EBV

HEIDE 104 A SALT CAVERN GASOLINE

AVERAGE CAVERN CONTENT vs. BOTTOM 10% AND 1% AND vs. FRESH PRODUCT

| | <u>AVERAGE (+)</u> | <u>BOTTOM 10% (+)</u> | <u>BOTTOM 1% (+)</u> | <u>1985 FRESH PRODUCT</u> |
|---------------------------------------|--------------------|-----------------------|----------------------|---------------------------|
| DENSITY (kg/m) | 768.9 | 772.1 | 775.6 | 766.2 |
| EXISTENT GUM (mg/100ml) | LT. BROWN | OILY, D. BROWN | DARK BROWN | LIGHT YELLOW |
| BEFORE nc7 wash | 60 | 310 | 2966 | - |
| AFTER nc7 wash | 3.0 | 1.0 | 0.6 | < 3 |
| IBP OC | 26 | 35 | 29 | 15 |
| 90 VOL% OC | 172 | 179 | 190 | 172 |
| FBP (OC) | 218 | 255 | 295 | 215 |
| IND. PERIOD (MINS) | > 1000 (*) | > 1000 | - | > 1000 |
| POTENTIAL GUM (mg/100ml) | | | | |
| (4h, 100°C, 7 Bar O ₂) | | | | |
| BEFORE nc7 wash | 120 | 1240 | - | - |
| AFTER nc7 wash | 18 | 1.0 | 210 | < 10 |
| DIENE NUMBER (g J ₂ /100g) | 0.26 | 0.62 | 0.39 | - |
| BROMINE No. (g BR ₂ /100g) | 3.1 | 7.55 | - | - |
| TOTAL AROMATICS (WT%) | 54.4 | 52.9 | 44.9 | - |
| BENZENE CONTENT (WT%) | 3.7 | 3.6 | 3.2 | - |
| OLEFINES (WT%) | 1.7 | 5.1 | 0.1 | - |
| RON | 95.2 | 92.4 | 88.1 | 95.3 |
| MON | 85.1 | 83.8 | 82.7 | 85.2 |

(*) NO BREAK OBSERVED FOR 2880 MINUTES (48 hi) | (+) 1990 ANALYSIS, CAVERN EMPTIED 1992

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**A STRATEGIC STORAGE PROGRAMME FOR DEVELOPING COUNTRIES -
TO BE OR NOT TO BE?**

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0. ABSTRACT

In the industrialised world agreements between countries or legislation will dictate that there shall be strategic fuel storage of "X" amount of days. What about the developing countries, the third world? For the most part they have no storage regulations. Should they consider a strategic fuel storage programme? If so, how can they go about it? What are the obstacles? Many have neither the technical expertise nor the monies. This paper will explore how developing countries can have a strategic oil storage programme - How they can plan, justify, finance, execute and operate such a storage without having a major impact on their countries.

1. INTRODUCTION

I am honoured to have been given the opportunity to address the delegates attending the 5th International Conference on stability and handling of Liquid Fuels. The stability of the International oil business today appears to be very different from what it was when we met in Orlando, Florida three years ago. Because of this, many in the developing countries question the need for building or maintaining strategic oil stockpiling programme.

Given the past history of political instability in the main oil producing areas of the world, it is very difficult to expect the political conditions in those areas 5 or 10 years from now to look anything like they do today. It is shortsighted for developing countries not to plan ahead for potential fuel crisis.

Many will say that housing, education and schooling should take precedence over stockpiling strategic materials. After working in developing countries in Africa for the past 6 years, and 25 years in the Middle East, I cannot dispute that, but developing countries can take care of all these needs if they plan ahead.

2. BACKGROUND

Since the Gulf War, countries, especially landlocked ones, have recognized that not only are they vulnerable to the political instability in neighbouring countries as well as to natural disasters, but also to the volatility of the main producing areas of the world. Escalation of the Gulf War would have caused very serious fuel shortages. Accurate missiles launchings could have led to wide - spread destruction of oil gathering centres, export terminals, and refineries. This would have resulted in a major world-wide supply shortage and would have created economic havoc.

Studies have been undertaken by many African countries on this subject and several have or are considering implementing strategic fuel stockpiling programmes - Lesotho Swaziland, Malawi, Zimbabwe and Botswana to name a few. I had been involved in a United Nations Development Programme in Botswana from 1988 until July of this year to develop the Petroleum Management capability of that country, which included assistance to their strategic fuel programme. This also provided me with a unique opportunity to study and advise other Africa countries on this special subject.

3. PLANNING

Can you picture the chaos in your country if you had only a few days of oil storage, if suddenly your oil supplies were cut off? This happened to Lesotho, a small Southern African country, during the mid - eighties. The result was that the Government was toppled.

Several questions need to be asked by Governments interested in having strategic fuel storage programmes -

- What do we gain by having a secure strategic oil storage facility?
- What do we lose if we don't have a secure strategic oil storage facility?
- Where can we obtain help, both financial and technical?
- How do we justify the expenditure for such a programme?

Firstly, it must be clearly understood that projects of a strategic nature cannot be evaluated within the framework of a classical cost - benefit analysis. These projects are in the nature of risk insurance in order to safeguard against the effects from various possible interruptions of oil supplies, which can have temporary retarding to disastrous effects on a countries economy and the living standard of the people.

One can say that the results of the money outlays are difficult to measure, or have intangible benefits. However often these benefits can be indirectly evaluated, for example -

What is a days production of gold or diamonds worth if you must shutdown operations because of lack of fuel?

With a Government strategic oil project, prior commitment by legislative action is often the underlying justification.

A strategic oil supply can gain a country political stability. It can ensure that industrial and food production continues in a reasonable manner during a fuel crisis. It can provide a buffer for erratic and rapid international fuel price fluctuations. It can pay its operating costs if you procure fuel supplies when prices are low and sell off when prices rise.

International assistance is available for funding and providing the technical know - how for strategic projects.

While we are addressing the developing countries of the world, we should not forget those countries classified as "least developed countries" or LDCs and listed in ANNEXURE I.

As well as considered as being the poorest nations in the world, many are landlocked and totally dependent on others for their oil supplies. Poor or not poor the LDCs must also plan for fuel shortages.

4. LEGISLATION

Government regulations and the enforcement thereof is one way to have cooperation between Oil Industry and Government in establishing and maintaining strategic petroleum reserves. Strategic storage regulations differ substantially from country to country especially in the method of financing and the level of obligations. Governments differ in the extent to which the cost of strategic reserves are borne by the tax payer through a general revenue fund, or are passed on to the Oil Industry and the petroleum end users. The cost of a strategic oil storage programme should in the end, be payed for by those who benefit the most.

This may work well in the industrialised or developed nations of the world but will the oil companies in, for example, Botswana (a country of 1.2 million people) be willing to provide 60 days of storage to complement 30 days by Government even if the costs pass on to the consumer. They might, but some of these strategic petroleum stocks might be with their industrial consumers, at the oil companies depot, or even in the underground tanks at service stations. Since these petroleum stocks varying daily and some of the stocks are in a remote service station tank located in the Kalahari desert, can they really be considered part of the strategic petroleum stocks? How accessible are they in an emergency? This is the type of stockpiling I found when I first came to Southern Africa and examined storage agreements between Governments and Oil Industry (Refer Annexure II).

To want a strategic oil programme is not enough. The regulations must be realistic and enforceable. Governments should never assume that oil companies will cooperate just for good-will. They are in business to earn money for their shareholders and not to provide secured supplies for Government emergencies.

5. FINANCING A STRATEGIC PETROLEUM PROGRAMME

With proper planning and legislation, a strategic petroleum programme can come to pass without undo hardship to the consumers and to the Government's development budget. The answer, in part, is the creation of a National Petroleum Fund, whose purpose is to meet the engineering and construction costs of the strategic storage facilities. A small levy or tax in the pump price is paid by fuel consumers to the oil companies, who monthly pay this levy into the Government's Petroleum Fund. (Refer ANNEXURE III). This fund should be managed by a private financial institution, such as a bank or other professional fund managers who have the

knownhow to prudently invest the fund to retain the real value of the assets.

EXAMPLE

1. A country with a population of 2 million
2. Number of vehicles: 150,000
3. Annual fuel consumption: 450,000,000 litres
4. Assume an average pump price of 26 US cents/litre (100 US cents/gallon).
5. Petroleum fund levy at 2 US cents/litre
6. Annual Petroleum fund: 9 million US dollars

This accumulated Petroleum Fund will form the basis for building the storage facilities. Prudent investment of the fund can annually earn an additional 1.2 million US dollars.

There are three main alternatives for the actual financing of a strategic petroleum project.

- concessionary or soft loans
- export credit financing
- commercial financing

Concerning soft and export credit financing, I have limited myself to considering financing from the Nordic countries and the multilateral World Bank institution, i.e. The African development Bank and The African Development Fund. This limitation has been made because I am very familiar with the conditions of the Nordic institutions. However each country has its own soft and export credit financing system and offers conditions that are normally comparable with those from the Nordic countries, which are in accordance with the organisation for Economic Co-operation and Development (OECD) rules.

As you will see in Annexure IV, these loans have long repayment periods with low interest, making it possible for repayment using the National Petroleum Fund.

Of course financing the project through loans will result on a drain on Government finances and in the case of foreign loans increase overseas debt burdens. However, this disadvantage will be outbalanced by the fact that this financing will be cheaper than commercial financing.

6. LEVELS OF STRATEGIC STORAGE RESERVES

The rationale for establishing the level of fuel reserves within a country has in it a large element of judgement, based on experience. One of the prime factors is the elapsed time during an emergency that it will take trying to find a new supplier, and the delivery time from the source of supply to the consumer. For a coastal country, many believe 60 days should suffice. For a landlocked country, it might take 90 days or more for supplies to reach consumers.

It should be noted that during any serious disruption in supply the rationalisation of the usage of petroleum supplies will extend the number of days available. This is, ofcourse an intregal part of strategic fuel planning.

The fuel consumption rate based on the level of industrialisation, and the size of the transport network within a country are also key factors in judging the levels to be stored. Southern African countries mainly receive their petroleum products from South African refiners/marketers. My experience in that part of the world has shown that to develop an alternative source of supply, including contract agreements ordering and delivery will take between 60 and 90 days.

7. TECHNICAL ASPECTS

Once Government decides that there shall be a strategic petroleum storage programme, the next step is to engage an internationally recognized consultant to study locations and the suitability and cost of the various types of possible fuel storage facilities - aboveground steel tanks, underground rock caverns, solution mined salt caverns or underground concrete caverns. The consultants should be familiar with these various types of storage facilities and when and where they are most applicable and what is the most cost-effective for your application.

Conventional welded steel tank farms, came into existence in the early 1920 in the United States and have been used around the world.

The storage of petroleum underground had its beginnings during World War II in rock caverns in Sweden. By 1969, the first large scale storage of crude oil in salt caverns started in Europe and today is extensively used in the United States Gulf Coast region since it is the cheapest form of storage and very secure.

Converted mines and underground or semi-buried concrete caverns were used by the South Africans for strategic petroleum supplies when sanctions were applied in the mid - seventies.

Since salt caverns are limited to the United States, some parts of Europe and possibly some parts of the former Soviet Union, there has been a trend to study and build facilities in rock caverns. Cost trends for storage aboveground have entailed that it is now economic to construct caverns even in "poor - quality" rock. ANNEXURE V refers.

ANNEXURE VI tabulates fuel storage plant costs in Southern Africa in 1992 in US dollars.

The advantages of underground storage facilities are:

- fire and explosion hazards are more or less non-existent.
- very high safety factors also in terms of potential sabotage considerations.
- environmental problems limited.
- valuable surface areas are not occupied.
- operation temperature constant thereby eliminating breathing and evaporation losses.

It has been traditional in the oil and gas industry, especially in developing countries, for the design and construction of facilities to be let on a "turnkey" basis. This method of contracting has been used successfully for petroleum storage projects.

Government officers should be assigned to the project as an active part of the Project Management Team to gain invaluable experience that can only be provided by a competent engineering company. It is most important for developing countries to be able to receive, retain and absorb relevant technological knowledge and action should be taken to ensure that acquired skills would not be lost by transferring trained personnel to other jobs.

Wherever possible indigenous engineering capabilities and construction skills should be developed within the framework of the project through sub - contracting some of the work.

I trust this has given you some insight into the problems and solutions for strategic petroleum projects in the developing world.

ANNEXURE I

LIST OF COUNTRIES

BY CATEGORY AND REGION

| LDCs (Least Dev. Countries) | Africa | Asia and the Pacific | Latin America | Arab States |
|--|---------------|---------------------------------|----------------------|--------------------|
|--|---------------|---------------------------------|----------------------|--------------------|

| | | | | |
|--|-----------------------------|---------------------|-------|----------|
| | Benin | Afghanistan | Haiti | Djibouti |
| | Botswana | Bangladesh | | Somalia |
| | Burkina Faso | Bhutan | | Sudan |
| | Burundi | Kiribati | | Yemen |
| | Cape Verde | Lao People's | | |
| | Central Af. Republic | Democratic Republic | | |
| | Chad | Maldives | | |
| | Comoros | Myanmar | | |
| | Equatorial | Nepal | | |
| | Guinea | Samoa | | |
| | Guinea Bussau | | | |
| | Liberia | | | |
| | Madagascar | | | |
| | Lesotho | | | |
| | Malawi | | | |
| | Mali | | | |
| | Mauritania | | | |
| | Mozambique | | | |
| | Niger | | | |
| | Rwanda | | | |
| | Sao Tome | | | |
| | Sierra Leone | | | |
| | Togo | | | |
| | Uganda | | | |
| | United Republic of Tanzania | | | |
| | Zaire | | | |
| | Zambia | | | |

| | | |
|------------------------|---------------|----------------------|
| "As if" LDC | Africa | Latin America |
|------------------------|---------------|----------------------|

| | | |
|--|---------|-----------|
| | Angola | Nicaragua |
| | Senegal | |

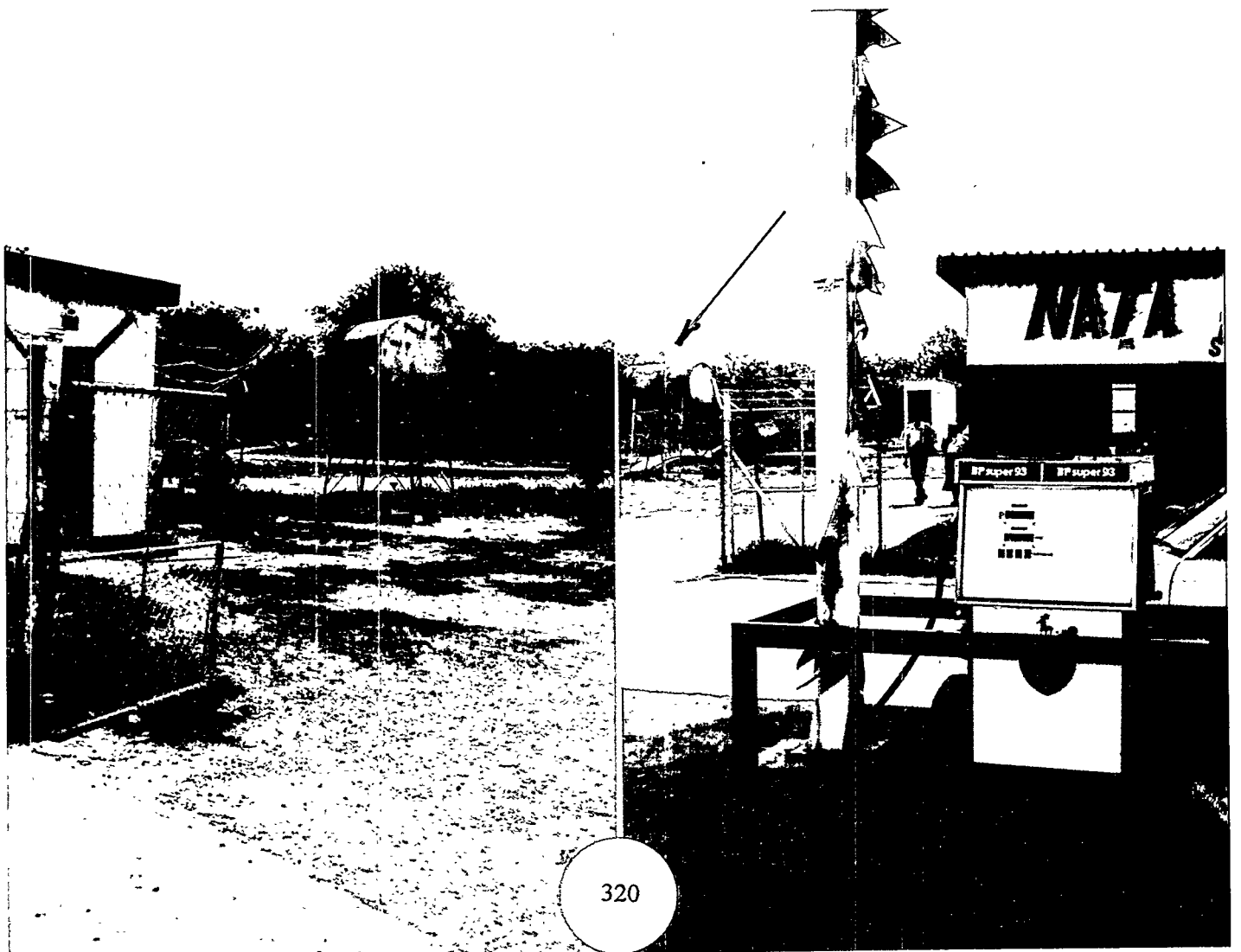
| | | |
|--------------|-----------------------------|----------------------|
| Other | Asia and the Pacific | Latin America |
|--------------|-----------------------------|----------------------|

| | | |
|--|----------|---------|
| | Tonga | Bolivia |
| | Viet-Nam | |

ANNEXURE II

THESE 4,500 AND 9,000 LITRE SERVICE TANKS ARE CONSIDERED PART OF STRATEGIC OIL STORAGE UNDER THE TERMS OF MANAGEMENT AGREEMENT.





ANNEXURE III

NATIONAL PETROLEUM FUND ORDER, 1992 (Published on 29th May, 1992)

ARRANGEMENT OF PARAGRAPHS

PARAGRAPH

1. Citation
2. Establishment of Fund
3. Purposes of the Fund
4. Administration of the Fund
5. Payments into the Fund
6. Disbursements from the Fund
7. Accounts of the Fund
8. Repeal of S.I. 45 of 1988

IN EXERCISE of the powers conferred on the Minister of Finance and Development Planning by section 25 of the Finance and Audit Act the following Order is hereby made —

1. This Order may be cited as the National Petroleum Fund Order, 1992, and shall be deemed to have come into operation on the 1st February, 1986. Citation
2. A special fund to be known as the National Petroleum Fund, hereinafter referred to as "the Fund", is hereby established. Establishment of Fund
3. The purposes of the Fund are to — Purposes of the Fund
 - (a) meet the engineering, construction and operational costs of the strategic storage facilities for Government fuel;
 - (b) purchase petroleum products for the Government's strategic oil stocks;
 - (c) stabilize prices charged by the oil industry;
 - (d) meet insurance premiums in respect of the insurance of Government's strategic oil installations and oil stocks.
4. (a) The Permanent Secretary, Ministry of Commerce and Industry, hereinafter referred to as "the accounting officer", shall be the public officer responsible for the administration of the Fund. Administration of the Fund
 - (b) The Minister shall appoint a management committee charged with determining the investment strategy and disbursement procedures of the Fund.
 - (c) The Minister may appoint an independent auditor to undertake audits of the Fund on such conditions as he shall in writing require.
 - (d) The management committee, shall, with the written approval of the Minister, cause the assets of the Fund to be prudently invested so as to retain the real value of the assets.
 - (e) The accounting officer may, with the written approval of the Minister, appoint a financial institution licensed in terms of the Financial Institutions Act, or a wholly owned subsidiary of such a financial institution, to undertake the day to day activities of the Fund. Cap 46:04
5. There shall be paid into the Fund — Payments into the Fund
 - (a) all monies received in respect of levies charged under the Control of Goods (Petroleum Products) (Levy) Regulations; Cap 43:07
Sub. Leg

ANNEXURE III

- (b) such other money as shall be received from Government or which Government instructs to be paid into the Fund;
- (c) income from the investment of moneys of the Fund.
- Disbursements from the Fund 6. There shall be paid from the Fund —
- (a) costs for the engineering, construction, and operation of the strategic storage, and distribution facilities for Government fuel;
- (b) sums of money to the oil industry for the stabilization of prices in respect of petroleum products;
- (c) such sums of money to the oil industry or Consolidated Fund as the Minister may from time to time determine;
- (d) costs of the purchase of petroleum products for Government's strategic oil stocks;
- (e) insurance premiums in respect of Government's strategic oil installations and oil stocks;
- (f) management and audit expenses of the Fund;
- (g) such other sums as the Minister may in writing approve.
- Accounts of the Fund 7. (1) The accounting officer shall —
- (a) keep and maintain proper accounts and records of the Fund;
- (b) prepare in respect of the Fund for each financial year a balance sheet and statement of income and expenditure in such form and manner as the Accountant-General may approve;
- (c) at the time of submission of the balance sheet and statement of income and expenditure, submit to the Minister proposals for dealing with any surplus in the Fund;
- (d) maintain an account in which shall be recorded all receipts into the Fund; and all disbursements from the Fund accounts shall be reconciled monthly.
- (2) The balance sheet and statement of income and expenditure shall be included in the annual statement of the Fund of the Accountant-General to the Auditor-General in accordance with section 34(2) of the Finance and Audit Act.
- Repeal of S.I. 45 of 1988 8. The National Petroleum Fund Order, 1988, is hereby repealed.

MADE this 15th day of May, 1992.

ANNEXURE IV

SOFT AND EXPORT CREDIT FINANCING

- A. The Swedish Agency for International Technical and Economic Cooperation (BITS). BITS co-operation is aimed at developing countries classified by the World Bank as low or middle income countries.

Financial Description

- Tenor: construction time + up to 10 years
- Interest: essentially none
- Fees: normal bank fees
- Security: Government guarantee.

- B. The Nordic Investment Bank (NIB).

NIB provides financing on normal banking terms for investment projects of Nordic interest within and outside the Nordic countries. These loans are granted to credit worthy developing countries and countries in Central and Eastern Europe.

Financial Description

- Tenor: Max. 5 + 15 years (normally 15 years)
- Interest: Market rate in respective currency
- Fees: Commitment fee 0.25 - 0.50% p.a. Management fee (sometimes)
- Comments: 15 - 20% of contract value originating from at least two Nordic countries. Possibility of co-financing with ADB.

- C. Nordic Development Fund (NDF).

NDF is part of the Nordic cooperation in the area of development aid to poorer developing countries. Particular importance is attached to projects with a positive impact on the environment.

Financial Description

- Tenor: Max 10 + 30 years
- Interest: 0.75% p.a.
- Fees: Commitment fee 0.50% p.a.
- Comments: Max amount 5 million US dollar co-financing offered with World Bank Group, Regional Development Banks and NIB.

- D. Swedish Export Credit Corporation (SEK) lending pertains mainly to the export financing of capital goods contracting assignments and consulting or service work.

Financial Description

- Tenor: Construction time + up to 10 years
- Interest: CIRR or market rate
- Fees: Normal bank fees
- Comments: Financing of Swedish exports
- Security: Government guarantee.

- E. African Development Fund (ADF)

Mainly projects and technical assistance financing as well as studies. Loans and grants are directed towards African member countries.

Financial Description

- Tenor: Construction time + 10 - 15 years
- Interest: market rate
- Fees: Normal bank fees
- Comments: Priority on project loans. Possibility of co-financing

- F. African Development Fund (ADF)

Loans and grants are directed towards the poorer members of ADB.

- Tenor: Construction time + max 50 years
- Interest: 0.75% p.a.
- Fees: Normal bank fees
- Comments: Priority on project loans with the possibility of co-financing.

Here caverns can be built.

The geological prerequisites for constructing caverns exist all over the world. Today storage facilities are constructed in granite, gneiss, schist, limestone, sandstone and chalk. Cost trends for storage above ground have entailed that it is now economic to construct caverns even in "poor-quality" rock. In these cases

special reinforcement work is required. Naturally the local possibilities must be specially appraised in each particular case.

Different areas on the world map can be divided into four groups—depending on the ground conditions for cavern storage.

Red area group

Plentiful supply of suitable areas for cavern storage.

Yellow area group

Good supply of suitable areas for cavern storage.

Green area group

Fair supply of suitable areas for cavern storage.

Non-coloured group

Sparse but usable supply of suitable areas for cavern storage.



ANNEXURE VI

FUEL STORAGE PLANTS COSTS

| | | |
|-------|---|------------------------------|
| * 1. | <u>BOTSWANA</u> - additional tanks only 3 x 2600 cubic metres. | 221 USD/cm (35 USD/Bbl) |
| ** 2. | <u>LESOTHO</u> - Grassroots Steel tank farm | 315 USD/cm (50 USD/Bbl) |
| * 3. | <u>BOTSWANA</u> - New Oil Industry tank farm, Horizontal tanks, Armoured Rock Covered | 870 USD/cm (138 USD/Bbl) |
| * 4. | <u>BOTSWANA</u> - Additional 1250 cm tank for existing Oil Industry tank farm | 225 USD/cm (35 USD/Bbl) |
| ** 5. | <u>BOTSWANA</u> - Grassroots Steel tank farm for 220,000 cm products | 200 USD/cm (32 USD/Bbl) |
| ** 6. | <u>ZIMBABWE</u> - Rock Cavern Storage for 360,000 cm products | 143 USD/cm (23 USD/Bbl) |
| ** 7. | <u>BOTSWANA</u> - Rock Cavern Storage for 220,000 cm products | 109 USD/cm (17 USD/Bbl) |
| ** 8. | <u>SOUTHERN AFRICA</u> - Grassroots - inground Concrete tanks | (136 USD/cm) (21 USD/Bbl) |
| ** 9. | <u>UNITED STATES</u> - Salt Dome Storage Caverns | 50 USD/cm (8 USD/Bbl) |

* Actual Cost

** Estimate

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

USE OF ASTM D5304 IN ASSESSING UNSTABLE DIESEL FUEL

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The storage stability, or the length of time a fuel can be stored, is of great concern to diesel fuel users. This paper reports on the use of the new ASTM accelerated test for storage stability by oxygen overpressure (D5304) to predict future storage life span of 63,000,000 gallons of a diesel fuel for U.S. Naval vessel use. This paper demonstrates the use of ASTM D 5304 at storage times of 16, 40 and 96 hours to accurately determine the length of time that this large quantity of diesel fuel could be stored at ambient temperatures before the maximum allowable amount of particulate contamination was reached.

INTRODUCTION

The Defense Fuel Supply Center (DFSC), Cameron Station, Alexandria, Virginia retained ownership of 1.5 million barrels of off-specification F-76 during the 1992-1993 time period. This fuel had originally been procured by DFSC using the military specification MIL-F-16884.¹ Although this fuel had passed specification requirements at the time of purchase, it rapidly showed signs of degradation when in storage.

Since the military conducts operations worldwide, it is necessary to store fuel at strategic locations for extended periods of time. The period of storage between production and usage varies greatly, depending upon tactical operations, therefore, there must be assurance that when the fuels are used they have not deteriorated during that time.

Storage quality is measured by the fuel's tendency to react with dissolved molecular oxygen to form undesirable products. These undesirable products can range from solid particulates and gums to highly reactive soluble fuel molecules of peroxides and acids. It is extremely important to the military that we include a test method within our procurement specification to address the predictive stability characteristics of the products at the time of production. Unfortunately, at the time DFSC had procured this particular F-76 product, the ASTM D 5304 (ASSESSING DISTILLATE FUEL STORAGE STABILITY BY OXYGEN OVERPRESSURE) had not yet been included in MIL-F-16884.

BACKGROUND

Beginning in 1992, the U.S. Navy and Coast Guard reported numerous problems during shipboard propulsion use of the suspect F-76. The complaints all indicated a degraded fuel product and were

reported from various sources. This fuel was reported to be a dark product which had very fine black particulates. This increased particulate was clogging filters, causing high filter change-outs. Also, there were some instances of a drop in fuel supply pressure to main engines at full power.

These problems were not isolated cases, but confined to vessels which had refueled on the U.S. West Coast area supplied by one refiner. Test results for this fuel in October 1992 revealed a color rating of ASTM 3 by ASTM D150 and had variable levels of particulate content. The storage stability test by ASTM D 2274 (OXIDATION STABILITY OF DISTILLATE FUEL OIL) indicated that about half of the fuel tested failed. Therefore, if this fuel were stored for more than six months it would not achieve acceptable standards of stability.

Over the next six months, this fuel was closely monitored and the user problems increased. Since ASTM D 2274 indicated that much of this fuel would continue to degrade with time, with the combination of high existent particulates along with predicted additional particulates, it became evident that a "clean up" procedure would be necessary.

In November 1992, DFSC funded the Naval Research Laboratory (NRL) to assess the extent of the problem and the magnitude of the particulate levels at the fuel storage sites. In addition to evaluating the current existent solid contamination, the potential solid production was measured using the ASTM D 5304 test. Finally, the "clean-up" procedure was assessed in the laboratory by simulating the field operation of filtration of existing particulates and the stabilizer additive injection to prevent further degradation.

Because of results obtained during this vigorous field simulated laboratory test, DFSC and the U.S. Navy were able to successfully "clean-up" and issue acceptable product to shipboard vessels without jeopardizing the rate of filter changes and plugging of shipboard coalescers.

RESULTS

ASSESSMENT OF THE EXTENT OF THE PROBLEM AND THE MAGNITUDE OF THE PARTICULATE LEVELS AT THE STORAGE SITES:

Samples were assessed by a modified ASTM D2276 for particulate contamination. This modified method consisted of immediately removing a 250 mL aliquot from the well shaken original container and filtering through a pre-weighted nylon membrane filter (0.8 micron porosity and 47 mm diameter). The resulting filter weight gain was multiplied by four to place the weight on a per liter basis and corrected by subtracting a blank filter weight change (usually 0.1 mg/L). The pass/fail use limit for this test for NATO F-76 type fuel is 15 mg/L for U.S. Navy use.

The results in Table 1 represent the currently existent particulate amount in the tanks from storage site #1. This is only true if a representative sample has been taken. The difficulty in obtaining small representative samples from very large tanks is demonstrated by examining some of the results in Table 2 which gives the results from a second set of samples obtained from storage site #1 in February 1993. The values for tanks 7 and 13 in Table 2 are about 25% lower, while the value for tank 8 is about 100% higher. Although this demonstrates the problems of obtaining a representative sample, it does not change the overall interpretation of the results from both Tables 1 and 2 that almost all of the tanks sampled at storage site #1 have very high particulate contamination levels which are above the use limit established by the U.S. Navy. These levels can be compared with values obtained by a recent worldwide survey of 22 OCONUS F-76 fuel storage depots. The average particulate contamination level from all level samples was less than 2 mg/L.² To put the very low

concentration of solid particulate in this fuel in the context of filtering very large volumes to remove the particulate, one can take the permitted solids value to 10 mg/L (ppm) and calculate that this is about 1.6 grams per barrel. Most Military fuel filters are qualified to be able to remove about 70 grams of solids per filter element at a cost of about \$20 per element. Most of this data represents about 10-60 mg/L of solids. Thus, in order to filter 10 mg/L from 1,000 barrels would require about 20 filters at a cost of about \$400. In order to filter 100,000 barrels of 10 mg/L solid would require 2,000 filters and a filter cost of about \$40,000, while filtering 1,000,000 barrels would require 20,000 filters at a filter cost of \$400,000. This represents about one cent per gallon additional cost. For 30 mg/L solid, this extra cost for filters would be three cents per gallon.

ASSESSMENT OF THE RATE OF FUTURE DEGRADATION IN INSOLUBLES AND COLOR AND THE USE OF STABILIZER ADDITIVES TO RETARD THIS DEGRADATION:

In addition to evaluating the current existent solids contamination levels above, the potential for future solids production was evaluated using the new ASTM D5304 test method. Using this test, a fuel is first filtered to remove all existent solids. Then, a filtered sample is heated at 90° C under a 100 psi oxygen atmosphere for 16 hours, cooled and then filtered to determine the amount of solids which formed during the accelerated oxidation test. The test conditions are roughly equivalent to the fuel being aged at room temperature for about 1 to 1.5 years in glass vessels under atmospheric air pressure.

Based upon results generated during the eight-year development of this new predictive storage stability test, it has been found that if a fuel does not exceed 1.5 mg/100 which is equal to 15 mg/L (i.e., 15 ppm) of filterable solids at the end of the test, then it can be considered a typical stable fuel suitable for bulk storage up to several years. Using this as a criterion for future additional particulate contamination, it can be seen in Tables 3 and 4 that most of the fuel at storage site #1 exceeds this upper limit.

The use of these predictive data may be further clarified by examining Figure 1. Using the criteria of future solids levels at 1.5 mg/100mL and 3.0 mg/100mL 15 and 30 mg/L (or ppm), one can effectively rank each of the tanks shown in both figures. Storage site #1 tanks 14, 34, and 10 were judged to have an effective future life of about three years, tank 7 had a future life of less than one year, tanks 8 and 36 should be consumed before six months and tanks 13 and 12 should be consumed immediately.

An additional test for even further future storage of these same samples was run by extending the test time of ASTM D5304 from 16 hours to 40 hours (on separate samples). The data for the fuels thus tested indicate no slowing of the increase of particulate production after very long storage times at ambient temperature (see Table #5). Similar data was also obtained from the other three storage sites.

Based on all of the above data, DFSC decided to attempt a filtration clean up of most of the fuel at storage site #1, followed by the addition of an after-market stabilizer additive. The predictive storage stability test data allowed DFSC to designate batches of fuel for immediate consumption all the way up to storage for three years, if necessary.

The new predictive test ASTM D 5304 was used to determine any future degradation of the fuel. As seen in figures 2-4, this fuel continues to degrade in a linear fashion. This behavior is quite unusual in that most fuels either never degrade or tend to degrade mainly in the first one to two years, followed by significant reduction in degradation.

Most of the F-76 samples/fuels were greater than six months old and thus the effects of adding a stabilizer at typical concentrations of about 24 ppm (w/v) would be expected to be much lower than adding the additive during the production at the refinery. There is a beneficial effect by adding a typical additive and the shelf life of the treated fuel would be expected to increase about 50 percent.

ASSESSMENT OF THE FIELD OPERATION OF FILTRATION/ADDITIVE INJECTION TO CLEAN UP THE PROBLEM F-76 FUEL

It was decided in order to "clean up" the fuel, it must be passed through a FAUDI precoat filtration system. This system consisted of diatomaceous earth pre-coated filters coupled with a micronic filter system. Downline of the filtration system, a stabilizer additive injection system was installed to inject 24 ppm of the additive.

The laboratory samples collected to establish the effectiveness of this procedure were:

- A representative all-level sample of fuel from the feed tank;
- A line sample just before the FAUDI pre-coat filter system;
- A line sample just after the FAUDI filter;
- A line sample just after the downstream micronic paper filter and stabilizer injection; and
- An all-level sample from the full holding tank at the end of the process.

Microscopic examination of the particulate contamination from the post FAUDI filter line sample indicated that a significant part of the weight was due to diatomaceous earth from the filter. It was estimated that the FAUDI filter probably was removing about half of the 15 mg/L of original solid contamination but adding about an equal weight of diatomaceous earth. From the viewpoint of settling out of fuel, the diatomaceous earth (density about 2.2 g/mL) would settle much more rapidly than the organic sludge contamination (density about 0.9 g/mL). However, from the viewpoint of potential abrasive harm to pumps, injectors and engines, the diatomaceous earth would be much worse than an equal weight of non-abrasive organic sludge contamination.

The final sample after additive injection after micronics paper filtration gave a particulate contamination level of about 12 mg/L. This 12 mg/L sample also showed significant diatomaceous earth contamination. This means that either break-through of the micronics paper filter has occurred or that fines from the diatomaceous earth are capable of passing through the intact filter.

In all cases, the addition of 24 ppm of the additive was quite beneficial regarding the future storage stability as gauged by long and very long term ASTM D5304 accelerated tests. The effect of the additive was essentially to double the future storage life of this fuel. Unfortunately, this would mean that instead of problems in the 6 to 12 month future time frame, the fuel would begin to exhibit problems in the 12 to 24 month time frame. That is, the additive slowed the solids formation rate by half but did not stop it.

CONCLUSIONS

Using the new ASTM D5304 accelerated storage stability test, it was possible to accurately assess the storage life of most of the bulk tanks containing then up to 1.5 million barrels of product. This

allowed DFSC to initiate an orderly issue schedule for most of the product which minimized problems for the U.S. Navy.

The ASTM D 5304 test also allowed DFSC to make a decision to add the storage stabilizer additive as part of the clean up operation. Finally and most importantly, the ASTM D5304 test was instrumental in convincing the refinery to change its processing so that F-76 fuel produced subsequent to January 1993 would be stable for long term storage. Since this storage instability was the major cause of high levels of sludge/solid buildup in the bulk fuel tanks, this means that future bulk stored samples should not exhibit this problem (which is manifested by the particulate contamination ASTM test D2276/D5452).

Regarding the use of diatomaceous earth coated (pre-coat) filtration to clean up high concentrations of existent solids (greater than 10 ppm or mg/L), it was found from laboratory tests that this method should not be used for F-76 diesel type fuels. It is important to note that this clean up technique has been quite successful at several field sites when used by DFSC in the recent past. However, all of these uses to date have involved jet fuel. These previous clean up processes use a particular diatomaceous earth specifically for jet fuels, which is not specified for diesel fuels. This is the probable reason for the current problems in clean up using this method. In addition, this diesel fuel had very high levels of contamination and thus presented a much more serious challenge to any type of filtration clean up method.

It was found that during the movement of fuel through the Pacific supply line, the high levels of particulate were essentially diluted by other cleaner fuels in the system. This dilution factor, coupled with the filtration/injection procedure, successfully cleaned up the fuel to an acceptable particulate level. Most of the fuel was issued and consumed by November 1993.

(The views expressed in this article are those of the author and do not reflect the official policy or position of the Department of Defense or the U.S. Government.)

Literature Cited:

- (1) MIL-F-16884, Military Specification for Naval Distillate, F-76.
- (2) Shaver, Bryan D. and Rigstad, Dennis A., DTNSRDC; Modetz, Henry J., Acurex Corp.; Shay, Joanna and Woodward, Paul, NIPER; "Worldwide Survey and Characterization of Commercial Marine Fuels, SAE Technical Paper, 8-10 June 1987.

FIGURE 1

STORAGE STABILITY BY ASTM D5304

Samples From Storage Site #1 (Nov. 92)

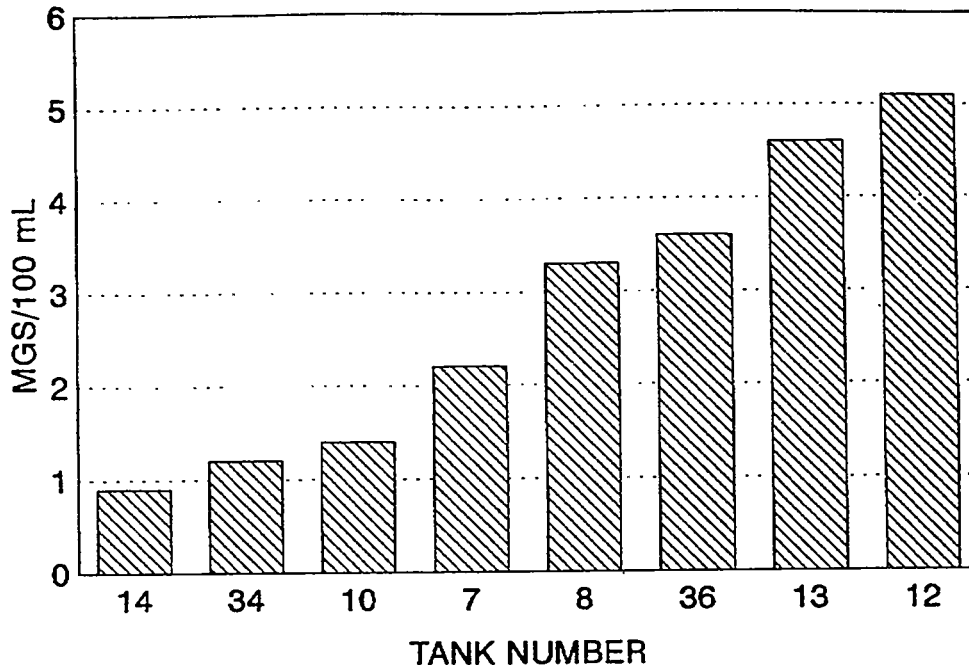
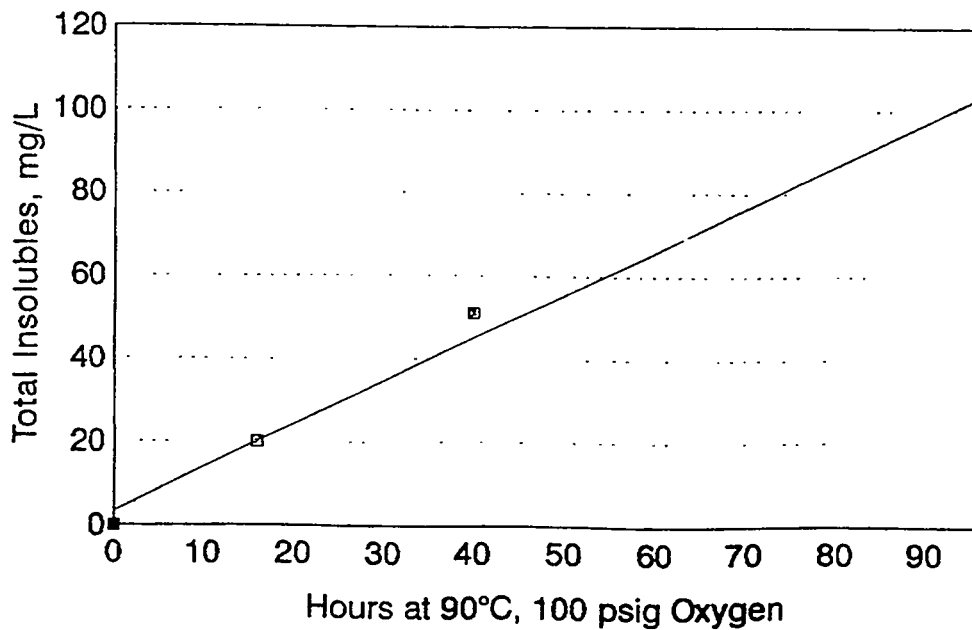


FIGURE 2

D5304 RESULTS

Storage Site #1, Tank #7

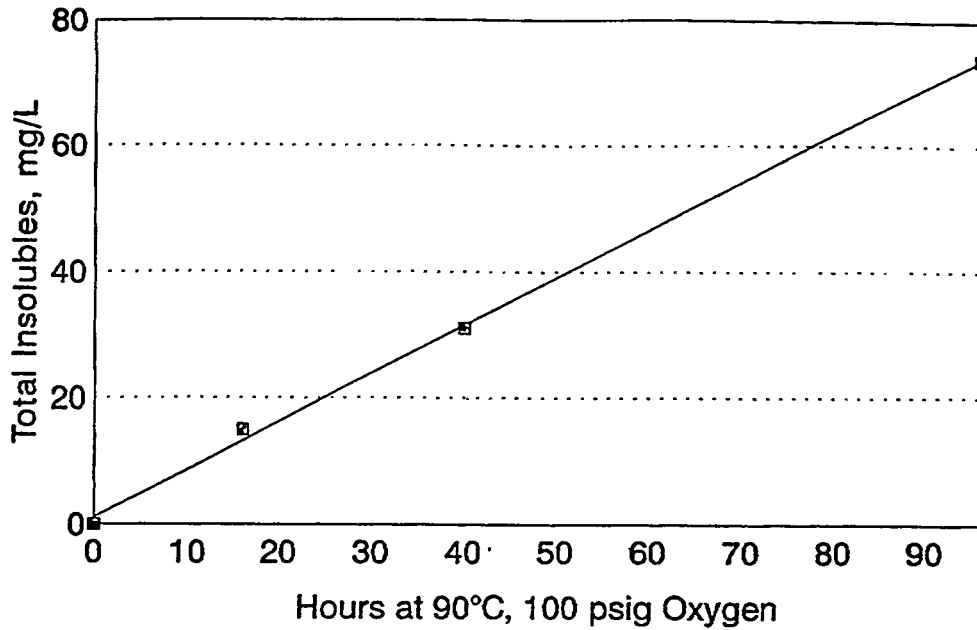


R squared = 0.991

FIGURE 3

D5304 RESULTS

Storage Site #1, Tank #16

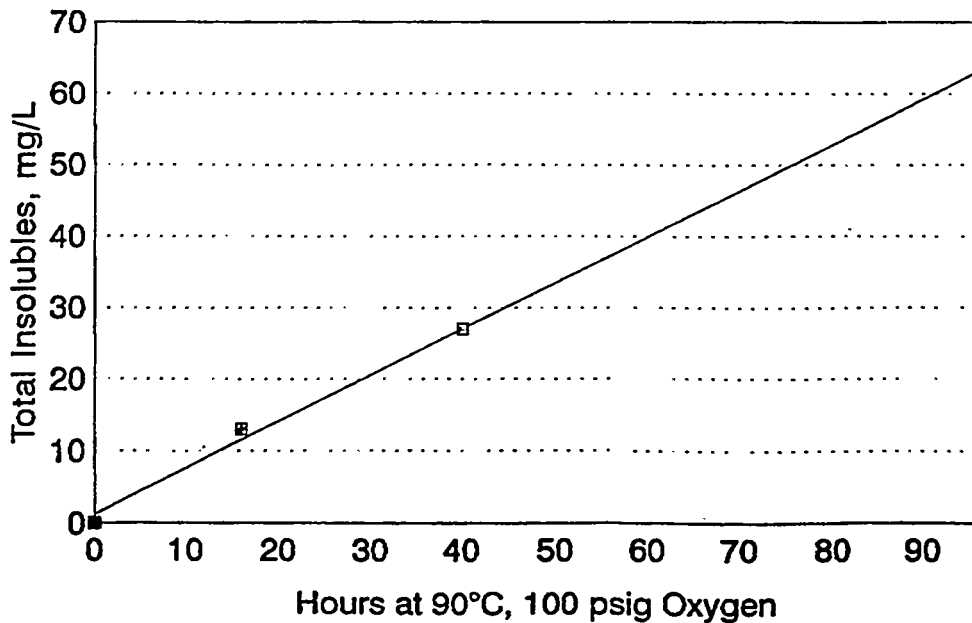


R squared = 0.999

FIGURE 4

D5304 RESULTS

Storage Site #1, Tank #9



R squared = 0.098

Table 1

PARTICULATE CONTAMINATION BY ASTM D5452 (MODIFIED)
250 mLs of sample filtered

Samples From Storage Site #1
November 1992

| Tank Number | Sample Level (from bottom) | Contamination mgs/L |
|-------------|----------------------------|---------------------|
| 7 | 10' | 32.0 |
| 8 | 10' | 16.4 |
| 10 | 10' | 11.6 |
| 12 | 8' Tap (Lowest) | 38.8 |
| 13 | 10' Tap (Lowest) | 32.8 |
| 14 | 75' | 38.8 |
| 34 | All Level | 16.8 |
| 36 | All Level | 20.0 |

Table 2

PARTICULATE CONTAMINATION BY ASTM D5452 (MODIFIED)
250 mLs of sample filtered

Samples From Storage Site #1
February 1993

| Tank Number | Sample Level (From bottom) | Contamination mgs/L |
|-------------|----------------------------|---------------------|
| 7 | 10' | 26.0 |
| 8 | 10' | 30.4 |
| 9 | 10' | 22.0 |
| 10 | 10' | 15.2 |
| 13 | 10' | 23.6 |
| 16 | 10' | 11.6 |
| 36 | All Level | 14.8 |
| 37 | All Level | 19.2 |

Table 3 (also see Fig. 1)

**STORAGE STABILITY BY ASTM D5304
16 hour stress time**

**Samples From Storage Site #1
November 1992**

| Tank Number | Contamination mgs/100 mL |
|-------------|--------------------------|
| 7 | 2.2 |
| 8 | 3.3 |
| 10 | 1.4 |
| 12 | 5.1 |
| 13 | 4.6 |
| 14 | 0.9 |
| 34 | 1.2 |
| 36 | 3.6 |

Table 4

**STORAGE STABILITY BY ASTM D5304
16 hour stress time**

**Samples From Storage Site #1
February 1993**

| Tank Number | Contamination mgs/100 mL |
|-------------|--------------------------|
| 7 | 2.0 |
| 8 | 3.9 |
| 9 | 1.3 |
| 10 | 1.7 |
| 13 | 3.7 |
| 16 | 1.5 |
| 36 | 2.9 |
| 37 | 0.9 |

Table 5

**STORAGE STABILITY BY ASTM D5304
40 hour stress time**

**Samples From Storage Site #1
November 1992**

| Tank Number | Contamination mgs/100 mL |
|-------------|--------------------------|
| 7 | 4.0 |
| 8 | 7.3 |
| 12 | 9.0 |
| 13 | 9.7 |
| 14 | 1.1 |

*5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
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METAL-DEACTIVATING ADDITIVES FOR LIQUID FUELS

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ABSTRACT

The metal-deactivating and the antioxidant properties of 1-phenyl-3-methyl-pyrazolone-5 derivatives have been investigated both in the model reaction of low temperature oxidation of ethylbenzene and in gasoline oxidation. The study of the ability of these derivatives to reduce the catalytic effect of copper naphthenate demonstrates that they are promising as metal deactivating additives for light fuels. Some of the pyrazolone compounds appear to be of special interest for the long-term storage of liquid fuels due to their action as multifunctional inhibitors.

INTRODUCTION

The problems concerning the fuel stability during their long-term storage and operation have been the subject of intense research in recent years¹⁻³. Increased emphasis is being placed on the development of ecological nonmetal-containing multifunctional additives for various fuels. Of special interest are compounds that may function as a multidentate ligand to chelate copper and exhibit radical-scavenging properties⁴. The conventional packages for light fuels comprise besides the antioxidant additive a metal-deactivating one. The Schiff bases, i.e. the condensation products of salicylic aldehyde with polyethylenepolyamines^{5,6} derivatives of 8-hydroxyquinoline, pyridinecarboxylic acids¹ are among the most popular metal-deactivating additives. A problem related to their utilisation is their low thermal stability which may be of concern for the stabilisation of fuels and lubricating oils under more severe operational conditions. Acylpyrazolone derivatives being polyfunctional compounds are widely used as chelate reagents in the analytical practice. These compounds possess high

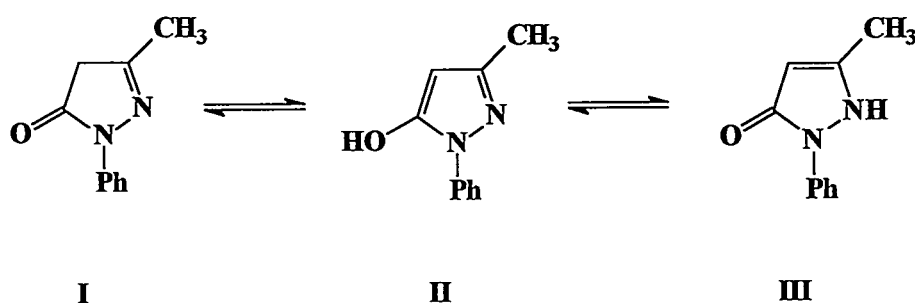
complexion ability which makes quite possible their using as metal deactivating additives for various lubricants.

The aim of this paper was to assess not only the reducing properties of some acyl pyrazolone derivatives towards the catalytic effect of copper, but also their efficiency as radical scavenging agents during gasoline oxidation and in model oxidation system.

EXPERIMENTAL

1-Phenyl-3-methyl-pyrazolone-5 derivatives were synthesized according to procedure described in Ref.7. The pyrazolone derivatives which have been the subject of the present study are presented in Figure 1.

It is known that these derivatives are used mainly for the production of medicinal compounds and they are highly soluble in water. Their ability to tautomerize is shown below. The tautomeric forms I and III are most the probable species in nonpolar medium as gasoline/ethylbenzene.



The radical-deactivating properties were assessed by the duration of the induction period (τ_{ind}) and the metal-deactivating properties by the degree of the reduction of initiation rate (W_i) during the oxidation of ethylbenzene/gasoline containing copper naphthenate as initiating additive.

The efficiency of the pyrazolone derivatives was evaluated by applying two test methods:

Test A - gasoline oxidation

The investigations were carried out in autoclave equipment as described earlier⁸. Two gasoline samples A-86 and A-86p have been studied. The base sample A-86 contains 50 % catalytically cracked fraction, 0.2 % wt. Pb as ethylate and 0.6 % wt. dycer. This gasoline sample has been additionally subjected to purification in order to eliminate the metal ions and the natural macromolecular compounds, and thus sample A-86p was obtained. For this purpose 1 l gasoline was passed through a column packed at the bottom with silica gel HS₂₅₄ and HS₆₀ (Merck) - 20 g. and at the top with silica gel HS₂₅₄ (40 g.) previously treated by bis-(4-carbonyl-pyrazolone-5)-p-phenylene (2.5 wt % with respect to silica gel).

Test B includes a model oxidation reaction of ethylbenzene at 353 K, P = 0.1 MPa in the presence of azobis-isobutyronitrile (AIBN) as radical initiator and copper naphthenate (CuNf) as a source of soluble copper ions. Neat ethylbenzene was purified according to the procedure in Ref. 9. The initiator AIBN was used after recrystallization from ethanol, acetone and benzene. Copper naphthenate was synthesised and purified as described in Ref.10. The rate of oxygen absorption was measured in manometric apparatus¹¹.

RESULTS AND DISCUSSION

Test A: The results from the oxidation of gasoline A-86 and A-86p in the presence of the pyrazolone additives DM-3 -DM-8 are given in Table 1. The inhibiting properties of the compounds studied are evaluated by comparing the value of the induction period with that of the typical radical acceptor of phenolic type -4-methyl-2,6-di-tert-butylphenol (further denoted as ionol). An essential difference in the behaviour of the pyrazolone derivatives towards the oxidation of the base gasoline A-86 and the purified one A-86p has been observed. All compounds tested are not effective in scavenging of the active free radicals generated in the course of the oxidation of A-86p (τ_{ind} is the same as τ_{ind} of the pure gasoline)

However, the oxidation of A-86 is found to be successfully inhibited by additive DM-4 (with terephthalic bridge between the pyrazolone cycles) and its antioxidant activity is similar to that of ionol ($\tau_{ind} = 238$ min for DM-4 and 236 min for ionol, respectively). The additive DM-8 which has an analogous structure to that of DM-4, but without possibility for conjugation between the two pyrazolone cycles does not manifest any significant inhibiting properties - the induction period (168 min) is the same as without it (160 min)

On the basis of the kinetic data the rate of the thermal initiation for the both samples and the concentration of the natural inhibitor can be estimated:

$$\tau_1 - \tau_2 = f [C_o]/W_i \quad 1)$$

where: τ_1 is the induction period of the gasoline oxidation in the presence of additives in sec.;

τ_2 is the induction period of gasoline without inhibitor;

f is the stoichiometric coefficient of inhibition showing the number of free radicals deactivated by a molecule inhibitor;

$[C_o]$ is the initial concentration of the additives, mol/l ;

W_i is rate of initiation, mol./l. s .

For A-86p gasoline the value of W_i is found to be $6.1 \cdot 10^{-8}$ mol./l .s and the concentration of the natural inhibitor = $1.4 \cdot 10^{-4}$ mol./l.s. For A-86 these parameters have the following values: $W_i = 8.8 \cdot 10^{-8}$ mol./l .s and $4.2 \cdot 10^{-4}$ mol./l . These data show that the "purified" gasoline sample A-86p practically does not contain natural inhibitor (its concentration is reduced almost three fold). From the other side, the reduction in the value of W_i points also to the removal from the stock gasoline of components possessing initiating properties. The data suggest that the mechanism of action of the tested pyrazolone derivatives during the oxidation of the both gasoline samples is more complex and requires further research. Another interesting and at the present state unexplained observation is the behaviour of the most efficient antioxidant additive DM-4 (with respect to the oxidation of the base gasoline sample A-86) during the oxidation of A-86p which does not contain Pb compounds, artificially introduced nitrogen-containing dyers, natural high molecular compounds, etc. It does not exhibit any inhibiting properties ($\tau_{ind} = 72$ min and 187 min for ionol, respectively). It could be assumed that the pyrazolone additive either interacts with some of these components resulting in the formation of more efficient antioxidant or forms synergistic mixtures with them.

The stoichiometric coefficient of inhibition of DM-4 ($f = 2.1$) has been determined by applying eqn.1 and is found to be similar to that of ionol

In Table 2 are presented the results of the study on the metal-deactivating properties of the pyrazolone derivatives. As a standard metal-deactivator we have used N,N-disalicylidene diethylenetriamine (DM-2) whose mechanism of action has been studied earlier^{8,12}. It can be seen that the additives DM-4 and DM-8 demonstrate high complexing ability towards copper ions thus reducing its catalytic activity in the promoted gasoline oxidation. The value of the induction period in its presence is similar to that of the standard

DM-2 additive. In addition the results of the oxidation of gasoline with DM-4 which has been kept for 24 hours followed by filtration reveal an unusual increase in τ_{ind} (215 min for reaction B against 170 min for reaction A, respectively) and the stoichiometric coefficient of inhibition estimated by eqn.1 amounts to 51.2. This suggests that the formed copper complex of this derivative appears to be effective antioxidant compound. Most probably, the increased efficiency observed in reaction B is due to the better dissolving of the polar pyrazolone additive with the time (the equilibrium is shifted to tautomers I and III) and thus its effective concentration is increased in the non polar medium.

Test B- oxidation of ethylbenze.

The data obtained from the gasoline oxidation provoke us to check whether these compounds can be used both as antioxidant and metal-deactivating additives. Another goal of the present research as to find more simple, reliable and quick test method for preliminary evaluation of their multifunctional effect. For this purpose, we have carried out a model low temperature oxidation reaction of ethylbenzene and tried to characterise this complex inhibiting action by performing two model reactions: reaction A and reaction B.

Reaction A comprises the oxidation of ethylbenzene in the presence of AIBN and the compounds studied (Table 3). The rate of the initiation was determined in the presence of ionol whose f is equal to 2. The radical-scavenging properties of the pyrazolone derivatives were evaluated on the basis of the experimentally determined induction periods and are characterised by the value of f . Some of the compounds, i.e. DM-5, DM-9 and DM-10 appear to be efficient radical acceptors with f similar to that of ionol. Taking into consideration the various tautomeric forms of the acyl pyrazolone compounds their deactivating properties towards free radicals might be due: for tautomer I- to electron transfer; for tautomer II - to the hydrogen abstraction from the hydroxy group and for tautomer III, which in our opinion is the most probable reactive species in the system studied, to the presence of sterically hindered NH group. The effect of the structure of these derivatives on their inhibiting properties could be also explained by the changes occurring in the equilibrium constant of this tautomerism.

Reaction B - In order to assess the metal-deactivating properties of the pyrazolone derivatives we have carried out the oxidation of ethylbenzene (353 K) both in the presence of AIBN and copper naphthenate as a source of soluble copper ions. The rate of

the initiation due to the presence of copper naphthenate (W_i^{CuNf}) was determined by subtracting from the value of the total rate of the initiation (ΣW_i , calculated by the method of the inhibitor -Table 4) the value of initiation rate due to the presence AIBN (W_i^{AIBN} determined in reaction A, Table 3). Taking into consideration the value of f (from Table 3) and the experimentally obtained τ_{ind} we have estimated the rate if the initiation in their presence (W_i^B). Subtracting from these values the value of (W_i^{AIBN}) we obtain the rate of the initiation which is due to the remained (noncomplexed) copper ions. In order to compare the metal-deactivating properties of the various pyrazolone derivatives with that of the standard (DM-2) we have introduced a parameter MDA which is given by the following expression:

$$MDA \% = 100 - [(W_i^B - W_i^{AIBN}) / W_i^{CuNf}] \cdot 100$$

where: W_i^B is the initiation rate given in Table 4

W_i^{AIBN} is equal to $1,33 \cdot 10^{-6}$ mol/l.sec

$W_i^{CuNf} = \Sigma W_i - W_i^{AIBN}$ and is equal to $2,47 \cdot 10^{-6}$ mol/l.sec

This parameter shows the degree of the reduction of the initiation rate with copper naphthenate in their presence and is a criterion of the copper-deactivating efficiency of the compounds studied. The data of Table 4 reveal that some of the pyrazolone derivatives possess metal-deactivating properties similar to those of DM-2. Among them, the additives DM-4, DM-14 and to a some extent DM-12 show remarkable metal-deactivating efficiency and are superior to the standard additive. Evidently, the various bridges between the pyrazolone cycles affect this parameter. However, the elucidation of this effect needs some more experimental evidences which will be the subject of future investigations.

The low values of the rate of the initiation obtained in the presence of the additives DM-4 and DM-14 ($W_i^B = 0.61 \cdot 10^{-6}$ mol/l.s and $0.70 \cdot 10^{-6}$ mol/l.s, respectively) suggest that the formed copper complexes of these additives are efficient radical acceptors during the ethylbenzene oxidation. These data support the results of test A with respect to the behavior of DM-4. Generally, the data of Table 4 reveal that although some of the pyrazolone derivatives are not efficient antioxidants (as their f values show) the additives DM-4 and DM-14 manifest excellent multifunctional action in the presence of soluble copper and are very promising as antioxidant additives.

CONCLUSIONS

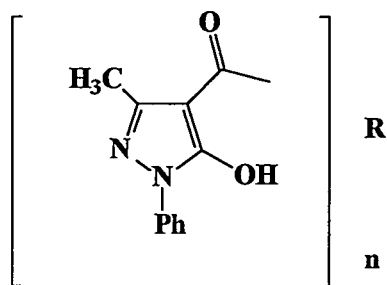
1. The model oxidation reaction of ethylbenzene can be successfully used for preliminary evaluation of the antioxidant and metal-deactivating properties of various compounds.

2. Some of the pyrazolone derivatives, as DM-4, DM-12 and DM-14 manifest good deactivating properties towards copper.

3. The additives DM-4, DM-12 and DM-14 show both high antioxidant potential and significant metal-deactivating properties and appear to be promising as multifunctional inhibitors for the long-term storage of liquid fuels.

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| compound | n | R |
|----------|---|-------------------------------|
| DM-3 | 1 | |
| DM-4 | 2 | |
| DM-5 | 2 | |
| DM-6 | 1 | |
| DM-7 | 1 | |
| DM-8 | 2 | $-\text{CH}_2-\text{CH}_2-$ |
| DM-9 | 2 | |
| DM-10 | 1 | |
| DM-11 | 1 | |
| DM-12 | 1 | |
| DM-13 | 1 | $-\text{C}_{11}\text{H}_{23}$ |
| DM-14 | 1 | $-\text{C}_{15}\text{H}_{31}$ |

Figure 1. Structure of the acyl pyrazolone derivatives studied.

Table 1. Inhibiting properties of pyrazolone derivatives during the oxidation of gasoline A-86 and A-86p at 393 K, $P_{O_2} = 1,0$ MPa, $[C_0] = 2 \cdot 10^{-4}$ mol/l.

| No | Additive | A-86, τ_{ind} , min | A-86p, τ_{ind} , min |
|----|----------|--------------------------|---------------------------|
| 1. | - | 160 | 78 |
| 2. | ionol | 236 | 187 |
| 3. | DM-3 | 140 | 77 |
| 4. | DM-4 | 238 | 72 |
| 5. | DM-6 | 148 | 80 |
| 6. | DM-7 | 146 | 78 |
| 7. | DM-8 | 168 | 72 |

Table 2. Metal-deactivating properties of pyrazolone derivatives during the oxidation of gasoline A-86 at 393 K, $P_{O_2} = 1,0$ MPa, $[C_0] = 1 \cdot 10^{-4}$ mol/l.

| No | Additive | Reaction A, τ_{ind} , min | Reaction B, τ_{ind} , min |
|----|----------|--------------------------------|--------------------------------|
| 1. | - | 40 | 40 |
| 2. | DM-2 | 170 | 170 |
| 3. | DM-3 | 44 | 65 |
| 4. | DM-4 | 162 | 215 |
| 5. | DM-6 | 44 | 52 |
| 6. | DM-7 | 42 | 59 |
| 7. | DM-8 | 152 | 172 |

Table 3. Kinetic data of ethylbenzene oxidation in the presence of pyrazolone derivatives at 355 K, P O₂ = 0,1 MPa, W_i = 1,33.10⁻⁶ mol/l.sec.

| Additive | Concntr. mol/l.10 ³ | τ_{ind} , min | f |
|----------|--------------------------------|--------------------|------|
| DM-2 | 4,0 | 6 | 0,12 |
| DM-4 | 2,0 | 16 | 0,5 |
| DM-5 | 0,5 | 10 | 1,6 |
| DM-9 | 1,0 | 21 | 1,7 |
| DM-10 | 1,0 | 17 | 1,4 |
| DM-11 | 1,0 | 9 | 0,7 |
| DM-12 | 4,0 | 19 | 0,4 |
| DM-13 | 4,0 | 10 | 0,12 |
| DM-14 | 4,0 | 11 | 0,23 |

Table 4. Kinetic data of ethylbenzene oxidation in the presence of pyrazolone derivatives, AIBN and CuNf at 355 K, P O₂ = 0,1 MPa, W_i^{AIBN} = 1,33.10⁻⁶ mol/l., [CuNf] = 5.10⁻⁵ mol/l

| Additive | Concentr. mol/l.10 ³ | τ_{ind} , min | W _i ^B mol/l.sec .10 ⁶ | MDA in % |
|----------|---------------------------------|--------------------|--|----------|
| DM-2 | 4,0 | 6 | 1,30 | 100 |
| ionol | 1,0 | 9 | 3,70 | - |
| DM-4 | 1,0 | 14 | 0,61 | >100 |
| DM-5 | 0,5 | 7 | 1,70 | 84,4 |
| DM-9 | 1,0 | 8 | 1,77 | 81,3 |
| DM-10 | 1,0 | 12 | 1,94 | 74,3 |
| DM-11 | 1,0 | 6 | 1,90 | 76,0 |
| DM-12 | 1,0 | 5 | 1,30 | 100 |
| DM-13 | 4,0 | 12 | 1,10 | 84,4 |
| DM-14 | 4,0 | 18 | 0,70 | >100 |



5th International Conference
on Stability and Handling
of Liquid Fuels

Rotterdam, the Netherlands, October 3 - 7, 1994

The EBV Quality Prediction System (EQPS)

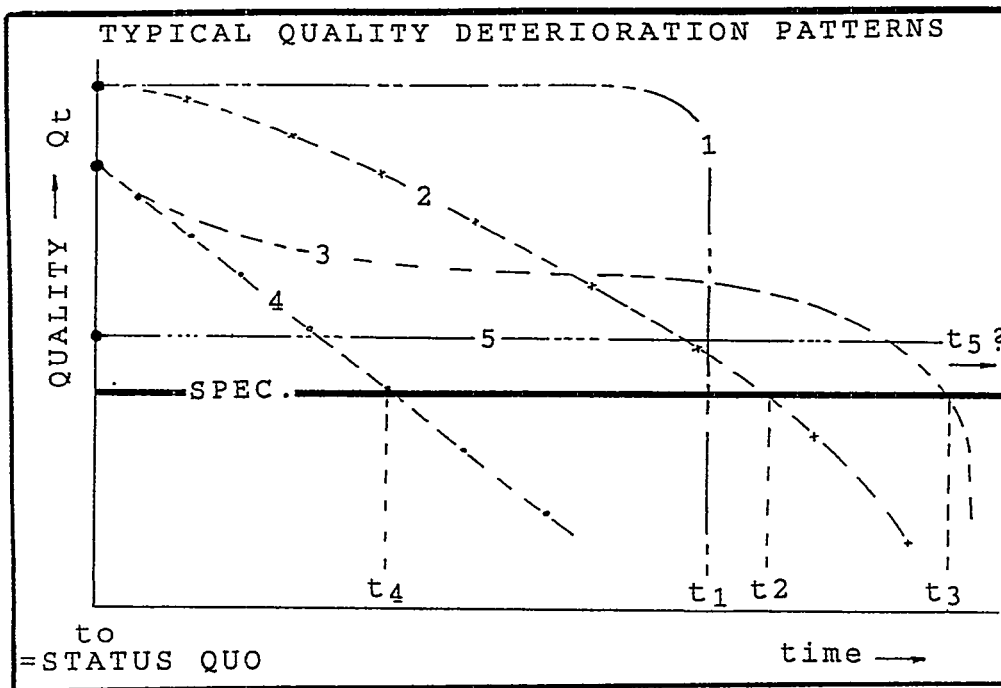
J.W. Joachim Koenig
ERDÖLBEVORRATUNGSVERBAND
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Chairman, Ladies and Gentlemen,

An oil product is said to be ageing, if over time it changes appearance, performance characteristics or environmental properties. Ageing - and so is quality - is a summary term - embracing many influencing factors and observed behaviours. Ageing quality is a function of inherent or added immunity, environmental factors or exposure and of course age. Inherent factors are themselves a function of raw materials from which the product was made and the manufacturing processes used in the refinery.

| WHAT IS OIL QUALITY DETERIORATION | |
|--|--|
| $Q_t = f(I_i, E_j, T)$ $I_i = g(M, S)$ | |
| <p><u>CONDITIONS</u></p> $Q_t = \left\{ \text{SPEC}_k \right\}_{k=1..n} + \left\{ R_{k_t} \right\}_{k=1..n}$ $R_{k_2} - R_{k_1} > 0$ | <p> Q_t = product quality at time t I_i = inherent ageing susceptibility and protection factors i E = environmental factors j T = time since virginity M = manufacturing process S = source material (e.g. crude) SPEC_k = quality specification indicators k R_{k_t} = quality reserve at time t k_2 = target life time (date) k_1 = current date $\left\{ \right\}_{k=1..n}$ = set of all indicators 1 to n </p> |

Quality is generally expressed by a set of quality indicators (measurements), which are themselves constrained by specified max or min values. If measurements do not meet specification values there is a positive or negative quality reserve. If quality indicators change with time, a fresh product should have a quality reserve, whose size establishes the storage life span of a product.

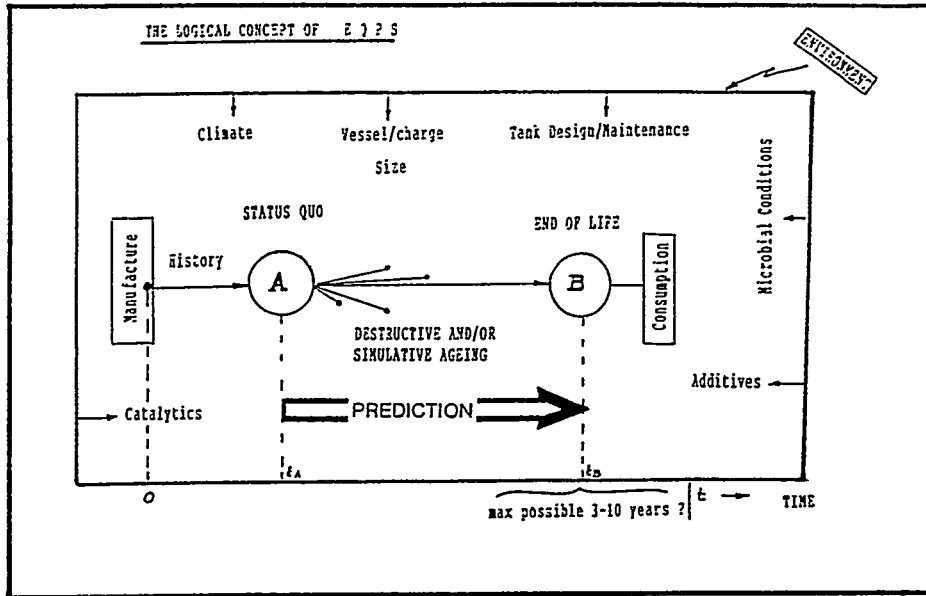


Product quality - used here as the summary term - changes with time along many possible and remarkably different paths, some of which can be observed well in strategic stocking of the "first generation", which stored mainly hydroskimming type products (FDO (Denmark) and Berlin Senatsreserve stocks).

EQPS is an attempt to predict the quality change = ageing through analysing as many as possibly influencing factors, whose effects often can not be well explained but qualitatively or even quantitatively measured.

Let me define ageing in another way:

Product starts ageing when it is created i.e. through manufacturing where its inherent qualities are "laid down". Normally it gets into our (EBVs) hands later, when it has reached the "status quo" position. At that point we test it, sometimes by simulative tests (often "product destroying" methods like forced oxidation) which normally do not predict



future ageing behaviour well. On the path from creation to the final consumption external factors like climate, vessel size (average temperature), tank maintenance, microbes, additive and all sorts of other catalytic effects influence the ageing paths, retard it or accelerate it. The objective of EQPS is to capture as many as possible of such external factors and join them with the inherent product quality into a prediction of the most likely lifetime.

What looks so simple as a general formula shown above becomes extremely complicated if one would attempt to build a mathematical model joining all the factors in a set of reaction kinetic, chemical/physical and energy balance describing equations. Even if we could know all those equations, we could not really fill them with data. The dream of having one simple ageing equation will possibly never be fulfilled.

AGEING THEORY/MODEL BEHIND EQPS

- o VARIOUS DIVERSE THEORIES, SOMETIMES CONTRADICTIVE
 - TAKEN IF EXPERIENCE SHOWED, THAT IT HAPPENED -
 - EXPERT WORD TAKEN FOR GRANTED, EVEN IF REASON. PARTLY CONCLUSIVE ONLY
- o NOT A MATHEMATICALLY DERIVED SINGLE AGEING FORMULA
 - TOO MANY COMPONENTS INFLUENCING (E.G. 90 FOR DIESEL) -
- o RISK ANALYSIS WITH PROBABALISTIC ELEMENTS
 - SO CALLED "EXPERT SYSTEM" USING LOGICAL DEDUCTIONS FROM DECISION TREES
 - PROGRAMMED DECISION OPTIONS, DECIDED ON BY EXPERT PROGRESSING ALONG DECISION TREE BRANCHES, STRICTLY LOGICALLY
- o PROBLEM TOO LARGE FOR HUMAN BRAIN TO CONSIDER ALL OPTIONS
 - ELIMINATES "PET FAVOUR" DECISIONS BY EXPERTS

Should we give up at this point? NO! There are many experts out in the field who can predict an ageing process without being able to explain why it all happens, it is just experience: "it always happens that way". If such experience could be gathered and logically formulated into a "cause--->result" system and linked to some kind of probability that under the various different circumstances it really happens, then a prediction could be made. There is a mathematical technique called "expert system", which does exactly that. Dr. Hartman will describe this in detail in the following presentation.

The problem is too large for the human brain to handle all the options simultaneously and quickly; every expert has his own view, why ageing occurs, he normally follows one or two theories, because they fit to his personal experience. He tends to overlook facts, which do not fit into his theory or which he considers marginally important only. The EQPS does not discard any fact, it weighs it, but if many marginal danger signals appear, it decides often against the experts. EQPS combines theories, which have their value taken on their own, but do not fit all together; it takes an expert opinion for granted concluding that experience showed once a problem under those given circumstances, thus there is a potential risk that it may occur again.

| <u>E Q P S - G A S O L I N E - AGEING PREDICTION.</u> | <u>MAJOR COMPONENTS</u> |
|---|--|
| <u>STATUS QUO</u> | APPEARANCE/COLOR ACIDITY UNSATURATES |
| <u>ARTIFICIAL AGEING</u> | INDUCTION ANALYSIS GUM FORMATION |
| <u>AGEING PRECURSORS</u> | OLEFINS/AROMATICS NITROGEN OXIGENATES |
| <u>ENVIRONMENT</u> | TANK (CONDITIONS, CONSTRUCTION, CLIMATE) PROCESS CHEMISTRY (MANUFACT., BLENDING, ADDITIVES) MICROBIAL (EXISTING & POTENTIAL) |

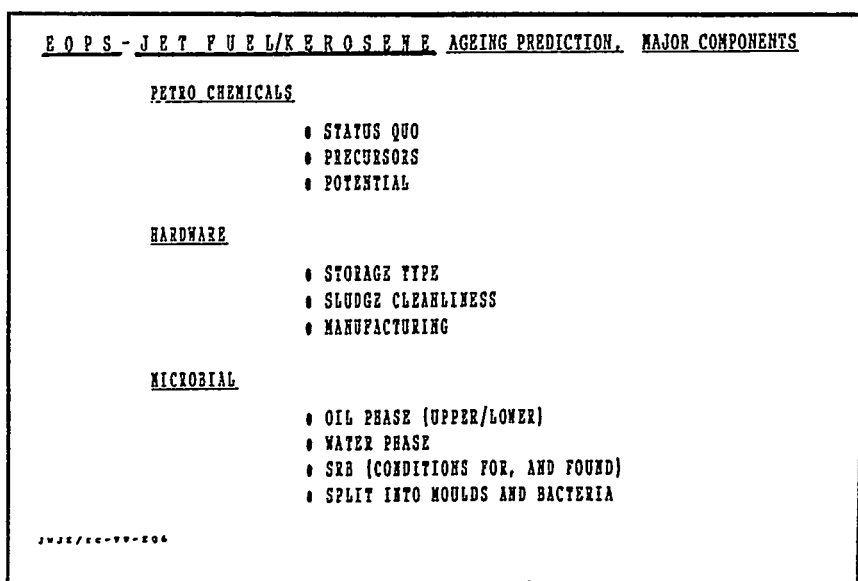
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Gasoline ageing Prediction

Certainly those "given circumstances" are normally manifested as laboratory test results, knowledge about the manufacturing process, storage conditions etc; thus EQPS does not encapsulate the "gut feeling" or "crystal ball" rather stays on firm ground of measurable (quantifiable) facts and observations.

For gasoline the main components are a set of data about the current quality (status quo), behaviour under forced oxidation ageing (artificial ageing), a chemical analysis allowing the indentification of compounds which have not yet but may lead to ageing (precursors) and a set of environmental facts ranging from storage conditions, climate over manufacturing processes to microbial spoilage, the latter being "low rated" as it still seldom occurs in gasolines.

The full structure and complexity of the EQPS gasoline module can be illustrated by the hirarchical block diagramme, which we call "flow plan", a term taken from chemical engineering, even though here information of course is "flowing" through it only. It just shows, how the various parameters are logically linked. There will be more explanation of such structures and its use in the following paper by Dr. Hartman.



The jet fuel/kerosene module is much simpler, mainly due to the fact that international airline and military have boxed-in jet fuel qualities by such tight specifications, that at least the petrochemical part leaves little room for variations. It also is a chemically much simpler product than gasoline or diesel/gasols.

There is of course a petrochemical section dealing with some straight forward indicators of the status quo quality and any chemicals, which may in future cause ageing problems. The biggest part of the system however deals with outside influences on a basically stable product.

The microbiological section is rather detailed, since biological deterioration is the main danger to paraffinic hydrocarbons of a chain length $C_8 - C_{18}$.

E Q P S - D I E S E L / G A S O I L A G E I N G P R E D I C T I O N .

MAJOR COMPONENTS

SPOILAGE/AGEING

- o EXISTING: APPEARANCE, CORROSIVITY, GUM/SEDIMENTS
 - o POTENTIAL: PRECURSORS: - CATALYTICS
 - NITROGEN/SULFUR
 - UNSATURATES/PARTICULATES
- OXIDATION: 13 OPTIONS

PROMOTERS

- o ACTIVATORS (SULFONIC ACIDS, ELEMENTAL SULFUR, NITROGEN COMPOUNDS etc)
- o PROCESSING HISTORY
- o TANK: CONDITIONS, CONSTRUCTION, MAINTENANCE, CLIMATE
- o MICROBIAL (EXISTING, POTENTIAL, PROMOTERS)
- o SLUDGE AND FALL-OUTS (e.g. WAX)

NOTE: KEY PARAMETERS CHECKED BY DIFFERENT TEST METHODS

.....

The EQPS module for diesel, gasoils and light heating oil is so far the most complex. Again the emphasis is on existing quality or spoilage and any potential for further deterioration. The ageing theories behind it are of course quite different from those assumed to be applicable for gasoline and jet fuel.

There is an extensive set of oxidation methods measuring essentially the same; but since the ASTM D 2274 now contained in the EN 590 spec is notoriously inaccurate and most other similar tests are not much better, the system tries to draw conclusions from tests controlling other tests. Besides this the standard environmental factors like storage facilities, climate, microbiology are of course there. In addition the system evaluates strong ageing promoters like acids, elemental sulfur, basic nitrogen compounds etc. Another speciality is a section on sludge formation, incompatibility and fall-outs.

As you can see from the "flow plan", the non straight chemical part of the system is almost the biggest. You will also note, that several measurements are used in double activity, e.g. describing the status of spoilage as well as being enhancers, promoters, catalysts for further ageing.

MAIN AGEING MECHANISMS BEHIND E O P S I

| |
|--|
| <p><u>GASOLINE</u></p> <ul style="list-style-type: none">• POLYMERIZATION/CONDENSATION• HYDROPEROXIDE FORMATION/PEROXYRADICALS• CATALYTIC PROMOTION<ul style="list-style-type: none">- METALS FROM TANK STRUCTUREMETAL SALTS/OXIDES FROM SLUDGEMETALS IN FUELCLIMATEMICROBIAL AS MINOR EFFECT• MANUFACTURING PROCESSES <p><u>JET FUEL</u></p> <ul style="list-style-type: none">• POLYMERIZATION• SULFUR/NITROGEN EFFECTS/ACIDIFICATION• MANUFACTURING PROCESSES AND TREATING• CATALYTICS (MAINLY TANK, SLUDGE, CORROSION ON HARDWARE)• MICROBIOLOGY (EXTENSIVE DETAIL) |
|--|

JUNE/CC-77-008

Ageing mechanisms used by EQPS

As said earlier EQPS does not subscribe to one single ageing theory. Thus it "worries" about several.

With gasoline of course polymerisation/condensation into gums, peroxyradical formation and all sorts of catalytic promotion is in the forefront. This is directly or indirectly linked to the manufacturing processes.

With jet fuel polymerisation is considered a minor effect (as it contains none or hardly any conversion components in Europe) but sulfur, nitrogen and acidification reactions are being watched and a lot of emphasis is laid on microbiological spoilage both as acid and biomass producer as well as catalysing other ageing reactions.

MAIN AGEING MECHANISMS BEHIND E O P S II

| |
|---|
| <p><u>DIESEL/LIGHT HEATING OILS/GASOILS</u></p> <ul style="list-style-type: none">• OXIDATION• NITROGEN/SULFUR COMPLEX COMPOUNDS (e.g. CYCLICS)• ORGANIC ACIDS• REACTIVE OLEFINS• STRAIGHT POLYMERISATION (AS MINOR EFFECT ONLY) <p>FOR DETAILS SEE DERST PAPER ON MECHANISMS: THIS CONFERENCE</p> <p><u>OTHER PROMOTERS AND RETARDERS</u></p> <ul style="list-style-type: none">• CATALYTICS<ul style="list-style-type: none">METALSACIDSSULFUR, N-COMPOUNDSSLUDGE/MAINTENANCE/CLEANLINESS OF TANK• PROCESS ORIGIN (REFINERY)• MICROBIOLOGY• ADDITIVES (TO BE ADDED TO THE SYSTEM) |
|---|

For diesel/light heating oils/gasoils the presence and/or formation sulfur/nitrogen compounds are being predominantly analyzed, less so any straight polymerisation reactions. Weight is also laid on all sorts of catalytic promotion possibilities and the processing origin of the product.

The system deals with stocks containing none or few additives only (antioxidizer, wax antisetling). It does not deal with the modern "additive culture" at the diesel loading rack, where today up to 12 additives are being mixed with the diesel fuel for multiple purpose. The system could be expanded into this field but the EQPS users do not see any need for it since they store "base stock" product without those additive packages. Many of those additives lose their activity over time, but experience is limited - often company secret. The extension could be very complex.

E Q P S - IN OPERATION AT EBV

• R O U T I N E CHECK OF ALL TANKS OWNED STOCK

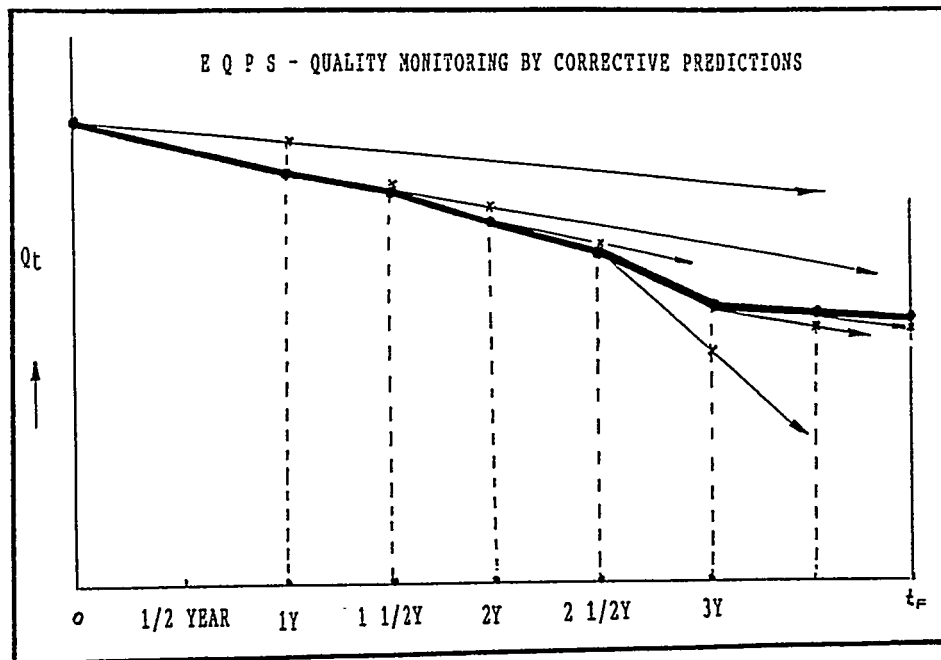
- PREDICT LIKELY LIFETIME
- HIGHLIGHT POTENTIAL PROBLEMS
- TRIGGER EXCHANGE
- CORRECT ACTUAL AGEING PATH EVERY 6 MONTHS

• T E S T P R O S P E C T I V E STOCK

- EVALUATE PURCHASE OPTION
- DECIDE ON STORAGE TYPE (e.g. FIT FOR CAVERN)
- SUGGEST NEGOTIATING VALUE

WJL/CC-V8-0013

How is EQPS being used? The system is available since over a year and has been in test use prior to that for almost also a year. Results are pleasing. Some scaling work is still going on for the diesel/gasoil module. The programme is PC based and can be/is being used by quality inspectors with little knowledge on chemistry, oil manufacturing and oil quality. Since decisions are recommended by the system which can be extremely costly, there should always be an expert at hand to do a brief plausibility analysis - as I said - when it becomes costly. A vast number of cases can be decided solely on EQPS. In general EQPS tends to judge ageing somewhat on the pessimistic side.



EBV tests all old and marginal tanks every 6 months and adjusts the ageing predictions accordingly. Good and perfect tanks with a "life" prediction of 3-5 years are checked annually. While predictions are generally accurate for the next 18 months, with fresh products, the variations between predicted and experienced quality loss generally increases with the age of the products.

Incoming cargoes, purchases etc. can also be assessed by EQPS, which gives advice as to buy or not to buy or buy at discount, or buy just for keeping it 1-2 years, or fit for long term cavern storage etc.

The analysis highlights every potential problem in plain language and quantified, much more than you ever wanted to release to the customer or seller. The system also indicates off-spec situations on non ageing relevant parameters, but this is done in the peripheral data base system. Automatic data transfer from 7 labs into EQPS will start early 1995 for EBV.

E O P S - A TRUE JOINT INTERNATIONAL EFFORT

- MANAGED BY EBV - HAMBURG
- DEVELOPMENT-TEAM: EBV (HAMBURG), IIBR/J.H. CON.EX (ISRAEL)
- FINANCIAL CONTRIBUTORS AND CURRENT USERS:
CARBURA (SWITZERLAND), COVA (NETHERLANDS), EBV (GERMANY)
FDO (DENMARK), SAGESS (FRANCE)
- TWO NEW PROSPECTIVE USERS MAY JOIN SOON, AVAILABLE FOR ALL STOCK ENTITIES
- 15 INTERNATIONAL OIL QUALITY EXPERTS LENT EXPERTIZE (INCL. UK, US, EUROPE)
- SALE TO COMPANIES CONSIDERED, NOT YET DECIDED
- EXPANSION INTO CRUDE OIL INCOMPATIBILITY HAS BEEN STARTED, LOOK FOR PARTNERS

INJL/CC-77-1012

EQPS is not only used by EBV. Its development was a true international effort. The origins go back to an 1989 British Institute of Petroleum meeting on microbiology, during which an expert system concerning the microbial spoilage of jet fuel was presented. Out of this grew a strong EBV interest to expand the concept to overall oil product quality deterioration. EBV joint with CARBURA of Switzerland and FDO of Denmark to finance such undertaking, later COVA of Netherlands and SAGESS of France joined. All five organizations are currently EQPS users. We are in the process to talk to potential new customers, predominantly stock holding agencies.

Over a period of 2 1/2 years the development team of EBV Germany and IIBR, later J.H. ConEx of Israel joint forces with input by 15 top international quality experts from member countries and elsewhere, which were interviewed to place their expertize into the hands of the team. The late Nahum Por was among them.

The work is by no means complete. We just finished work on lab input automation and look forward to join up with other customers to expand into the field of crude oil incompatibility and sludging, possibly under the umbrella of an International Energy Agency joint project.

Dr. Hartman, who was the key man on the Israeli side of the development team, will now go into more detail on the functioning and structure of EQPS

Thank you for you attention

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*5th International Conference
Stability and Handling of Liquid Fuels*

Rotterdam, the Netherlands

October 3-7, 1994

**THE MATHEMATICAL APPROACH TO EQPS -
AN EXPERT SYSTEM FOR OIL QUALITY PREDICTION**

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1. INTRODUCTION:

EQPS is an expert system for prediction of ageing processes in long term storage of oil products. EQPS contains a data base with detailed information on the user's stored stocks, and a diagnostic Expert System which is used for analysis, evaluation and quality prediction of a given storage site. An extensive body of knowledge and information concerning oil products is included in the program. Petrochemical and petrobiological laboratory test results, source and product processing data, storage conditions, environmental and climatic factors, are all considered in the evaluation.

The objective of EQPS is to serve as a tool which allows a quality control of strategic oil reserves, assistance in oil purchase decisions, selection of appropriate storage site for a given product, and to provide guidance consultation and instruction in the field of product ageing.

EQPS is a rule based expert system. The rules are expressed mainly in form of decision trees. Each input item is rated according to its potential relevance to ageing of the product. Various 'functions', expressing ageing phenomena are defined and assessed. Finally, a recommendation and indicative remarks conclude the assessment.

The system applies Artificial Intelligence concepts. Implementation uses PDC - Prolog software, one of the leading Logical Programming tools. [Forsyth (7) and Bratko (8)].

In references [1], [2], [3], earlier expert systems for microbial problems in jet and diesel fuel were discussed. EQPS deals with the whole spectrum of ageing, chemical, physical and biological. The knowledge acquisition and logical structuring was done with the help of more than a dozen international experts in various facets of the problem. Special mathematical and programming tools were developed to accommodate the extensive knowledge, information, and reasoning capabilities of the system.

We emphasize in this paper, the mathematical structure, logical architecture and programming tools. The subject matter will be discussed in [Koenig (9)].

2. AGEING OF A PRODUCT:

A product is said to be 'ageing', if over time it changes its performance, appearance, or environmental properties. Ageing may be caused by chemical reactions (sometimes promoted catalytically), physical treatment, exposure, climatic situation, storage conditions, and microbial attack.

Ageing will have usually detrimental results. Formation of chemical compounds (e.g. acids), attacks and may destroys engine components. Filter plugging may result from formation of heavy molecules by polymerization or condensation. Heavy molecules, which boil at higher temperatures than the original product components, lead also to carbon black formation (smoke), mechanical corrosion, poor combustion (energy loss), and pollution. Formation of biomass, which often is related to increase in acidity, plugs filters, corrodes and blocks pipes, and sometimes destroys components necessary for performance.

Ageing could be prevented or slowed down by additivation, such as antioxidants, anti corrosion, metal deactivator, biocides, wax dispersors and others. Maintenance conditions of storage sites is an important factor in ageing. Manufacturing modifications may also be applied to this end.

Obviously, it is desirable to detect an ageing trend as early as possible, then effective prevention methods could be applied. EQPS is intended to give an early warning - prediction of an ageing trend. The system estimates the present degree of ageing by looking at color, existent gum, sediments, pour point, CFPP, microbial counts etc. In addition to the current deterioration level, forced (artificial) ageing tests (potential gum, ASTM 2274, VEBA airblow, TUV/ESSO test etc.) are considered. Outside ageing factors such as climate, tank design, tank cleanliness, oxygen exposure, water and others, coupled with inherent ageing potential caused by manufacturing (olefins, aromatics, nitrogen, sulfur, phosphorous etc.) complete the predictive picture.

EQPS contains at the present three product modules for assessment of gasoline, diesel/heating oil, and jetfuel.

The gasoline module will be used in the demonstration of the system. The structure of the other modules is similar.

3. EXPERT SYSTEMS:

An expert system is a computer program that encapsulates specialist knowledge about a particular domain of expertise. It should be capable of making intelligent decisions within its domain. Such a system is a simulation of the human expert knowledge and his way of reasoning.

In general, an expert system contains three main components:

1. The knowledge base.
2. The inference engine.
3. The user interface.

The knowledge base consists of facts or assertions and rules that summarize the field of expertise. PROLOG a special declarative-logical programming language which have been developed for this purpose allows convenient expression of the knowledge base as a set of logical rule of the type 'If A then B'. Unlike conventional data bases which are normally passive, an expert system tries actively to conclude logical consequences of the rules. In case of partial information, the system attempts to fill in the gaps. An expert system should be able to "think" creatively. Thinking is due to the inference engine, which supplies the system with reasoning capabilities. This component generates a 'line of reasoning' leading from known facts (input data) to logically consistent conclusions.

The user interface is the channel of communication between the user and the program. This component allows the user to enter data into the program in a simple manner and displays the system's conclusions and decisions in a clear and intelligible form.

An expert system should have a sort of 'growing' capability. As time passes, new information, knowledge and experience are usually acquired. These are incorporated, automatically or manually in the system. As a result, the system improves, and it's predictions become more accurate. Thus an expert system is viewed as a dynamic body of knowledge and experience, which could give up to date expert advice to the user.

4. EQPS GASOLINE MODULE STRUCTURE:

EQPS contains a specially designed database which can handle data of many oil storage sites. Each storage site (above or below ground tank) record file includes data on the site and it's environment, and laboratory test results of samples taken at various points in time.

The following is a typical tank data screen.

| | | | | | |
|--|---------------------------|-----------------------------|---------------|-----------------|-----------------|
| Product: | <i>gasoline</i> | Grade: | <i>S V K</i> | Last Fill Date: | <i>15/11/92</i> |
| Tankfarm owner/operator: | <i>Bominflot</i> | | | | |
| Location: | <i>Hamburg</i> | | | | |
| Location detailed address: | <i>Tankweg 1</i> | | | | |
| | <i>2000 Hamburg</i> | | | | |
| | <i>Tel.:040-740007.20</i> | | | | |
| Tank number: | <i>81</i> | Status of tank: | <i>active</i> | | |
| Year of construction: | <i>1956</i> | Capacity (m ³): | <i>9583</i> | | |
| Safety classification: | <i>A1</i> | | | | |
| Diameter/height ratio: | <i>2/1</i> | | | | |
| Tank Underground? | <i>no</i> | | | | |
| Roof fixed/floating: | <i>float</i> | Double seal: | <i>yes</i> | | |
| Floating roof inside of fixed roof tank: | <i>no</i> | | | | |
| Closed System: | <i>no</i> | | | | |
| Automatic gauging/sampling: | <i>no</i> | Coloring (outside paint): | <i>gray</i> | | |
| Drainage facilities: | <i>yes</i> | | | | |
| Operation (static/rare turnover/continuous turnover): | <i>static</i> | | | | |
| General Maintenance: | <i>weak</i> | | | | |
| Last date cleaning: | <i>06/91</i> | | | | |
| Sludge found: | <i>no</i> | | | | |
| Method of last cleaning: | <i>water washed</i> | | | | |
| State of internal corrosion: | <i>light</i> | | | | |
| Naked steel (e.g. sandblasted bottom or walls): | <i>no</i> | | | | |
| Coating Material: | <i>---</i> | | | | |
| Coating Extent: | <i>---</i> | | | | |
| some - bottom and lower walls | <i>---</i> | | | | |
| Copper piping: | <i>no</i> | | | | |
| Brass/bronze fittings: | <i>no</i> | | | | |
| Climatic Region (continental/inland(moderate)/seashore): | <i>sea</i> | | | | |
| Sudden temperature shocks: | <i>few</i> | | | | |

The gasoline content of this tank will be evaluated later in this paper by EQPS.

Corresponding to the tank data, the system holds a history of test results of samples taken from the tank. The test list is comprehensive, meant to include all known and conventional

tests on the specific product. Obviously, the more input data points supplied to the program, prediction accuracy and reliability improves. The system, however may reason and assess the storage site, even in cases where less than a dozen input values are available. Each test is defined by known methods and standards. EQPS contains extensive 'help' texts defining the test, its methods, precision, significance, repeatability, etc. The texts could be easily retrieved on screen by the user. Specs depend on regulations in the storing country, and on the different types of product. The system allows the user to alter, add, or delete tests, and to modify the help texts accordingly. The following is an example of a few tests from the gasoline module.

| Type of Test | Units | Method | Specs | Expert System Ranges | | |
|-----------------|-------|--------|-------|----------------------|--------|------|
| | | | | low | medium | high |
| Bright & Clear | | Visual | | yes | odd | no |
| Climatic Region | | | | sea | mod | cont |

| Type of Test | Units | Method | Specs | Expert System Ranges | | | |
|---------------------|-------|----------|---------|----------------------|-------|-------|------|
| | | | | <-l-> | <-m-> | <-h-> | |
| Density at 15C | g/ml | ISO 3675 | .74-.79 | 0.60 | 0.74 | 0.78 | 0.88 |
| Research Octane No. | RON | ISO 5164 | >95 | 70 | 90 | 97 | 120 |

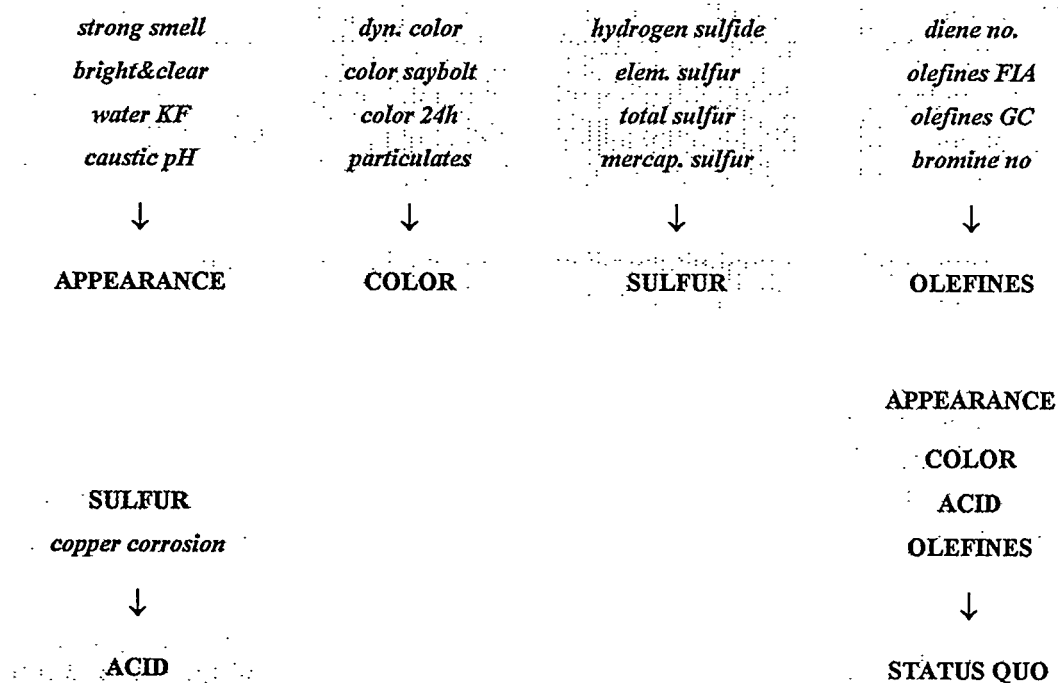
EQPS classifies input items into 'high', 'medium' or 'low', according to their impact on the product's ageing process. Thus the visual test of 'bright & clear' will be classified low (risk), if test result is 'yes', high if result is 'no', and 'medium' if input is 'odd'. Tank items, such as 'Climatic Region', are also classified. Numerical values in the second table, have also classification ranges. 'Density at 15C' test result will be graded low for values X if $0.60 \leq X \leq 0.74$, medium if $0.74 < X < 0.78$, and high if $0.78 \leq X \leq 0.88$. A value X, such that $X < 0.60$, or more $X > 0.88$, is considered by the system an input error, and prompts a message on screen. The permitted range, as well the classification range could easily be modified by a non programmer user.

Some items are calculated by the system, expressing the difference between previous and current measurements, or averages of certain values, and not actual test values. The system will label the calculated value as high medium or low.

The next task performed by EQPS, is to divide the tests into relation groups. The groups, represented by predefined functions, exhibit an ageing relevant aspect, or situation. This serves as an intermediate decision related to the product's ageing. For instance, the olefines function in gasoline, which influences the existing ageing, is evaluated using four test values; 'diene

number', 'olefines FIA', 'olefines GC', and 'bromine number'. Depending on the classifications of the four input parameters, function 'OLEFINES' will be classified into high, medium, or low. To distinguish between input test values and evaluated functions, the latter will be designated in capital letters. Functions will be evaluated even if some input parameters are missing. Test values may enter several functions, and functions often have other function classifications, as their input parameters.

The following displays the logical flow diagram of function STATUS QUO, which assesses the current deterioration level. The lower case values are individual input values, whereas the capital letters represent functions. SULFUR for example, is evaluated by a tree with input parameters listed above it. ACID function will consider the level of SULFUR, and the levels of total acid number and copper corrosion test result. All input parameters of STATUS QUO are function classifications.



A passage through a function box, depicted by capital letters, involves an activation of an appropriate decision tree. For any combination of available input values, the system will apply a different decision tree. In the following section, decision trees will be discussed.

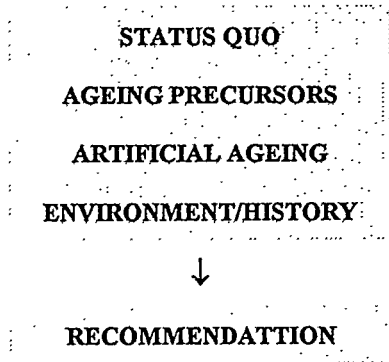
Similarly, three additional (main) functions as follows, will be evaluated. Each has its own logical flow diagram.

AGEING PRECURSORS - Combines chemical measurements and some physical data which are known to be potential degradation promoters.

ARTIFICIAL AGEING - Various tests which simulate deterioration by bringing the product under severe condition for a short period of time.

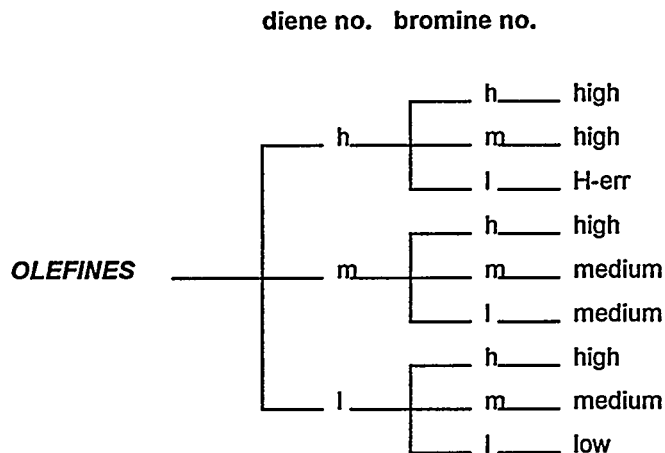
ENVIRONMENT/HISTORY - Combining risk factors based on storage

Each main function could be classified in one level out of three, therefore there will be 81 different combinations, each corresponding to a diagnosis-recommendation.



5. DECISION TREES:

Function evaluations are performed by an appropriate predefined decision tree. **OLEFINES** for example, in case of 'olefines FIA' and 'olefines GC' missing, will be evaluated by the following tree.



Thus, if diene and bromine number are classified low and high respectively, **OLEFINES** function will be classified high. The decision tree, built according to expert knowledge, places

more weight on bromine number. This implicit weighing of input parameters, both test values and function classifications, exists of course in all the hundreds of trees EQPS contains. The H_err symbol attached to the high-low path, is a high classification, with an error message, which is issued by the system. The message conveys an expert opinion that a sample with a high diene and low bromine numbers is unlikely, and may be an error. Individual decision trees exist for all EQPS defined functions.

Decision trees are flexible, in the sense that any number of input parameters will trigger a decision. This is achieved by defining a tree for each combination of input parameters. For OLEFINES function, for example, there are 16 possible parameter combinations, as follows

1. All four input values available. (1)
2. Three out of four available. (4)
3. Two out of four. (6)
4. Only one available. (4)
5. None of the four. (1)

A special tree exists for each case. Therefore for OLEFINES, the system stores 15 decision trees. If no parameter exists, no decision is made, and the next tree (STATUS QUO in this case), will miss the OLEFINES input. The same is valid for many functions in each of the different product modules.

To store in the computer the large volume of trees, and to allow quick retrieval and assessment, a special tree structure was designed. Automatic logical tree consistency checks are built into the system, to avoid clashes between tree decisions.

A trees may contain contradictions between its own branches. For example, the rule for SULFUR function based on elemental sulfur and mercaptane sulfur is high if the first test has low result and the second has high. If the same tree will contain a rule saying that SULFUR function will be rated as medium when the first test yields medium and the second high, the tree is obviously inconsistent. Similarly any branch in a tree may be inconsistent with other branches. EQPS will automatically color any branch decision blue if an upper branch contradicts it. Thus the high in the first branch in the previous example will have a blue color.

Inconsistencies may occur between trees of different size belonging to the same function. Take the previous example where SULFUR function is high when elemental sulfur is high and mercaptane sulfur is low. Assume that SULFUR function in the presence of the three tests elemental sulfur, total sulfur, and mercaptane sulfur is not high when elemental sulfur is high, mercaptane sulfur is low, independent of total sulfur. This case is an inconsistency between a 2-tree and one of its 3-trees. Branch decisions in these cases are colored red.

6. FINAL ASSESSMENT:

EQPS creates a final site assessment which lists all input data items and defined functions with their risk classification. The final report consists of several additional parts:

1. A list of comments, which point at some warning sign as a result of an important function or test result classified as risky.
2. A recommendation, an action to be taken. This could be a time span before deterioration is likely to occur, an advice whether to purchase the product if offered as cargo etc.
3. A comment related to the age of the product in storage. That is, an advice how to consider the previous recommendations given the storage time.
4. Any inconsistencies concerning the test results.
5. A list of all test values which have been classified by EQPS as high risk.

The system displays the final assessment on screen, and prints it upon request.

The following is an EQPS assessment of the previous gasoline tank example. Missing values are labeled by the symbol -?-.

GASOLINE EXPERT SYSTEM EVALUATION

of samples taken at 01/10/93 Tank No 81

Product: *gasoline* Location: *Hamburg* Owner: *Bominflot*

*** *This Assessment is Using 39 Items* ***

| <u>TEST</u> | <u>VALUE</u> | <u>LEVEL</u> | <u>TEST</u> | <u>VALUE</u> | <u>LEVEL</u> |
|------------------------|--------------|--------------|--------------------------|--------------|--------------|
| Hydrogen Sulfide | 0.99 | low | Strong Smell | no | low |
| Elemental Sulfur | -?- | -?- | Bright&Clear | yes | low |
| Total Sulfur | 0.02 | low | Water KF | 105 | low |
| Mercap Sulfur | 3 | medium | Caustic pH | 6.7 | low |
| SULFUR ⇒ medium | | | APPEARANCE ⇒ low | | |
| Total Acid no. | 0.01 | low | Diene No | 0.6 | low |
| SULFUR | | medium | Olefines FIA | 8.3 | medium |
| Copper Corrosion | 1 | low | Olefines GC | | -?- |
| ACID ⇒ low | | | Bromine No | 24 | medium |
| | | | OLEFINES ⇒ medium | | |

| | | |
|--------------------|------|-----|
| Dy Color Saybolt | 6 | low |
| Color Saybolt | -16 | low |
| Color 24h Daylight | -?- | |
| Particulates View | none | low |

| | | |
|-------|---|-----|
| COLOR | ⇒ | low |
|-------|---|-----|

| | | |
|------------|--|--------|
| APPEARANCE | | low |
| COLOR | | low |
| ACID | | low |
| OLEFINES | | medium |

| | | |
|------------|---|-----|
| STATUS QUO | ⇒ | low |
|------------|---|-----|

| | | |
|-----------------|-------|-----|
| Alcohol Content | 0.499 | low |
| Ether Content | 0.199 | low |
| Total Oxygen | 0.499 | low |

| | | |
|------------|---|-----|
| OXYGENATES | ⇒ | low |
|------------|---|-----|

| | | |
|----------------|--------|--------|
| Aromatics FIA | 29.4 | medium |
| Density at 15C | 0.7425 | medium |
| (FBP+90%)/2 | | -?- |
| DY MON Fall | 0 | low |

| | | |
|-----------|---|--------|
| AROMATICS | ⇒ | medium |
|-----------|---|--------|

| | | |
|----------------|--|--------|
| OLEFINES | | medium |
| Total Nitrogen | | low |
| OXYGENATES | | low |
| AROMATICS | | medium |

| | | |
|---------------|---|-----|
| AGEING PRECUR | ⇒ | low |
|---------------|---|-----|

| | | |
|------------------|------|-----|
| Ex. Gum Unwashed | 3.4 | low |
| Ex. Gum Washed | 0.99 | low |
| DY Ex. Gum W | 0.09 | low |

| | | |
|---------------|-------|-----|
| Pot. Gum Un | 4.0 | low |
| Pot. Gum W | 0.991 | low |
| DY Pot. Gum W | 0.991 | low |

| | | |
|---------------------|---|-----|
| EXISTENT GUM | ⇒ | low |
|---------------------|---|-----|

| | | |
|-----------------|------|-----|
| Induct Pd 1000m | 1000 | low |
|-----------------|------|-----|

| | | |
|---------------|-----|-----|
| Pot. Gum 7h W | 2.0 | low |
|---------------|-----|-----|

| | | |
|---------------------|-----|-----|
| Stickiness WG at 7h | dry | low |
|---------------------|-----|-----|

| | | |
|--------------|---|-----|
| BREAK | ⇒ | low |
|--------------|---|-----|

| | | |
|--------------|--|-----|
| BREAK | | low |
|--------------|--|-----|

| | | |
|---------------------|--|-----|
| EXISTENT GUM | | low |
|---------------------|--|-----|

| | | |
|----------------------|--|-----|
| POTENTIAL GUM | | low |
|----------------------|--|-----|

| | | |
|-------------------|---|-----|
| ART AGEING | ⇒ | low |
|-------------------|---|-----|

| | | |
|------------------|-----|--|
| Coke/Therm Crack | -?- | |
|------------------|-----|--|

| | | |
|-------------------|-----|--|
| Severe Hydrotreat | -?- | |
|-------------------|-----|--|

| | | |
|-------------------|-----|--|
| Merox/Unextracted | -?- | |
|-------------------|-----|--|

| | | |
|----------------|---|-----|
| PROCESS | ⇒ | -?- |
|----------------|---|-----|

| | | |
|---------------|----|-----|
| Copper Piping | no | low |
|---------------|----|-----|

| | | |
|---------------------|----|-----|
| Brass/Bron Fittings | no | low |
|---------------------|----|-----|

| | | |
|---------------------|---|-----|
| COPPER-BRASS | ⇒ | low |
|---------------------|---|-----|

| | | |
|-------------------|-----|--|
| Chemical ByBlends | -?- | |
|-------------------|-----|--|

| | | |
|----------------|-----|--|
| PROCESS | -?- | |
|----------------|-----|--|

| | | |
|------------------|--|-----|
| ADDITIVES | | low |
|------------------|--|-----|

| | | |
|---------------------|---|-----|
| PROCESS/CHEM | ⇒ | low |
|---------------------|---|-----|

□

| | | |
|--------|-----|--|
| Sludge | -?- | |
|--------|-----|--|

| | | |
|----------------|---|-----|
| POT GUM | ⇒ | low |
|----------------|---|-----|

| | | |
|----------|---|-----|
| Antioxid | 0 | low |
|----------|---|-----|

| | | |
|----------------|----|-----|
| Total Nitrogen | 15 | low |
|----------------|----|-----|

| | | |
|----------------|------|-----|
| Copper Content | 0.99 | low |
|----------------|------|-----|

| | | |
|---------------|-----|--------|
| Phosphor Cont | 1.2 | medium |
|---------------|-----|--------|

| | | |
|------------------|---|-----|
| ADDITIVES | ⇒ | low |
|------------------|---|-----|

| | | |
|---------------|----|------|
| Closed System | no | high |
|---------------|----|------|

| | | |
|-------------|----|-----|
| Naked Steel | no | low |
|-------------|----|-----|

| | | |
|-------------------|--|-----|
| COPP-BRASS | | low |
|-------------------|--|-----|

| | | |
|------------------|---|--------|
| CONSTRUCT | ⇒ | medium |
|------------------|---|--------|

| | | |
|--------------------|--|--------|
| CLEANLINESS | | medium |
|--------------------|--|--------|

Maintenance weak medium

Internal Corrosion light low

CLEANLINESS ⇒ medium

CONSTRUCT medium

Free Water -?-

CONDITION ⇒ medium

Capacity 9583 high

Fill Rate -?-

FILL-SIZE ⇒ high

Climatic Region sca low

Temp Shocks few medium

CLIMATE ⇒ medium

CONDITION medium

Water Acidity -?-

Microbs in Low Oil -?-

SRB in Water -?-

MICROBIAL ⇒ medium

CONDITION medium

FILL-SIZE high

CLIMATE medium

TANK ⇒ medium

TANK medium

MICROBIAL medium

PROCESS/CHEM low

ENVIR/HISTORY medium

Shaded areas display input values the next column shows the input value's level given by the system. Function level are displayed in framed areas, the function evaluation depends on the levels above. For example, ACID function has been evaluated as low, resulting from 'Total Acid no' (0.01) and 'Copper Corrosion', both being low, and SULFUR function evaluated as medium. The sequential evaluation process follows similarly. The major function evaluations are double framed.

A 'Full Recommendation' will take into consideration STATUS QUO, AGEING PRECURSORS, ARTIFICIAL AGEING and ENVIRONMENTAL/HISTORY. A 'Partial Recommendation' will not consider the last function. The later will be used when many data items related to the environment and/or product processing are not available. The system supplies the following text.

Partial Recommendation no. 27 (does not consider ENVIRONMENTAL/HISTORY)

Please note, that your information was not complete and can be improved by more quality data.

The following highlights some major quality issues of this product:

- * The color of the product does not give any cause of concern.
- * There is no potential gum problem detected.
- * So far, judging from the existent gum level, there has been little ageing.
- * The level of unsaturates could allow relatively fast ageing.

Concluding from the above major issues and all other available data, the following can be concluded:

This is an excellent product, which does not fall under any applied ageing condition and does not exhibit worrisome ageing precursors. Under the right storage conditions it could last up to 10 years. If offered you may buy it at substantial premia, perfect material for storage in caverns.

The product in hand has been stored in this tank by your organization for about 2 years. It is reasonable to assume that the product was fresh when it was taken in. Modern products containing cracked stocks are inhibited against ageing by additives, to maintain quality for 18 to 24 months. You are beyond this time frame already, thus any deterioration sign mentioned above should be taken seriously. There is a reasonable chance, that above life span is on an optimistic side.

Please pay attention to the following values rated 'High Risk':

Closed System - no

Capacity - 9583

Explanation capability is an important feature in expert systems, as it enhances the reliability of the conclusions. EQPS has a few features which provide means to justify the system's decision. The expert system assessment screen could be used as a logical spreadsheet, where it is possible to type in values and to observe their impact on the evaluation process. This could be used for instance to select the best storage site to a given product, by entering on screen all the test and product details and tank details of a particular site. The system will give a quality prediction of the product as if it is stored in that site. The user may ask for a list of all high risk and missing values, and for a complete reasoning sequence, listing the logical path of decisions.

7. CONCLUSIONS:

This paper describes an existing expert system geared toward product aging phenomena. The flexibility of the software, especially the separation between the logical shell structure and a specific knowledge base allows to replace the knowledge base to fit other fuels, e.g. crude oils. The namely aging prediction could also be replaced by another objective function, expressing for instance operability features of fuels. Thus, the system could be viewed as a logical shell for the general subject of fuel assessment and diagnosis.

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*5th International Conference
on Stability and Handling of Liquid Fuels
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**A RAPID COLORIMETRIC METHOD FOR PREDICTING THE STORAGE STABILITY
OF MIDDLE DISTILLATE FUELS**

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ABSTRACT

Present methods used to predict the storage stability of distillate fuels such as ASTM D2274, ASTM D4625, DEF STAN 05-50 Method 40 and in-house methods are very time consuming, taking a minimum of 16 hours. In addition, some of these methods under- or over-predict the storage stability of the test fuel.

A rapid colorimetric test for identifying cracked, straight run or hydrofined fuels was reported at the previous Conference. Further work has shown that while a visual appraisal is acceptable for refinery-fresh fuels, colour development may be masked by other coloured compounds in older fuels.

Use of a spectrometric finish to the method has extended the scope of the method to include older fuels.

The test can be correlated with total sediment from ASTM D4625 (13 weeks at 43°C) over a sediment range of 0-60mg/L. A correlation of 0.94 was obtained for 40 fuels.

INTRODUCTION

Middle distillate fuels that are unstable in long term storage have been reported for at least 30 years¹. The fuels darken in colour and form gums and microparticulate sediments. The insoluble degradation products can cause operational problems in fuel systems and engine components. Fuels containing unhydrogenated light cycle oil components have been shown to be particularly associated with such instability problems¹⁻⁴.

At present, the storage stability of middle distillate fuels is assessed by using one or more of a number of standard tests, such as Def Stan 05-50 Method 40, ASTM D2274 and ASTM D4625. These tests accelerate the ageing process using elevated temperature, with or without additional oxygen. The high temperature tests such as Def Stan 05-50 Method 40 (short test) and ASTM D2274 do not reflect the behaviour of some fuels in ambient storage conditions, in particular those fuels containing unhydrogenated light cycle oil^{5,6}.

Correct prediction of the storage stability of fuels is obviously a requirement of any predictive test. ASTM D4625 has been considered to reflect the sedimentation processes which occur at ambient conditions the most accurately of any of the accelerated ageing tests. However, the test is long term, taking up to 24 weeks to complete and hence while of use as a research tool, is not acceptable as a specification test.

Several researchers have developed alternative tests to overcome the shortcomings of the present tests. Bahn et al⁷ and Hardy et al⁸ developed tests at elevated temperatures and measured the subsequent sediment and colour change. Por et al⁹ accelerated fuel deterioration in a number of automotive diesel fuels by irradiation with laser light, measuring the sediment produced. White¹⁰ has reported improvements in repeatability of D2274 by using a pyrrole as a reference.

DRA and DSTO Australia have developed colorimetric methods to identify unstable fuels under a joint UK/Australia research co-operation agreement. Solly¹¹ described a rapid colorimetric method using a solid phase to identify fuels containing unhydrogenated light cycle oil. The test may also be used to quantify the concentration of LCO in automotive diesel fuels. The test is very rapid and requires little sample.

DRA Cobham has developed a liquid phase test in parallel with the DSTO method, and results obtained from using this method were reported at the previous conference¹². 5cm³ of fuel were mixed with a similar volume of a reagent mixture (immiscible with fuel). The phases were allowed to separate and the reagent phase examined visually after 30 minutes. For refinery fresh blends, a blue or green colour in the reagent layer indicated the presence of unstable fuel components; a pink or red colour indicated the presence of hydrofined products. Straight run fuels produced a yellow or brown coloration. Assessment of the colour of serial dilutions of the sample allowed an estimate of the storage stability of the fuel to be made.

This paper describes the continued development of the method to give a quantitative assessment of middle distillate fuel stability, and the application of the test to fuels other than refinery fresh products.

VISUAL ASSESSMENT OF FUELS: ASSESSMENT OF COLOUR AND INTERPRETATION OF RESULTS

Some initial instances of incorrect interpretation of results from operators led to the initiation of a programme to improve the robustness of the method.

A series of fuels including marine gas oils, F-76 diesel fuels and refinery fresh research blends were examined using the same procedure by 3 operators. Some of the fuels had been dyed for customs and excise regulations. The operators were requested to carry out the colorimetric test, report the colour obtained and obtain a visible spectrum of the reagent layer for each sample. The fuel samples were also tested for the presence of chemical species

known to be present in and peculiar to unstable LCO components, namely phenalenones and phenalenes using HPLC^{13,14}. The fuels ranged in age from refinery fresh to 1.5 years, and their colour by ASTM D1500 ranged from <1.0 To 3.5. Samples were stored at -30°C until analysed and they were thawed in the dark to maintain the integrity of the sample.

The results are given in Table 1. Visual colour assessment, even with a reference colour card, often varied widely between operators. The best correlation was, as expected, for refinery fresh blends where fuels containing unstable LCO were readily identified. As fuels age additional reactions may occur which mask the colours observed in fresh fuels.

The spectra obtained for each fuel were identical from each operator and correctly identified those fuels containing unstable products, even when the fuels were known to be up to 1.5 years old. The presence of unstable components was correctly identified in fuels containing dyes.

This data, coupled with the information presented at the last conference, indicated that a spectrometric finish to the test procedure, giving a numerical estimate of storage stability, would be feasible.

DEVELOPMENT OF SPECTROMETRIC FINISH TO METHOD.

Serial dilution was previously used¹² to estimate the stability of the fuel sample. This indicated that the method could be further developed to give a quantitative finish and hence be used as a rapid test to define unstable fuels.

Fresh gas oil components were obtained from a number of UK and European refineries, which process crudes from sources including several North Sea crude oils and also Middle East crudes. Components included straight run light gas oil (LGO), untreated LCO, and hydrofined LCO (both from catalytically and thermal cracking plant). Raw cracked components had been stored at -30°C until blending took place.

22 fuels were blended from these components: blends of 2%, 8%, 12% and 20% LCO in LGO or stable gas oil blends, and blends of 25% and 50% hydrofiner product in LGO. 17 gas oil components from these refineries were also tested. 7 samples of diesel fuel were tested (Table 2).

The storage stability of the fuels was assessed using ASTM D4625 (13 weeks storage at 43°C). Each fuel was tested in duplicate. The total sediment in mg/L was recorded.

The fuels were also analysed in duplicate using the colorimetric test. The visible spectrum of the reagent layer was obtained for each sample and the absorbance measured.

The storage stability of the fuel as measured by ASTM D4625 was plotted against the absorbance obtained from the reagent layer for each fuel. This is shown in Figure 1. Linear regression carried out on these results gave a correlation of 0.94 for the 46 fuels.

An absorbance of greater than 0.2AU was found to equate to a total sediment by ASTM D4625 (13 weeks at 43°C) of greater than 10mg/L. The specification limit for storage stability of F-76 diesel is 10mg/L (using Def Stan 05-50 Method 40).

Fuels blended from old components (5 years) also followed the correlation shown in Figure 1. Results for fuels giving greater than 60 mg/L total sediment by ASTM D4625 have been

included for correlation purposes, although the absorbances recorded were extremely high - above 1.0AU.

The repeatability of the procedure was good, results obtained on duplicate analyses were within ± 0.008 AU for absorbances up to 0.40 AU.

The results of this programme indicate that the colorimetric test may be used as a rapid test to determine the storage stability of middle distillate fuels. Further samples of fuels, including marine gas oils are being tested (colorimetric test and ASTM D4625) to extend the database and improve the reliability of the test. It is anticipated that a test kit, including a portable spectrometer will be field tested in the near future for fuels testing.

SURVEY OF MARINE GAS OILS USING THE COLORIMETRIC TEST.

201 samples of marine gas oil (MGO) were obtained during 1993 and the colorimetric test was used to determine their storage stability. This work is part of an ongoing programme to survey the properties of such fuels, which were obtained from world-wide sources.

The results are summarised in Figure 2 and Table 3.

The highest number of fuels were obtained from Europe (94), with smaller sample numbers obtained from the USA, Central and South America, Africa, the Middle East and Asia. Overall, 51 of the samples showed the presence of unstable components - 25% of the sample. Approximately half of these gave absorbances in excess of the limit of 0.2AU, indicating the presence of high concentrations of unstable components in these fuels.

All the fuel samples from the USA were obtained from the Eastern Seaboard and all the

samples gave very high absorbances, indicating high concentrations of unstable components in the fuels. No fuels obtained from Asia or Africa showed high absorbances, although the majority of these samples were known to be straight run products. Hence low absorbance readings would have been expected. Fuels containing unstable components, obtained from the remaining areas, have been placed in one of three categories: those giving absorbances greater than 0.2AU; those with "borderline" absorbances (0.15 -0.2AU) and those fuels giving lower absorbances (0.1-0.15AU) which would be expected to contain low concentrations of unstable components. These latter fuels were tested for the presence of phenalenones using HPLC and all showed trace levels (1-5mg/L). The distribution of these fuels is shown in Figure 2.

CONCLUSIONS

The colorimetric test has been developed to provide a numerical estimate of storage stability of middle distillate fuels which correlates well with ASTM D4625 total sediment measurements when stored at 43°C for 13 weeks. Use of a spectrometric finish has extended the scope of the method to include older fuels. The correlation was found to be 0.94 for 46 fuels.

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Figure 1 Correlation between ASTM D4625 total sediment and Colorimetric test absorbance for 46 fuels

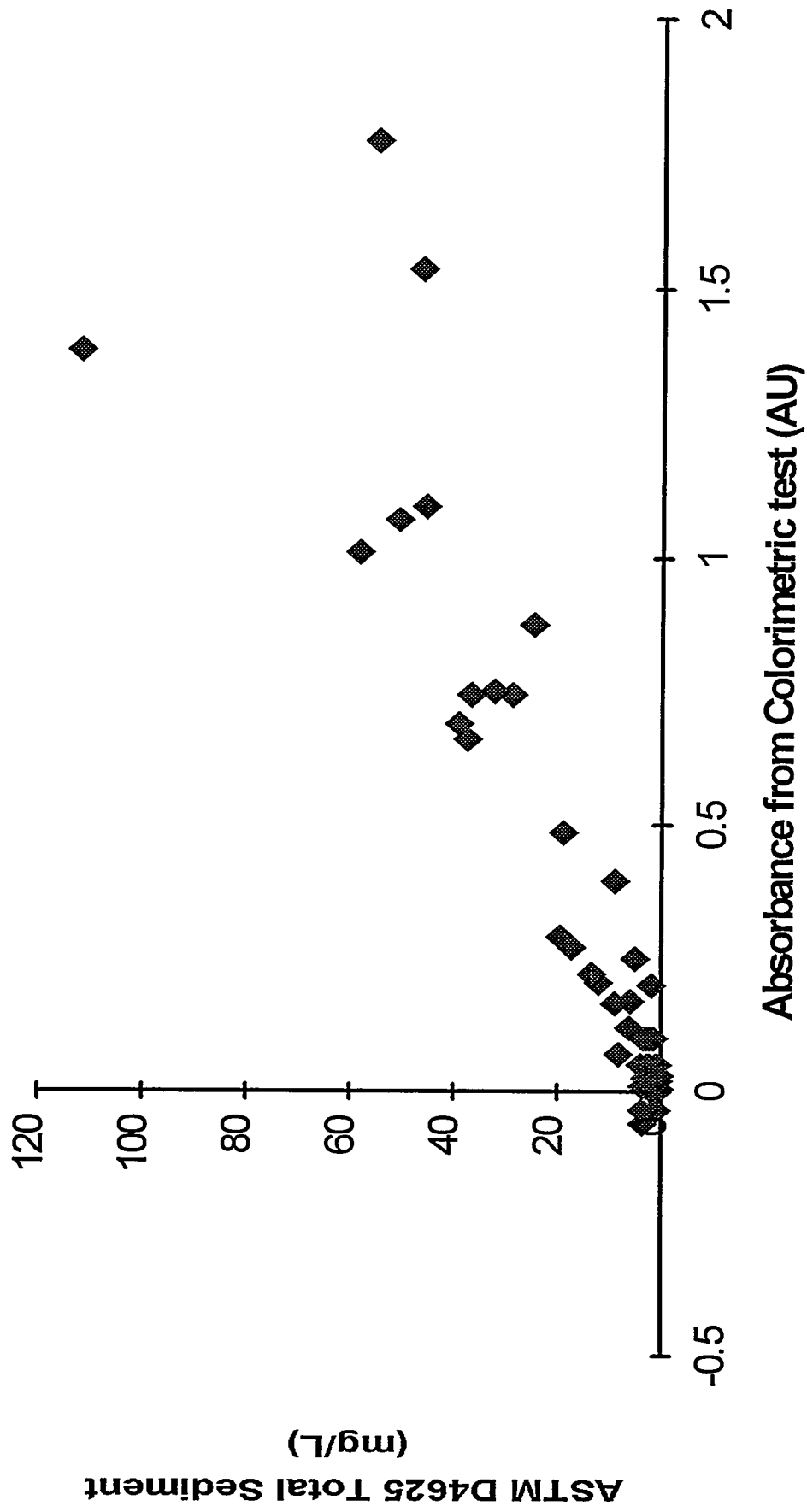


Figure 2 Distribution of marine gas oils tested by geographical area

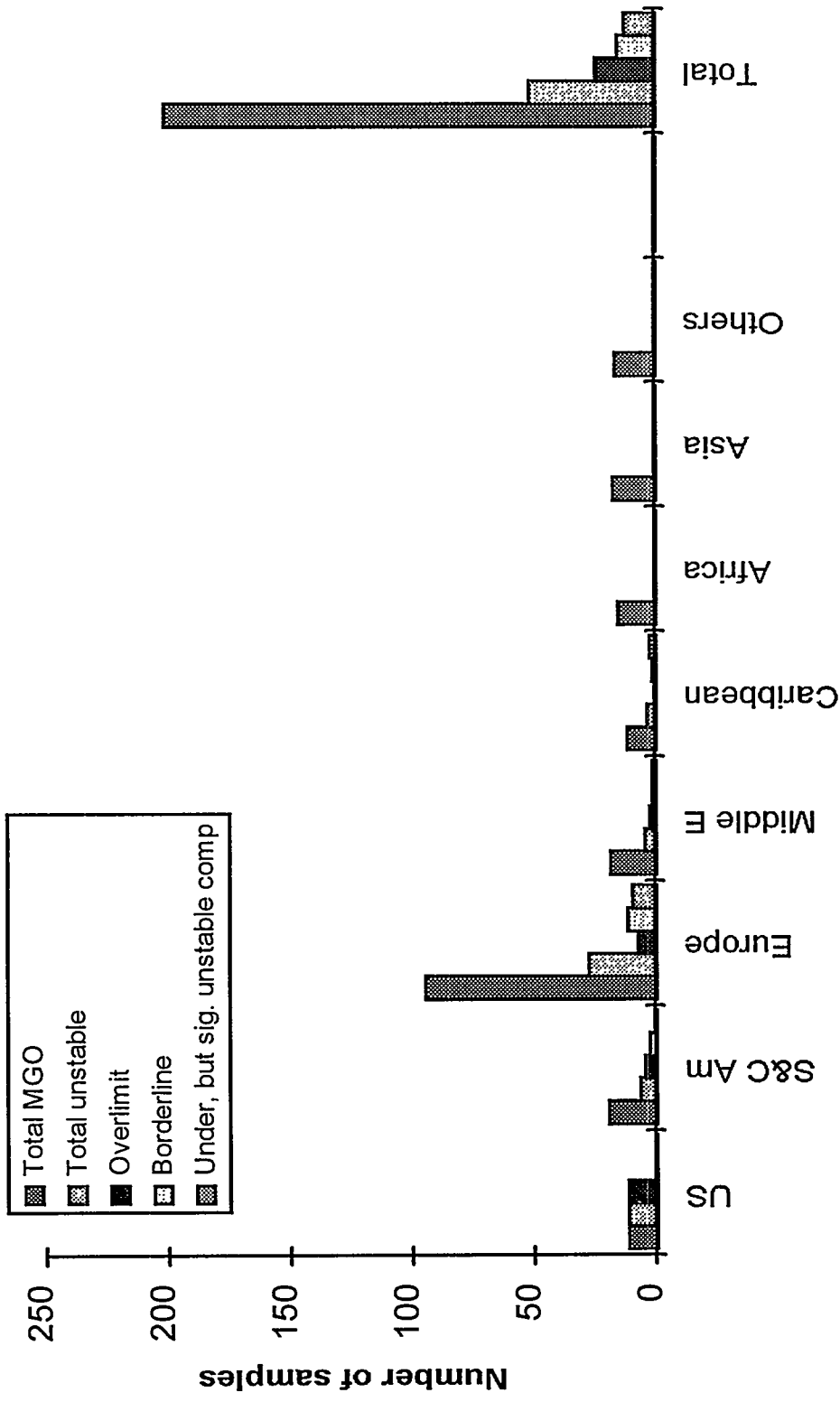


Table 1: Results of visual assessment of fuels using the colorimetric test

| Fuel | Colour of reagent layer reported | | | Phenalene/ Phenalenone present | Absorbance max above 580nm |
|---------------|----------------------------------|-------------|-----------------|--------------------------------------|----------------------------------|
| | Operator 1 | Operator 2 | Operator 3 | | |
| A | Green | Green | Dark Green | 20 mg/L | yes |
| B | Brown | Olive green | Dark Grey | Not Detected | no |
| C (dyed fuel) | Brown | Deep purple | Deep red | Not Detected | no |
| D | Brown | Khaki | Green | 2 mg/L | yes |
| E | Green | Green | Dark Green | 6 mg/L | yes |
| F | Dark blue-green | Green | Dark Green | 28 mg/L | yes |
| G | Yellow | Khaki | Light Green | Not Detected | no |
| H | Brown | Khaki | Brown | Not Detected | no |
| J | Yellow | Yellow | Yellow | Not Detected | no |
| K dyed | Brown | Brown | Black | 2 mg/L | yes |
| L | Dark Green | Dark Green | Dark Green-blue | 40 mg/L | yes |
| M dyed | Brown | Brown | Dark Green | Not Detected | no |

Table 2 Fuels tested for correlation of colorimetric test with ASTM D4625 (13 weeks at 43°C) total sediment

| Source | Composition of samples tested |
|------------|---|
| Refinery 1 | 2%, 8%,12%, 20% LCO in Gas Oil Blend 1 |
| | Light Gas Oil (LGO) |
| | Heavy Gas Oil - 2 samples |
| | Medium Gas Oil |
| Refinery 2 | 2% LCO in Gas Oil Blend 2 |
| | Low S Gas Oil |
| | High S Gas Oil |
| | Desulphurised Gas Oil |
| | Kerosine blend |
| | Heavy gas oil |
| Refinery 3 | 2%, 8%, 12%, 20% LCO in Gas Oil Blend 3 |
| | Desulphurised Gas Oil - 2 samples |
| | Blending Kero - 2 samples |
| | Straight run gas oil |
| Refinery 4 | 2%, 8%, 12%, 20% LCO in LGO |
| | 25%, 50% hydrofined product in LGO |
| Refinery 5 | 2%, 8%, 12%, 20% LCO in LGO (fresh components) |
| | 2%, 8%, 12%, 20% LCO in LGO (components aged 5 years) |
| | Straight run gas oil |
| Refinery 6 | Blending kerosine (straight run) |
| | Diesel (straight run) |
| | |
| | Automotive gas oils (NATO F-54) - 3 samples |
| | Gas Oil (NATO F-76) - 2 samples |
| | Marine gas oil - 2 samples |

Table 3 Survey of marine gas oils using the colorimetric test to monitor storage stability

| Source | Total MGO Samples | Total of unstable samples | No. over limit | No. border-line | some unstable product present, but below limit |
|-------------|-------------------|---------------------------|----------------|-----------------|--|
| USA | 11 | 11 | 11 | | |
| S&C America | 30 | 9 | 4 | 3 | 2 |
| Europe | 94 | 27 | 7 | 11 | 9 |
| Middle East | 18 | 4 | 2 | 1 | 1 |
| Africa | 15 | 0 | | | |
| Asia | 17 | 0 | | | |
| Others | 16 | 0 | | | |

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**THERMAL STABILITY AND FILTERABILITY OF JET FUELS CONTAINING
PDR ADDITIVES IN SMALL-SCALE TESTS AND REALISTIC RIG
SIMULATIONS**

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Specification, small-scale and realistic fuel simulation tests have addressed concerns about the impact of pipeline drag reducer (PDR) flow modifying additives on jet fuel handling and performance. A typical PDR additive tended to block filters which were similar to those used in the specification Jet Fuel Thermal Oxidation Tester (JFTOT) and other thermal stability test apparatus. Blockages reduced flow rates and PDR concentrations downstream of the filters. Consequently two PDR additives (A & B) were tested in JFTOT apparatus without the usual in-line pre-filters as part of a Ministry of Defence (MoD) co-ordinated Round Robin exercise. Some fuel/PDR additive combinations caused decreases in JFTOT breakpoints. Effects were additive- (type, concentration and degree of shear) and fuel-dependent; most failures were caused by filter blockages and not by a failing lacquer rating. In further work at Thornton, the thermal stability characteristics of similar fuel/additive combinations have been examined in non-specification tests. In Flask Oxidation Tests, PDR additives caused no significant increase in the liquid phase oxidation rates of the fuels. Additives were tested in the Single Tube Heat Transfer Rig (STHTR) which duplicates many of the conditions of a heat exchanger element in an engine's fuel supply system. B produced an average two-fold decrease in thermal stability in a Merox fuel; A had no significant effect. In hydrotreated fuel, B reduced the thermal stability up to five-fold. A had little effect below 205°C, while at higher temperatures there may have been a marginal improvement in thermal stability. Again, certain jet fuel/PDR combinations were seen to reduce thermal stability.

In the late 1980's NATO became interested in using pipeline drag reducer additives (PDR) in middle distillate fuels, particularly kerosine, that were being transported through strategic pipelines. Typically, PDR additives are exceptionally long chain polymers (homo- and co-polymers) derived from various α -olefin monomers. When additive/fuel blends pass through high shear regions, PDR average molecular weights (M_w) are degraded from about 20-30 million to about 1-2 million, and drag-reducing properties diminish. The manufacturers claim that these sheared PDR molecules are invisible to the end use of the fuel product. The additives are already approved in some instances for use in diesel and gasoline fuels; tested at 10-25 times their usual dose rates, the only specification test that registers a change is that for gum¹. Used throughout the USA's extensive network of pipelines, they substantially reduce energy losses associated with fluid drag. One can increase product flowrate for a given amount of input energy (i.e. number of pumping stations²) or achieve the

same flowrate with fewer pumping stations³. For jet fuel, however, there was concern that very high M_w PDR additives would affect fuel handling and filtration, as well as subsequent performance properties such as thermal stability and combustion spray patterns⁴. Increased local viscosity around the filter pores or pore blockages could affect the filterability of a PDR-doped fuel. Should the molecules, even in their sheared states, pass through the final stages of filtration (1 μm nominally, but there can be holes up to about 26 μm) before entering the aircraft fuel tanks, they might contribute to fuel thermal degradation products, being incorporated into lacquers or filterable deposits.

Thornton's research effort has addressed the related concerns of filterability and thermal stability and has involved specification, small-scale and realistic fuel rig simulation tests. Some of the work has been performed in a Round Robin exercise organised by the British Ministry of Defence (MoD) Thermal Stability Working group, involving five other independent laboratories⁵⁻⁷ and using the Jet Fuel Thermal Oxidation Tester (JFTOT) to examine the behaviour of jet fuels doped with two PDR additives, A and B. (N.B. The JFTOT is used in the fuel certificate of quality test (ASTM D3241) and so ought to highlight any operational problems that might be expected from PDR introduction.) A necessary preamble to thermal stability tests was to investigate PDR filterability; all thermal stability rigs use a high degree of prefiltration (0.45 μm Millipore) to ensure that the system responds to fuel stability and not contamination. At a realistic doping rate, some PDR could fail to reach the JFTOT test section and 17 μm downstream filter if the pre-filter were to be used, so the impact of PDRs on lacquer formation could be underestimated. The sequence and aims of tests at Thornton were as follows: (1) measure the filterability properties of PDR-fuel blends and determine how these might affect specification (JFTOT) testing and other thermal stability systems; (2) explore the thermal stability of PDR-fuel blends within the MoD JFTOT Round Robin, making use of different fuel types and additive, and additive shear rate; (3) derive some chemical mechanistic information on PDR systems via the flask oxidation test, and (4) determine fuel fouling rates within a large scale realistic rig, using PDR-doped fuels. The mode of action of these additives suggests that their behaviour might differ between turbulent and laminar flow conditions. Thus, the results of large-scale testing in the Single-Tube Heat-Transfer Rig (STHTR) could differ markedly from JFTOT studies.

Other large-scale rig testing of PDR additives had been performed by Rolls-Royce, Derby and the USAF, at their Wright-Patterson laboratories. However, while Rolls-Royce had claimed an increase in lacquering in their "Catacomb" rig, Wright-Patterson had not reported a consistent effect. Thornton's use of the STHTR for testing PDR thus provided the opportunity to produce, if not a definitive statement of PDR behaviour, one which would allow confirmation of certain findings.

EXPERIMENTAL SECTION

Apparatus. Figure 1 shows the rig used to measure the filterability of PDR-containing fuels. Fuel is pressurised within a vessel by a compressed air system and then flows under a constant known pressure to the filter housing via an on/off fuel valve. It is discharged through a filter into a beaker placed on a balance. Data are recorded as profiles of cumulative flow weight (filtrate weight) versus time, typically for 0-200 g of filtrate. A filterability index (FI) can be defined as

$$FI = (\text{flow time of 100 g of base fuel})/(\text{flow time of 100g PDR-doped fuel}) \quad 1)$$

The ASTM JFTOT⁸ assesses the thermal stability of a fuel by its propensity to lacquer the test section or to block a downstream (17 μm) filter by decomposition products. The test fuel is drawn from a reservoir and passes through a 0.45 μm pre-filter before entering the test section region. Normal operation requires a fuel flowrate of 3 ml/minute. The highest temperature at which a fuel still passes the test is called the JFTOT breakpoint.

Flask Oxidation Tests (FOT)⁹ are used to measure the liquid phase thermal oxidation rate of fuels and thereby determine their other oxidation characteristics. Perturbing the system with a radical initiator enables a fuel's intrinsic radical initiation rate to be determined. This rate has been found to be a good predictor of fuel deposition tendency.

The STHTR¹⁰ is used to study the deposition tendencies of fuels. It duplicates the dimensions, fuel flow rates and metallurgy of an aircraft fuel-cooled oil-cooler element. The configuration used for the PDR studies is shown schematically in Figure 2; the additive injection system was reconfigured to bypass the prefiltration step and thus prevent any PDR loss due to filtration. There is a turbulent flow regime (i.e. Reynolds number $\gg 5,000$) within the test element, the Test Heat Exchanger, T.H.E.; the JFTOT and many other rigs only produce laminar flow conditions. The temperatures are increased to ensure measurable deposition. Three heating stages are arranged in series: (1) a 20 litre glass tank in which the fuel is subjected to moderate heating (95-125°C) for about an hour (simulating the wing tank of a supersonic aircraft, in which the wing skin experiences frictional heating, or the collector tank of a military aircraft that has some form of recirculatory fuel system.), (2) a tubular pre-heater which heats the fuel to 165-210°C (simulating fuel heating due to the cabin air, avionics and hydraulic oil coolers), and (3) the Test Heat Exchanger (T.H.E.) which represents one element of a multi-element fuel-cooled engine oil cooler. The T.H.E. consists of a thin walled, dimpled stainless steel tube through which fuel is heated to 190-242.5°C. The fuel side heat-transfer coefficient (htc) decreases due to the insulating effect of any deposits laid down on the interior of the tube and is calculated from

$$htc = \{M C_p (T_2 - T_1)\} / \{A \Delta T_m\} \quad 2)$$

where: T_1 and T_2 are, respectively, temperatures of fuel entering and leaving T.H.E., M = fuel mass flow rate, C_p = specific heat of fuel, A = surface area of T.H.E. and ΔT_m = arithmetic mean temperature difference across the T.H.E. Temperature and flow rate data are collated and sent to a computer. The rate of deposition on the inside of the T.H.E. is determined by measuring the change with time of the heat transfer coefficient across the tube. The % per hour loss of heat transfer efficiency, ΔHTC , for each test condition of the T.H.E. can then be determined by

$$\Delta HTC, \%/hour = \{d/dt(10000/htc)/(10000/htc)_\infty\} \times 100 \quad 3)$$

where $(10000/htc)_\infty$ is the reference value of $10000/htc$ at the start of the test series, i.e. when the tube is clean, and $d/dt(10000/htc)$ is the change in $10000/htc$ with time, obtained from the gradient of the post induction rate.

The initial period where there is slow and little deposition on a clean metal surface is termed the induction period. The period of running the rig to lay down deposits on the inside of a new T.H.E. until there is no more clean metal surface, and hence overcoming the induction period, is termed tube pre-conditioning. N.B. the T.H.E. surface is not accessible for polishing to a given finish. Pre-conditioning mimics practice with real engines, where fuel system components soon become lacquered in service. A lacquered surface also provides a more consistent surface finish and, unlike a virgin metal surface, one which does not over-respond to surface active species in the fuel; experience has shown such surfaces produce more repeatable and therefore more reliable results. The post-induction rate, when Δhtc becomes time invariant at that test temperature, measures the much greater rate of deposition that occurs on a fouled surface. As this rate is constant for a given fuel at a given temperature, it is the most useful parameter for comparing fuels' deposition tendencies.

Reagents. Filterability tests used a clean hydrotreated fuel (Y), low in polar species, while a Merox-treated fuel (AD) was used for oxidation tests. The large scale rig programme used three hydrotreated fuels (AM, AO and AQ), and two sweetened Merox fuels (AP and AN), with high polars contents; key analytical properties of all seven fuels are given in Table 1. Two additives types were tested, A and B, in unsheared and fully-sheared forms, and at final polymer concentrations up to 50 ppm by mass in the fuels. (A 100% sheared additive produces no increase in fuel flow in a flow loop rig). Only additive A (in sheared and unsheared forms) was supplied in sufficient quantity for the large-scale fuel blending needed to perform filterability trials, oxidation studies and preliminary thermal stability rig work.

Procedures. 1) JFTOT filterability: A drop count method was used to measure flowrates for fuel Y in the JFTOT as a function of time rather depending on a calculated average flowrate at the end of test. The JFTOT method uses 8 μm coarse filtration (Whatman No. 2) when loading the fuel reservoir and a 0.45 μm prefilter (Millipore) when leaving the

reservoir. In some experiments only the base fuel was subjected to the coarse filtration prior to the addition of PDR. In others, the entire finished blend was coarse filtered.

2) STHTR. Apart from base fuel characterisations, preliminary STHTR tests used a single rig condition, a T.H.E fuel exit temperature of 225°C. Later studies adopted a generalised test sequence of: i) full temperature characterisation of base fuel, ii) full temperature characterisation of fuel + 20 ppm additive, iii) single point (225°C fuel outlet) determination of fuel + 5 ppm additive, and iv) repeat one temperature (225°C fuel outlet) of the base fuel, to further improve repeatability. Where possible, the full sequence was performed using the same T.H.E..

3) Particulates analysis. Effluent samples for tests involving fuels AO and AP were collected from two locations within the STHTR (points S1 and S2, Figure 2), to clarify whether PDR was having an effect on the generation of insolubles. Particulate contamination was determined by passing samples through 0.22 µm filters, in a scaled down version of IP 216/ASTM D2276: single rather than duplicate measurements were made, and 1 rather than 5 litre samples were used.

RESULTS AND DISCUSSION

Filterability experiments - JFTOT and FI rig: Figure 3 shows results for unsheared PDR blends in fuel Y tested with a 5 µm rather than a standard 0.45 µm pre-filter. Up to 100 minutes, flowrate profiles are constant with time; higher PDR concentrations produce lower flowrates because of the local viscosity increase as fuel passes through the filter. At longer times and higher doping rates (beyond 100 minutes and 40 ppm PDR), flowrates progressively decline, indicating filter blocking.

All concentrations of unsheared additive show a decline in flowrate with time (see Figure 4) when the finer pre-filter (0.45 µm) is used, i.e. there is steady blocking of the pre-filter. Coarse filtration of the entire blend, however, reduces the filter plugging considerably; for instance, 40 ppm coarse filtered blend produces similar plugging to 20 ppm of unfiltered additive blend. The coarse Whatman No. 2 paper filter (nominally 8 µm) affects particles in a range similar to that of 0.45 µm Millipore membrane filter. Similarly, Whatman No. 1 (nominally 11 µm) is effective in a range similar to 0.8 µm Millipore. The sheared additive is only 60% as effective as the unsheared additive in terms of filter plugging, i.e. 50 ppm sheared additive blend behaves like 30 ppm unsheared additive blend.

Clearly, a number of PDR/fuel combinations were capable of blocking the standard JFTOT pre-filter. The above results suggest that the PDR molecules themselves are responsible for filter blocking as opposed to poor cleanliness of the additive, by-products of synthesis or chance contamination. In addition, the fact that the filter plugging is more evident for the 0.45 µm than the 5 µm Millipore filter leads to the conclusion that many of the particles which cause plugging are in the range \approx 0.45 to 5 µm. It is possible that large (fuel

solvated) PDR molecules align themselves with the flow in fast flow systems whereas in the JFTOT the extremely slow flow prevents this alignment and thus aids filter plugging by such large molecules. Order of magnitude calculations of the length of the unsheared PDR molecules yield figures around 40 μm , thus only a well-aligned molecule will pass through a 0.45 μm filter.

FI can be used as a guide to the concentration of PDR in a system assuming no shear (or constant level of shear) within the samples. A series of flowrate versus time lines (see Figure 5) show slight but significant curvature, indicating that the flowrate is not only impeded by a local viscosity increase in the pores but also that there is some measure of filter blockage. Fuel flow times were measured under a number of different rig conditions. The best discrimination among the blends was achieved at the lower pressures (0.0524 bar, 21" water) and finer filter size, i.e. Whatman No.1. Figure 6 is the PDR calibration graph for this most discriminating system. PDR-FI calibration graph and flowrate profiles (Figures 5 and 6) were applied to samples derived from the JFTOT rig before and after the prefiltration step. One can estimate that the 0.45 μm prefiltration will reduce a PDR concentration of 40 ppm down to 25 ppm, i.e. by 37%. This means that JFTOT and other thermal stability rigs using the same high degree of filtration could be testing significantly lower levels of additive than anticipated and thus, if used unmodified, would underestimate the performance of similarly doped fuels in real situations.

FOT. These experiments required a fuel, Merox-treated AD, that yielded a repeatable and inhibited oxidation trace. With 5ppm additive A, a non-polar species, in AD there was no tendency to increase the fuel's radical initiation rate. It was assumed that the same would be true for additive B.

JFTOT Round Robin. The MoD wished to investigate a "worst case" of a pipeline with ten pumping stations, additive injection at each station and no loss of additive. For these reasons JFTOT testing was performed with doping rates of 50 ppm and 15 ppm (by mass) active matter, to reflect 10x old and new recommended in-service dope rates. The MoD-sponsored Round-Robin exercise used the JFTOT without the usual pre-filter in place. Instead, fuels were pre-filtered externally to the JFTOT and then the PDR additive concentrates were doped into the filtered fuel. Breakpoint temperatures were determined for various fuel/additive combinations. The results from the six laboratories involved are reported in detail elsewhere⁵⁻⁷. Briefly, they showed that PDRs could reduce breakpoints significantly (by up to 50°C in one case), with sheared additives tending to have more effect than unsheared additives. The magnitude of the breakpoint reduction also depended on fuel (hydrotreated or Merox) and additive type. Most JFTOT failures were caused by excessive pressure drops (a result of post test section filter blockage) and not by lacquer formation.

STHTR - Preliminary tests. The object of these rig studies was to compare and contrast the behaviours of two different fuel types, in particular to identify whether they

responded similarly to the presence of two different types of PDR additives. Because only small samples were available, preliminary STHTR work was restricted to the additive A. The additive injection pump was able to provide a final concentration in the fuel of 20 ppm PDR, but not the 50 ppm level of the JFTOT Round Robin. Unsheared A was studied in both hydrotreated (AM) and Merox-treated (AN) fuels at 5 and 20 ppm, and in sheared form in AM. Within the repeatability of the STHTR, unsheared A had no propensity to increase lacquering in either fuel (see Table 2); in fact, the evidence might have suggested a reduction of lacquering at the higher dope rate in the Merox fuel. Tests with the fully-sheared additive in AM failed to produce any lacquer on the test section.

Full STHTR characterisations - a) base fuels. Displaying $\log_{10}(\Delta HTC)$ results as a function of temperature produces pseudo Arrhenius plots. These will be referred to as Arrhenius plots hereafter although, strictly, true Arrhenius plots are for single mechanism systems; past work at Thornton¹⁰ has shown that limited treatment of STHTR data with such plots can be informative. The lower the rate of loss of heat-transfer efficiency at a given fuel outlet temperature, the more thermally stable the fuel. Figure 7 displays results for base fuels used in the STHTR studies. As expected, results for the Merox-treated and hydrotreated fuels occupy different areas of the plot. Linear regression fits for data for the three hydrotreated fuels indicate fuels of comparable stability while the two Merox fuels are 10 to 15 times less stable.

The rate of deposition for some hydrotreated fuels can be too low to be measured easily or with any great precision at lower rig operating temperatures. Unfortunately, the logarithmic scale of the Arrhenius plot accentuates the problem and low temperature data can have undue influence on the regression lines of Figure 7. The larger supply of fuel AQ allowed testing in an order that would highlight if any of the results were affected by the pre-conditioning Merox fuel lacquer. Improved confidence in the regression data for the last test on AQ was achieved by testing at two additional, intermediate, temperatures where reliable lacquer measurements were possible. The results, shown in Figure 7, were similar to those of fuel AO.

Experiments with the Merox fuel, AP, produced significantly higher fouling rates and probably benefited from the better pre-conditioning possible with Merox fuels. Fuel AP produced a good fit and was more stable than the Merox fuel, AN, used in the earlier PDR studies.

Full STHTR characterisations - b) additivated fuels. In later studies, only fully sheared additives were tested. Additive B at 20 ppm in fuel AO produced a plot almost parallel to that of the base fuel but shifted to lower stabilities (Figure 8). This shift represents an average 5-fold increase in fouling across the range of test temperatures. There was also a shift when B was doped into fuel AP, corresponding to a 2-fold increase in fouling rates across much of the temperature range (see Figure 8). This is a smaller increase than seen with

hydrotreated fuel; the PDR's contribution is less significant in the naturally "dirtier" (i.e. more polars), less stable fuel. The single point determination for 5 ppm B in AP produced an increase on the base fuel figure of 1.7-fold. This is only slightly smaller than the effect for 20 ppm; the difference between the 20 and 5 ppm cases probably is not significant within the repeatability of the rig. (STHTR repeatability has been estimated to be, at best, $\pm 25\%$.) This lack of sensitivity to the 4-fold increase in PDR concentration, seen also with the hydrotreated fuel, may indicate that a critical threshold for PDR additives to have an effect is at or below the 5 ppm level.

Figure 9 shows the best line through the three measurable results for fuel AO plus 20 ppm additive A. The gradient seemed much too shallow, with the 0.005% intercept suggesting an extremely unstable fuel. At the time, the results were discounted. There was insufficient fuel to repeat the experiment, except with another hydrotreated fuel, AQ. The experimental 10,000/htc trace at the 207.5°C condition was not clear, i.e. the gradients that could be measured after the first few hours were very varied and no single value seemed more reasonable than another. Figure 9 indicates (with *) extremes of values (i.e. upper and lower plausible gradients) that could be computed from the trace. As with fuel AO results, extrapolation to lower temperatures using the higher 207.5 °C value produces a totally unrealistic gradient and 0.005% intercept, consistent with a relatively unstable fuel. If the lower value at 207.5°C is to be believed, the inference is that A's presence has produced a real improvement in fuel stability at all temperatures. The two point fit to the data, although undesirable, is more realistic and suggests that at temperatures above about 205°C additive A perhaps improves the fuel thermal stability (by a factor of about 2 at 225°C). Below 205°C, there is no convincing conclusion to be drawn about the fuel's performance.

The odd behaviour appears to occur for both hydrotreated fuels suggesting that it is not an anomaly. The kinetic analysis and software for the STHTR experiment assume a one-way reaction, or an overall process with a single rate determining step (RDS) throughout the temperature regime being investigated. For additive-free systems, in particular, this assumption has proved reasonable in the past. If, however, there are a series of finely balanced equilibria that produce, for instance, a change in the overall RDS over the temperature regime studied, artefacts could be produced and a single Arrhenius plot treatment of the data would be misleading.

Addition of 20 ppm A to Merox-treated fuel AP produced no significant change to the fouling rate (Figure 10). Likewise, the 5 ppm result at 225°C was not significantly different.

Particulates measurements. Table 4 summarises data obtained for samples taken during STHTR testing of fuels AO and AP. The ambient temperature contaminants levels seem to increase in AO when 20 ppm additive B is introduced to the base fuel. However, there is no obvious effect of higher T.H.E. temperatures on the contaminants levels in the additivated fuel. If the base fuel particulates levels (not measured) at non-ambient

temperatures were to be temperature independent, this would mean that all of the contaminant level increase could be ascribed to the presence of the additive, and not to normal fuel lacquer precursors.

At a given temperature and in either fuel, contaminants levels appear to be greater when additive B rather than A is used, by up to as much as 90%. This agrees with the STHTR results which suggest that additive B reduces fuel thermal stability. It is also consistent with most of the JFTOT Round Robin results, where the majority of failures were due to fuel insolubles (causing pressure failures) rather than due to excessive lacquer deposition^{6,7}, and which found that additive B tended to produce larger breakpoint depressions than additive A. With the Merox fuel, unlike with fuel AO, there is evidence for an increase in contaminants levels with increasing temperature; the particulates more than double on changing from the 190°C to 242.5°C conditions. This may, however, be more of a reflection on the inherent poorer stability of this fuel than a PDR effect; again, particulates levels were not measured for base fuel which had passed through the rig. The 5 ppm and 20 ppm results are not very different.

General STHTR Discussion. Tables 2 and 3 summarise the STHTR results at 225°C for unsheared and sheared additives, respectively. Data are normalised to the base fuel's result, using the "best straight line" value wherever possible rather than the actual 225°C result (the base fuel figures for fuel AM and AN are from single point (225°C) determinations, not linear regression fits). Data for unsheared A had shown no deterioration in thermal stability, with a possible improvement in performance suggested by data for 20 ppm loadings in both the hydrotreated and Merox fuels.

In sheared form, additive A was only tested in fuel AM. For this test, base fuel both with and without PDR gave "negative" fouling rates (i.e. a clean-up effect, with 10,000/htc decreasing throughout); these data have not been tabulated since no meaningful conclusions regarding thermal stability performance could be drawn. The later data (Table 3) for fully sheared A show an improvement in thermal stability in the hydrotreated fuel but show no significant effect in the Merox fuel.

Tabulated and graphical results (Figure 8) confirm that in certain cases, low levels of additive B reduce the thermal stability of both hydrotreated and Merox fuels in a realistic high temperature rig. Problems manifest themselves as increased lacquers and increased levels of particulate contamination, though not increased filter blockage, with the PDR contribution being more noticeable in hydrotreated fuels. Previously, data from the Working Group Round Robin^{6,7} had indicated that PDR additives were likely to increase fuel filter insolubles rather than cause surface lacquers in the JFTOT apparatus; JFTOT failures were caused by pressure drop failures rather than by higher lacquer ratings.

Also obvious from the tables and graphs is that 5 ppm and 20 ppm loadings of a given additive in a given fuel produce similar results. This may suggest that there is a critical

concentration of PDR above which no further deposit formation can be produced; this may provide a route to conjecturing on the deposition mechanism.

The rig data do not warrant detailed mechanistic discussion but provide scope for conjecture. They resolve some of the apparent differences between earlier results generated by Rolls-Royce and Wright-Patterson laboratory. The interim Rolls-Royce results¹¹ had related to a Merox fuel, with 50 ppm of fully sheared additives. There was possibly an improvement in thermal stability caused by A. B, however, had caused significant increase in deposit rates in both temperature regimes studied and more pressure build up across filters. Neither fuel had indicated any problems when JFTOT breakpoints were measured. Fuel and additives details of the Wright-Patterson work are not available, but USAF claimed that the PDRs did not worsen thermal stability performance. The STHTR results provide convincing proof that additive B can produce more lacquer in realistic rigs, as Rolls-Royce had claimed, and that the effect may be more dramatic in a hydrotreated than in a Merox fuel. The additive A data are in general agreement with those from Rolls-Royce. Any effect for this additive is negligible or slightly beneficial, and there may be a different temperature dependence for such behaviour than that seen with unadditivated fuels.

CONCLUSIONS

PDR filterability experiments have confirmed that the concentrations of PDR additives reaching test sections of unmodified thermal stability test rigs could be significantly reduced by the pre-filters. Flowrates of PDR-doped fuels are retarded by two mechanisms: (i) an increase in local viscosity in the test filter pores and (ii) trapping of additive molecules in the test filter pores producing partial blockage. The Filterability Index method would suggest that up to about 40% of PDR additive concentration could be held back by a JFTOT prefilter.

A comprehensive set of tests looking at a matrix of a) fuel processing type, b) additive type, c) additive concentration and d) temperature has been performed in a reliable, established turbulent flow rig (STHTR), modified to allow for filtration effects. Data from the STHTR show that addition of low levels of fully sheared additive B (< 20 ppm) to jet fuels can cause up to a 5-fold reduction in the thermal stability of the fuel. The effect is more pronounced with a hydrotreated fuel than with a Merox treated fuel. Similar levels of fully sheared additive A added to a Merox treated fuel cause no significant change to the fuel's thermal stability but in a hydrotreated fuel cause, if anything, a slight improvement in the fuel's thermal stability above about 205°C. The effect of PDR additives on STHTR behaviour appears independent of additive concentration, suggesting that there may be a critical concentration level, about or below 5 ppm, above which further PDR addition has no further impact.

These rig experiments confirm the MoD working group's JFTOT studies, i.e. with certain jet fuel/PDR combinations, the PDR additive can reduce the fuel's thermal stability. It

is not invisible to end use. The STHTR data do not show the same additive concentration dependence as the JFTOT studies but are in broad agreement with those from the Rolls-Royce "Catacomb" rig, i.e. some fuel/PDR additive combinations are less thermally stable than the base fuel alone. Both sets of rig data support the view of the JFTOT Round Robin exercise that current generation PDRs should not be used in jet fuel systems. Should any PDR material manage to pass the final stages of fuel-handlers' filtration, it could produce early component blockages as well as more rapid lacquer build-up and consequent reduction in component lifetimes.

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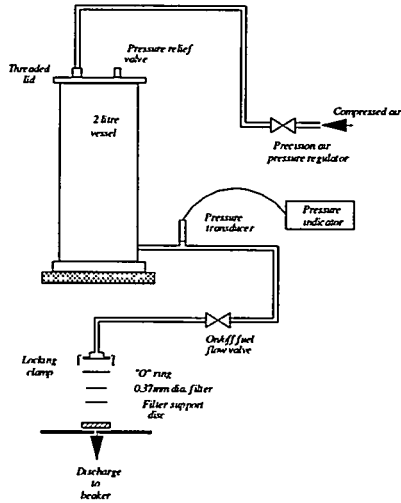


FIG. 1 - Schematic of filterability index rig

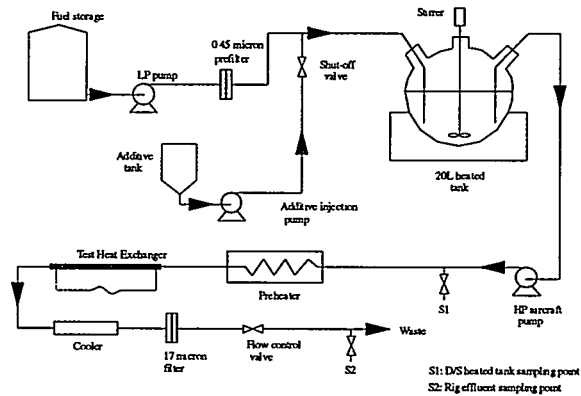


FIG. 2 - Schematic of STHTR rig showing main heating elements and sampling positions (S1 and S2)

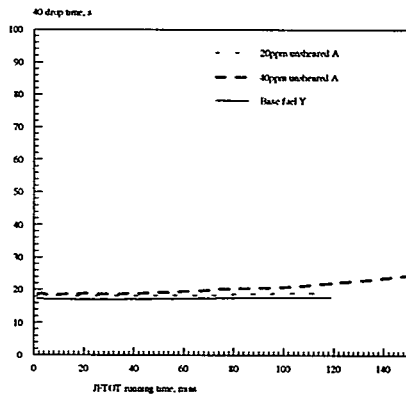


FIG. 3 - PDR-JFTOT flow-rate effects for fuel Y and unsheared additive A with 5 micron pre-filter in place

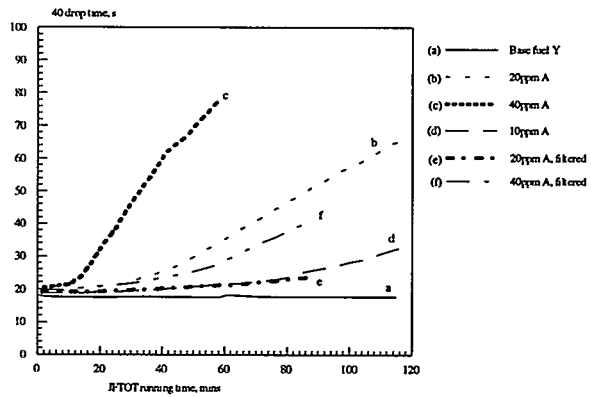


FIG. 4 - PDR-JFTOT flow-rate effects for fuel Y and unsheared additive A with 0.45 micron pre-filter in place

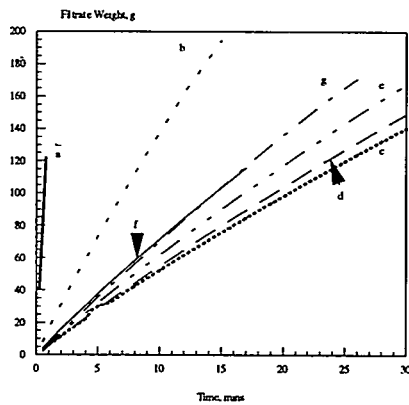


FIG. 5 - Filterability of unsheared A in FI rig

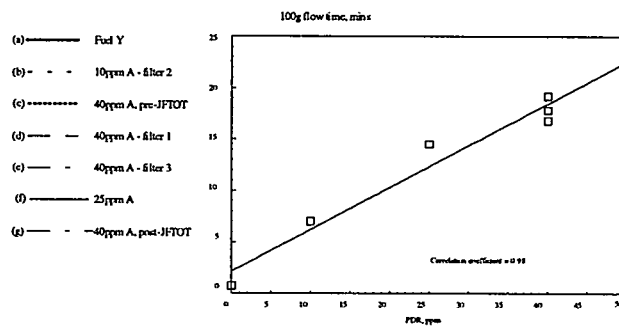


FIG. 6 - 100g flow time as function of unsheared additive A concentration in fuel Y

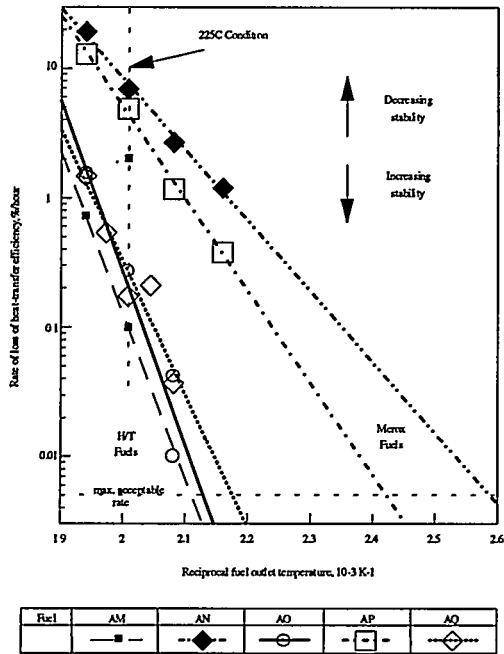


FIG. 7 - Base fuel lacquering rates in the STHTR as a function of fuel outlet temperature

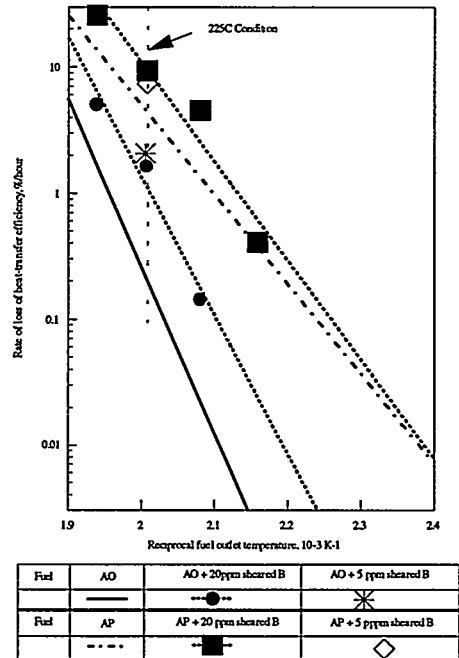


FIG. 8 - Effect of additive B on lacquering rates of fuels in the STHTR

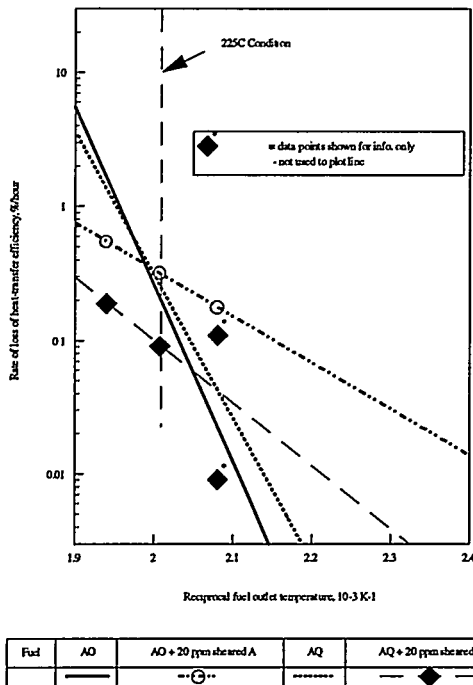


FIG. 9 - Effect of additive A on lacquering rates of hydrotreated fuels in the STHTR. Points marked * not fitted

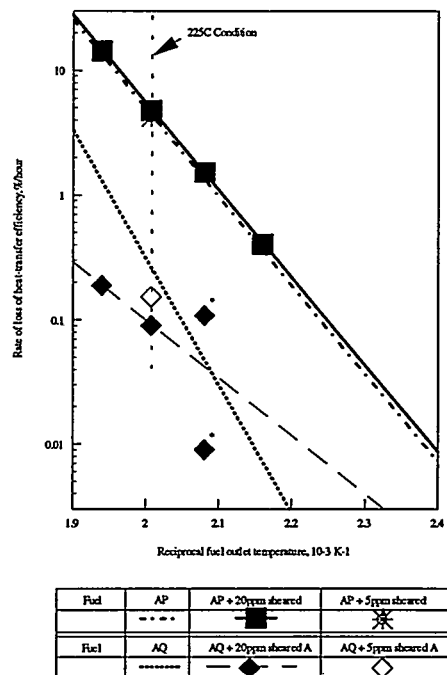


FIG. 10 - Effect of additive A on lacquering rates of fuels in the STHTR. Points marked * not fitted

Table 1. Properties of Hydrotreated (HT) and Merox-treated (M) fuels used in study.

| PROPERTY | Method | Fuel code: | | | | | | | |
|------------------------------------|--------|------------|-------|-------|-------|-------|-------|--------|--|
| | | AD | Y | AM | AN | AO | AP | AQ | |
| | | Treatment: | | | | | | | |
| | | M | HT | HT | M | HT | M | HT | |
| Aromatics, %v | D1319 | 18.0 | 16.0 | 13.5 | 17.7 | 17 | 17.6 | 17.4 | |
| Olefins, %v | D1319 | 0.5 | <1.0 | <1.0 | 0.3 | <1.0 | 0.5 | 0.4 | |
| Total sulphur, ppm m/m | D2622 | | 17 | | 200 | 200 | 500 | | |
| | D1266 | 720 | | <1 | | | | 100 | |
| Mercaptan S -Doctor test | D235 | | Neg | Neg | | Neg | | Neg | |
| ppm m/m | D3227 | 11 | | | 12 | <3 | <6 | 2 | |
| Acidity, mg/KOH | D3242 | 0.005 | 0.004 | 0.005 | 0.006 | 0.005 | 0.005 | <0.001 | |
| JFTOT Breakpoint, °C | | 275 | 285 | 285 | 275 | 285 | 280 | 295 | |
| Radical initiation rate | | | | | | | | | |
| 10 ⁻⁷ mole/Ls | | 8.26 | 0.93 | 0.72 | 5.25 | 0.71 | 5.43 | 0.58 | |
| Induction period, min | | | | 46 | | 52.3 | | 53.1 | |
| STHTR, %/h at 225°C | | 0.68 | 0.19 | 0.1 | 7.46 | 0.2 | 4.37 | 0.26 | |
| Distillation, C | D86 | | | | | | | | |
| IBP | | 165.0 | 155.0 | 155.0 | 154.5 | 159.5 | 147.0 | 153.0 | |
| 50% | | 192.5 | 200.0 | 198.5 | 195.5 | 200.0 | 193.0 | 197.0 | |
| FBP | | 254.0 | 259.0 | 251.0 | 255.5 | 256.5 | 252.5 | 256.0 | |
| Density at 15 C, kg/m ³ | D4052 | 798.0 | | | 800.6 | | 796.5 | | |
| | D1298 | | 796.0 | 789.1 | | 794.7 | | 788.8 | |
| WSIM (MSEP) | D3948 | 76 | 95 | 97 | 97 | 92 | 78 | 95 | |
| Copper, microg/L = ppb | ICP-MS | 12 | <2 | <2 | 18 | <3 | <3 | <2 | |

| ADDITIVES | Class | | | | | | | |
|------------------|------------|------|------|-----|------|-----|------|------|
| Hitec 4733, mg/L | AntiOxid | | | 20 | | | | |
| RDE/A/609, mg/L | AntiOxid | | | | | 23 | | 19.0 |
| Ionol J65, mg/L | AntiOxid | | 19.0 | | | | | |
| ASA-3, mg/L | AntiStatic | | 0.7 | 0.7 | | | | |
| Stadis 450, mg/L | AntiStatic | 1.89 | | | 0.45 | 1.3 | 1.13 | 1.1 |

Table 2. STHTR fouling rates at 225°C normalised to base fuel rate for unsheared PDR

| Test fuel | ΔHTC at 225°C (normalised) | | |
|------------|----------------------------|----------|----------|
| | AM | AN | |
| | | 1st Test | 2nd Test |
| Base fuel | 1 | 1 | 1 |
| + 5 ppm A | 1.2 | 0.96 | - |
| + 20 ppm A | 0.87 | 0.78 | 0.83 |

Table 3. STHTR fouling rates at 225°C normalised to base fuel rate for sheared PDR

| Test fuel | Δ HTC at 225°C (normalised) | | |
|------------|------------------------------------|-----|-----|
| | AO | AQ | AP |
| Base fuel | 1 | 1 | 1 |
| + 5 ppm B | 9.2 | - | 1.7 |
| + 20 ppm B | 5.6 | - | 2.1 |
| + 5 ppm A | - | 0.8 | 1 |
| + 20 ppm A | - | 0.5 | 1.1 |

Table 4. Filtration studies on STHTR effluent samples of sheared PDR fuel blends

| Fuel / T.H.E. fuel outlet temperature | Particulate contaminants, mg/l | |
|---------------------------------------|--------------------------------|--------|
| | 0.38 (base fuel) | |
| AO at ambient | with B | with A |
| AO + 20 ppm PDR: at ambient | 0.90 | - |
| at 207.5°C | 0.55 | 0.50 |
| at 225.0°C | 1.40 | 0.80 |
| at 242.5°C | 1.09 | 0.67 |
| AP + 5 ppm PDR at 225.0°C | 2.29 | 2.10 |
| + 20ppm PDR at 190.0°C | 1.10 | 0.82 |
| at 207.5°C | 1.73 | 0.91 |
| at 225.0°C | 2.30 | 1.70 |
| at 242.5°C | 2.70 | 2.38 |

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SYSTEM EVALUATION OF IMPROVED THERMAL STABILITY JET FUELS

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Abstract: A single-pass, single-tube heat exchanger device called the Phoenix rig and a single-pass, dual-heat exchanger system called the Extended Duration Thermal Stability Test system are specific devices/systems developed for evaluating jet fuel thermal stability. They have been used extensively in the evaluation of various jet fuels and thermal stability additives. The test results have indicated that additives can substantially improve the thermal stability of conventional jet fuels. Relationships of oxygen consumption, residence time, bulk, and wetted wall temperatures on coking deposits that form in the heated tubes have also been investigated.

1. Introduction: Thermal management is a major factor in designing today's high-performance aircraft. The trends are towards larger and higher power avionics, higher power hydraulic and electrical systems, and more efficient, higher-temperature engines. Fuel is used as the primary heat sink for cooling of the aircraft and engine systems. Fuel operating temperatures will increase to accommodate the higher loads. Laboratory systems have been developed and tests conducted to establish the temperature limits for JP-8 fuels and to provide a baseline for evaluating improved thermal stability fuels (JP-8+100). JP-8+100 fuel is being developed by the U.S. Air Force to provide a 100°F (56°C) improvement in thermal stability. This paper covers laboratory test systems being used to evaluate JP-8 thermal stability limits and the test results with conventional JP-8 and JP-8+100 fuel candidates.

Temperature limits for engine fuel systems using conventional JP fuels were basically established by field experience. There are many tests, such as Jet Fuel Thermal Oxidation Tester (JFTOT) for evaluating the thermal stability of fuels. However, these tests do not provide data appropriate for system design considerations. These tests are normally conducted at high temperatures and for short durations to accelerate the test, and at low flow rates to conserve the amount of fuel required for the test. These tests emphasize the fuel's tendency to make deposits at the higher temperatures. For example, the minimum acceptable temperature for JP-8 fuel in

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the JFTOT is 260°C (500°F); whereas the general temperature limits that are used for engine design are 163°C (325°F) for bulk fuel and wetted wall temperatures of 205°C (400°F) in engine fuel injector nozzles. The systems and tests covered in this paper were directed toward developing an improved research device for evaluating fuel thermal stability and establishing fuel thermal degradation criteria for JP-8 fuels that can be used for aircraft system designers. These criteria are also required to evaluate the increased thermal stability temperature capability of the JP-8+100 fuel candidates.

2. Increased Fuel Thermal Stability Requirements: Advanced fighters that will be produced late in this decade will require increased cooling resources. Fuel will be subjected to higher temperatures, higher heat fluxes, and multiple heating and cooling cycles due to increased heat loads imposed by the aircraft and engine systems. Integrated aircraft thermal management is becoming a significant driver in the balance between providing sufficient cooling resources to maintain component integrity and life and the aircraft performance capabilities. Fuel is the primary heat sink for aircraft thermal management. Most current fighter aircraft recirculate the fuel on the airframe to maintain proper aircraft cooling and to maintain the aircraft/engine interface temperature to between 80°C (176°F) and 120°C (248°F). The fuel is cooled before it is returned to the main fuel tanks to prevent the bulk fuel from exceeding 66°C (150°F). The fuel is cooled via either ram air or natural convective/conductive cooling available in the metal wing tanks (Fig. 1).

The burn fuel flow for the engines now being developed will be too low during most of the flight mission to satisfy the increased system heat loads. To provide the required fuel cooling flow, fuel will be bypassed from the engine back to the aircraft fuel tanks by way of a ram air/fuel cooler. From a thermal management standpoint it is desirable for the aircraft and engine fuel systems to operate at higher temperatures to eliminate or reduce the size of the ram air/ fuel heat exchanger by reducing the required bypassed fuel flow and increasing the effectiveness of the heat exchanger. Bypassed flow with current fuels at low engine power settings can exceed 2.5 times the flow required to provide the engine thrust. In addition, it is anticipated that these aircraft using current fuel such as JP-8 will require increased fuel system maintenance to replace fouled engine components. The JP-8+100 fuel discussed later in this paper is being developed to

provide the additional heat sink capability and to eliminate the fuel fouling of fuel system components.

Looking ahead toward the beginning of the next century, the Integrated High Performance Engine Technology (IHPTET) program is developing technology that will potentially double the turbopropulsion capability of current engines. To achieve these goals, fuels will be stressed to considerably higher temperatures than present aircraft applications. New lubricants being developed under the IHPTET program will operate at temperatures of 316°C (600°F) for the next generation engines and 385°C (725°F) for the following generation. Present-day lubricants are limited to temperatures of 177°C (350°F). Future fuels must have a similar temperature capability increase to avoid fouling problems in the fuel/lube oil coolers. In addition, studies have shown¹ that the wetted wall temperature in main burner nozzles will be in the range of 260°C (500°F) to 300°C (572°F) compared to the maximum allowed wetted wall temperature of 204°C (400°F) for use with current fuels such as JP-8. The bulk fuel temperatures projected for the higher wetted wall temperature range from 204°C (400°F) to 218°C (425°F).

3. JP-8+100 Fuel Development: The United States Air Force embarked on a program in 1989 to improve the thermal stability of JP-8 fuel¹. Two approaches were initially explored. The first approach was to develop a new refinery specification for a more thermally stable JP-8 fuel. This approach was discarded early since a new fuel would be costly to obtain and would offer logistics penalties contrary to a single fuel for the battlefield. The second and preferred approach was to develop a thermal-stability-improving additive package that could be added to the JP-8 kerosene base fuel and increase its thermal stability by 100°F (56°C). Currently, the improved fuel is referred to as JP-8+100, but when the development is complete it is anticipated that the additive package will be listed in a Qualified Products List (QPL) for use in the JP-8 specification, Mil-T-83133. The cost goal for the additive package is \$0.001 per gallon of fuel.

Current research indicates that the additive package will contain four main ingredients: antioxidants, metal deactivators, detergents, and dispersants. The Air Force contacted major additive manufacturers and oil companies to provide thermal-stability-improving additives for evaluation. To date, more than 300 additives have been screened, and several show promise for meeting the thermal stability goals. A number of test devices have been developed or refined for

screening additives². The Phoenix rig and the Extended Duration Thermal Stability Test (EDTST) system are the primary flowing type test systems for evaluating the most promising additives identified by the other screening tests.

The Phoenix test rig was established as a research device for evaluating a fuel's tendency to form deposits at elevated temperatures. It is primarily used for short tests (under 24 hours) at accelerated temperature conditions. The EDTST system was established for longer duration tests (96 hours or higher) at aircraft fuel system simulated heat load, residence time, and temperature conditions.

4. Phoenix Test Rig: The Phoenix test rig is a single pass fuel flow system that heats fuel in a single steel tube. Fig. 2 is a flow schematic diagram of this rig which consists of a preconditioning tank, a positive displacement diaphragm pump, two copper blocks (one for heating, the other for cooling), a fuel supply system, filters, and instrumentation. Small-bore stainless-steel tubes (0.3175 cm o.d., 0.216 cm i.d., and 55.9 cm in length) are used as the test sections in the copper blocks. The internal surface of the tube has an roughness range of 0.2 to 0.38 cm. The heating block is a 45.7 cm long copper cylinder with an o.d. of 7.6 cm. The copper cylinder is split lengthwise into two halves, with each section containing a full-length cartridge heater. A lengthwise groove in the flat face of each cylinder surface was provided for clamping the 0.3175 cm diameter tube in between the cylinder halves. The cooling block is designed similarly, except that it is not provided with cartridge heaters.

5. Phoenix Test and Test Results: The Phoenix test rig is used to measure various aspects of fuel thermal stability, such as carbon deposition versus temperature, oxygen consumption, and methane production. The carbon deposition testing has been conducted primarily at three copper block temperatures (227°C (441°F), 270°C (518°F), and 300°C (572°F)). The flow rate for the 270°C (518°F) and 300°C (572°F) tests is 16 ml/min, and the 227°C (441°F) test is conducted at 4 ml/min. The test duration is 12 hours at 227°C (441°F) block temperature, and six hours for the other test temperatures. The residence time in the heater tube is about 25 sec at 4 ml/min and 6.2 sec at 16 ml/min. The 227°C (441°F) and 270°C (518°F) block temperature test results only are covered in this paper. The 300°C (572°F) block test is not considered to be applicable to JP-8+100 requirements.

At the conclusion of the tests, the test sections are removed, drained, cut into 50 mm segments, rinsed with hexane, dried in a vacuum oven, and analyzed for carbon deposits by a LECO RC-412 multiphase carbon analyzer.

Evaluation of the JP-8+100 additives has been accomplished by running repetitive tests with and without the additives in various Jet A and JP-8 fuels. Tests were run with a variety of fuels to ensure that the additive is effective in fuels from different base stocks and processing methods. Tests were also conducted with a JPTS fuel, which was established as a baseline fuel for the JP-8+100 overall program. Three Jet A fuels were primarily used as baseline fuels for evaluating the JP-8+100 additives: POSF-2926**, POSF-2980, and POSF-2827. Since JP-8 is the baseline fuel for this overall program, the fuels were doped with the standard additive package (corrosion inhibitor, anti-icing additive, and static dissipater additive) to make them into JP-8 type fuels.

POSF-2926 was considered to be the best (from a thermal stability standpoint) of the three baseline Jet A fuels. The refinery method for this fuel was not known. Comparisons of the carbon deposits of this fuel with and without a potential JP-8+100 additive package (JP-8+100 additive #1) for 227°C (441°F) and 270°C (518°F) block temperatures are shown in Figs. 3 and 4. JP-8 additive #1 consisted of 100 mg/ml of a proprietary dispersant (Betz 8Q405) and 25 mg/l of butylated hydroxy toluene (BHT) antioxidant. At the lower temperatures, the deposits for the fuel without the additive package reached a peak in the middle of the heater tube. Fuel deposits with this fuel at the 270°C (518°F) block temperature were increasing at the end of the heater tube. At the lower temperature, the deposit peak occurs where the oxygen is being consumed in the middle of the heater tube. At the higher temperature, the oxygen is not completely consumed in the heater tube. The oxygen consumption difference between the two temperature tests is caused by lower flow and associated longer residence time of the lower temperature test. At both temperatures, the deposits for the fuel with the JP-8+100 additive package were almost identical to each other and considerably lower than the fuel without the additive package.

The second Jet A fuel tested was designated as POSF-2980. This fuel was Merox treated during its refining process. The comparisons of the carbon deposits of this fuel with and without

** Each fuel acquired by the Air Force has been assigned a four-digit number (e.g., POSF-xxxx). POSF is indicative of the Air Force Branch which catalogued the fuel. These numbers are used for identification here to be consistent with other reports and tests which have been performed on these fuels.

the potential JP-8+100 additive #1 package are shown in Figs. 5 and 6. The deposits for this fuel with the JP8+100 additive package at both temperatures were considerably lower than for the fuel without the additive package. This fuel without the additive package had carbon deposit patterns similar to POSF-2926. A peak was reached at the lower temperature; at the higher temperature, the deposit continued to rise at the end of the heater tube.

The third Jet-A fuel tested was designated as POSF-2827. This fuel was refined by a straight-run process with no hydrotreating. The comparisons of carbon deposits with and without a potential JP-8+100 additive #2 package are shown in Figs. 7 and 8. This was not the same package as tested with the other Jet A fuels. Additive #2 consisted of 300 mg/l of a proprietary dispersant (MCP477), 100 mg/l Betz 8Q405, and 25 mg/l BHT. The other additive package has not been tested in this fuel. The deposits for this fuel without the additive package were considerably less than the deposits with the additive package. The deposits of the fuel with the additive package reached a peak in the heater tube at both block temperatures. This additive package is no longer a candidate for JP-8+100 fuel.

Tests were conducted with JPTS fuel at the same block temperatures. A comparison of the carbon deposit is shown in Fig. 9. The deposits on the heater tubes at both block temperatures were very low and significantly less than the other fuels tested.

An oxygen consumption test is another test that is conducted on the Phoenix test rig. This test is performed by increasing the tube wall heater temperatures in 5°C (9°F) or 10°C (18°F) increments while maintaining a flow of 4 or 16 ml/min. After the flow and temperature changes stabilize, the fuel upstream and downstream of the heated tube is analyzed for dissolved gases using a modified HP-5890 Series II gas chromatograph³.

Thermal stressing of the fuel causes the dissolved oxygen to react with the fuel to form both bulk and wall deposits, as well as trace quantities of methane gas. The oxygen consumption test is used to examine the effects of candidate additives on fuel oxidation rates. For example, an antioxidant additive may significantly increase the temperature at which the dissolved oxygen reacts with the fuel. Also, the amount of methane produced appears to correlate with the amount of deposit formed⁴.

Fig. 10 is a plot of oxygen consumption versus temperature characteristics of the four baseline fuels. The hydrotreated JP-TS fuel reacts with oxygen at the lowest bulk temperatures. POSF-2827 reacts with oxygen at the highest temperature and its slope is very gradual, significantly extending the oxygen-consumption temperature range. The higher oxygen-reaction temperatures for POSF-2827 are attributed to significant quantities of natural antioxidants in the fuel after refining. Fig. 11 shows the oxygen consumption comparison of the JP-8 and JP-8+100 additive #1 in POSF-2926 and POSF-2980. Here the oxygen-consumption temperatures were increased by the JP-8+100 additive for both fuels. Fig. 11 also shows the effect of oxygen consumption of JP-8+100 additive # 2 in POSF-2827. This additive produced the high hot tube deposits and is no longer a JP-8+100 candidate, as discussed previously.

6. EDTST System: The EDTST system was established by modifying an existing facility that was originally a "hydrotreater" for processing fuels. A schematic of the EDTST system is shown in Fig. 12. The system consists of a 60-gallon feed tank, an electrical motor-driven gear pump, two clam shell furnace heaters, and a scrap tank. Normally, fuel makes only one pass through the system. The first furnace heater (preheater) in the system is used to establish the desired fuel bulk temperature in the second heater. The fuel bulk temperature is representative of the fuel temperatures that are experienced due to aircraft and engine heat loads. Temperature is established in the second furnace heater (main heater) to represent the wetted wall temperatures associated with engine injection nozzles. Bulk fuel and wetted wall temperatures have been established because they are used to define limits for engine fuel systems design. The present bulk fuel temperature limit for engine control systems is 163°C (325°F). Engine fuel injectors are normally limited to wetted wall temperatures of 204°C (400°F) to avoid coking problems with conventional JP-type fuels. The desired capability for JP-8+100 fuel is to provide fuels that are thermally stable at wetted wall temperatures of 260°C (500°F) and bulk temperatures of 218°C (425°F).

Both furnace heaters are 0.81 meters long and resistively heated. Each has five heating element zones that are independently controlled. The fuel flows upward through a single stainless-steel tube in each heater. The tube in the preheater has a diameter of 0.96 cm and a wall thickness of 0.0889 cm. The tube in the main heater has a diameter of 0.32 cm and a wall

thickness of 0.0889 cm. Each tube is assembled inside a thick-walled furnace tube that has an i.d. of 2.54 cm and an o.d. of 5.08 cm. The tubes have thermocouples attached to the outer wall for establishing wetted wall temperature. The annular space between the furnace tube and heater tubes is filled with sand. A typical main heater assembly is shown in Fig. 13. Both furnaces have two sets of thermocouples in each heater element zone to control temperature. One set of thermocouples is used to control the heat input from the clam shell heaters; the other set is used for a safety shutoff control system.

During tests, the temperature of the heating zones of the preheater is increased to establish the desired bulk outlet temperature. Similarly, the temperature of the heating zones of the main heater is established to provide the desired wetted wall temperature as measured on the tube outer wall. The middle heating zone is set at the highest temperature to ensure that the desired wetted wall temperature occurs in this zone. A typical temperature profile for the main heater tube is shown in Fig. 14. A flow rate of 1 gallon per hour (gph) and a duration of 96 hours have been used for most tests. At the 1 gph flow rate, the residence time from the inlet of the preheater to the outlet of the main heater is 50 seconds. Similarly, the residence time from the inlet to the outlet of the main heater is 1.6 seconds. The Reynolds number in the heater tube is approximately 2500 at the 1 gph flow rate. The EDTST system is computer controlled and can run unattended for long periods.

7. EDTST Test and Test Results: POSF-2926 with the standard JP-8 additive package was tested with and without candidate JP-8+100 additive #1 at a wetted wall temperature of 260°C (500°F) and a bulk inlet temperature of 177°C (350°F). A comparison of carbon deposits for these tests is shown in Fig. 15. The segment numbers correspond to 5.1 cm segments that the heater tubes are cut into for carbon analysis. Segments 13 and 14 are in the middle zone of the heater where the maximum wetted wall temperature occurs. Total carbon is measured by burning off the carbon from the tubes in the LECO Carbon Analyzer. A test duration of 96 hours was used for these tests and for all the tests discussed later in this paper. There were essentially no deposits with the JP-8+100 additive added to this fuel for these temperature conditions. The deposits for the fuel without the additive were significant and peaked in the middle section of the tube. This same fuel with the additive was then tested at a wetted wall temperature of 288°C

(550°F) and a bulk inlet temperature of 177°C (350°F) to establish how much temperature improvement the additive provides. A comparison of the carbon deposits for this test and the previous two tests is shown in Fig. 16. Based on these results, the additive provides approximately a 28°C (50°F) wetted wall temperature improvement for this fuel. However, the additive in this fuel provided a margin of 28°C (50°F) in regards to the 260°C (500°F) wetted wall temperature goal. A test was also conducted on the JP-8+100 additive #2 candidate in this fuel at a wetted wall temperature of 260°C (500°F) and a bulk inlet temperature of 177°C (350°F). A comparison of the carbon deposits with this additive and the baseline fuel in both the preheater and heater is shown in Fig. 17. This additive resulted in significant deposits in the preheater tube and deposits throughout the heater tube with no peak. This result correlates with the Phoenix test rig findings that this additive reduces the temperature at which oxygen is consumed in this fuel.

Similar tests were conducted on POSF-2980 with and without the standard JP-8 additive package plus the JP-8+100 additive #1 candidate at the same conditions as run with POSF-2926. A comparison of carbon deposits for these tests with POSF-2980 is shown in Fig. 18. The deposits were approximately 50 percent higher with this fuel as compared with POSF-2926 and indicated that the JP-8+100 additive provided about the same wetted wall temperature improvement.

Tests were then conducted on the third Jet A fuel (POSF-2827) with and without the standard JP-8 additive package plus the JP-8+100 additive #1 package at the same wetted wall temperatures and bulk inlet temperatures as used for the other two fuels. A comparison of carbon deposits for these tests is shown in Fig. 19. The results of these tests indicate that the deposits from this fuel were similar to POSF-2980. The deposits with the JP-8+100 additive were higher than with the other two fuels. However, this deposit quantity is considered to be acceptable for meeting the JP-8+100 goals. The maximum thickness of the deposit is estimated to be 0.0002 inch. At this rate, it would take 5000 hours at these conditions to obtain a 0.010 inch deposit.

Tests were also conducted on JPTS fuel at a wetted wall temperature of 260°C (500°F) with a bulk inlet temperature of 177°C (350°F) and a wetted wall temperature of 288°C (550°F) with bulk inlet temperatures of 177°C (350°F) and 218°C (425°F). A comparison of the results of

these tests is shown in Fig. 20. This figure shows that the fuel formed significant deposits at 288°C (550°F) wetted wall temperatures at the higher bulk inlet temperature (218°C (425°F)) but did not have any deposits at the same wetted wall temperature at the lower bulk inlet (177°C (350°F)) condition. A comparison of the tube deposits in the preheater for these 288°C (550°F) wetted wall temperature tests are shown in Fig. 21. This figure indicates that the fuel forms deposits in the preheater at the 218°C (425°F) bulk inlet temperature. Therefore, the allowable bulk temperature (218°C (425°F)) for engine fuel system design desired by this overall program could not be met by the JPTS fuel tested. The result of this test also indicates that there is a definite induction time involved with deposits being formed on the hot tube walls, since significant deposits were not obtained for this fuel at higher bulk and wetted wall temperatures during the shorter duration Phoenix tests.

POSF-2980 with the standard JP-8 additive package plus the JP-8+100 additive was also tested at a 288°C (550°F) wetted wall temperature and bulk inlet temperatures of 177°C (350°F) and 218°C (425°F). A comparison of the carbon deposits from both the preheater and heater for these tests is shown in Fig. 22. Similar to JPTS, this fuel also formed deposits in the preheater at the 218°C (425°F) bulk inlet temperature. This fuel had higher heater deposits at the lower bulk inlet temperature condition. These higher deposits appear to have occurred because the fuel formed the deposit in the preheater instead of the heater at the higher bulk inlet temperature condition. Phoenix oxygen consumption tests suggest that the deposits formed as a result of the oxygen being depleted in the preheater with this fuel at these conditions. The JP-8 +100 additive candidate in this fuel also did not meet the desired bulk temperature requirement for this overall program. Other additive candidates and increased concentrations of the additive tested are to be evaluated to determine their potential to provide the desired capability. More tests of this additive package will also be conducted to determine its maximum allowable bulk operating temperature.

8. Summary: The development of an improved JP-8 fuel (JP-8+100) offers a significant payoff to the Air Force. The trends towards higher heat loads and their associated increase in fuel system temperatures are the main stimulus for this new fuel development. In addition to the higher thermal stability fuel, a need was also identified for improved test apparatus and/or test

techniques to evaluate the fuel. To date, tests conducted using the Phoenix test rig and EDTST have verified that additives can improve the thermal stability of JP-8 fuels. The goal for operating at wetted wall temperatures of 260°C (500°F) has been achieved. The goal for bulk fuel temperatures of 218°C (425°F) with no deposits has not been achieved. Further tests will be conducted on the most promising additives to determine their allowable temperature operating limits. Additional additive candidates will also be evaluated in both the Phoenix test rig and EDTST to identify potential additives to meet the wetted wall and bulk fuel temperature goals of this program. However, if the bulk temperature goal cannot be totally achieved, the JP-8 fuel specification will most probably be changed to take advantage of the wetted wall temperature improvement already demonstrated by a JP-8+100 additive candidate.

9. Acknowledgments: This work was supported by the U.S. Air Force, Wright Laboratory, Fuels and Lubrication Division, Aero-Propulsion and Power Directorate, Wright-Patterson Air Force Base, Dayton, Ohio, under contract No. F33615-92-C-2207, with Mr. Charles W. Frayne serving as the Air Force Technical Monitor.

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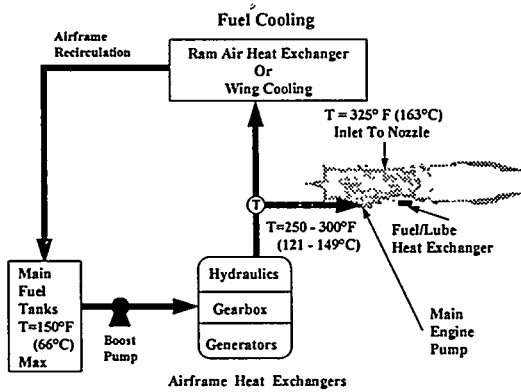


Fig. 1: Current Fighter Aircraft Thermal Management System

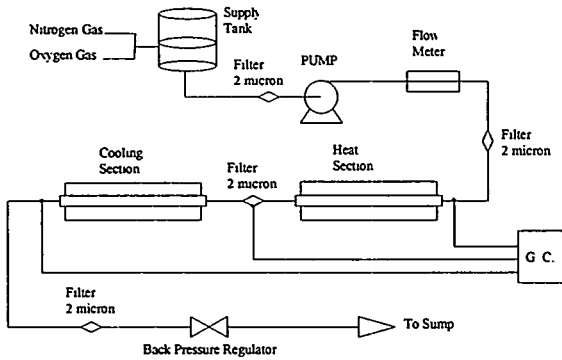
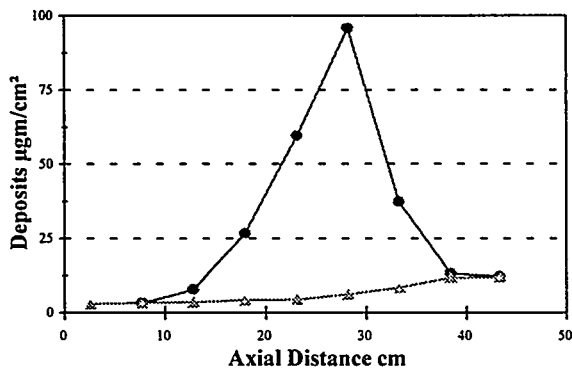
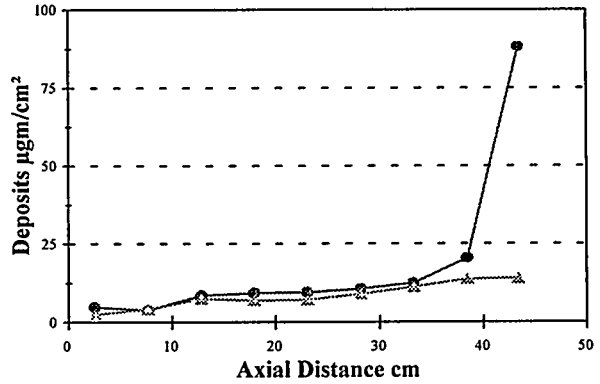


Fig. 2: Phoenix Rig Schematic



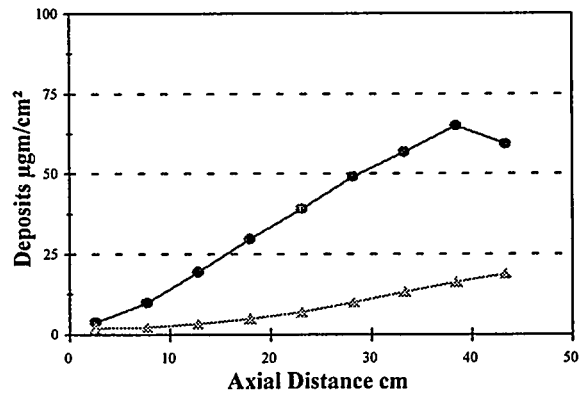
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Fig. 3: JP-8+100 Additive Effects in POSF-2926 at 227°C Block Temperature



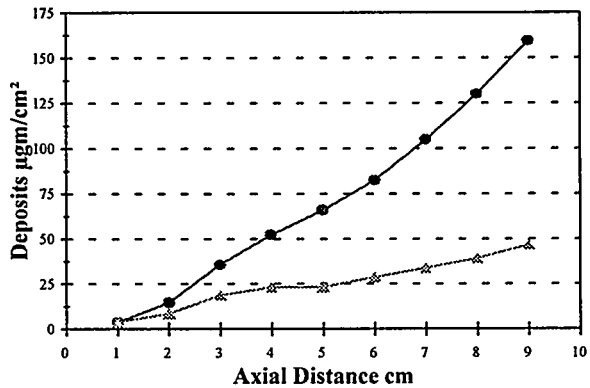
● JP-8 ☆ JP-8 + 100 Additive #1

Fig. 4: JP-8+100 Additive Effects in POSF-2926 at 270°C Block Temperature



● JP-8 ☆ JP-8 + 100 Additive #1

Fig. 5: JP-8+100 Additive Effects in POSF-2980 at 227°C Block Temperature



● JP-8 ☆ JP-8 + 100 Additive #1

Fig. 6: JP-8+100 Additive Effects in POSF-2980 at 270°C Block Temperature

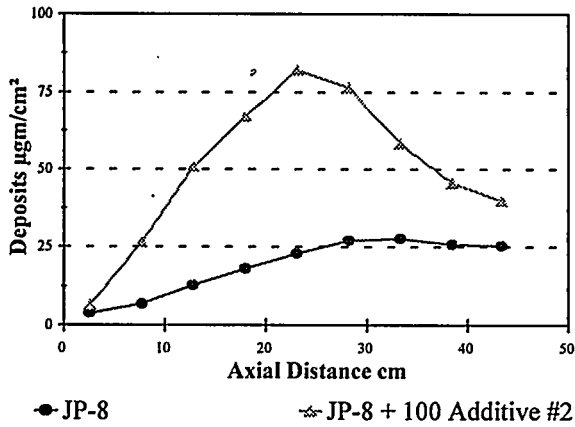


Fig. 7: JP-8+100 Additive Effects in POSF-2827 at 227°C Block Temperature

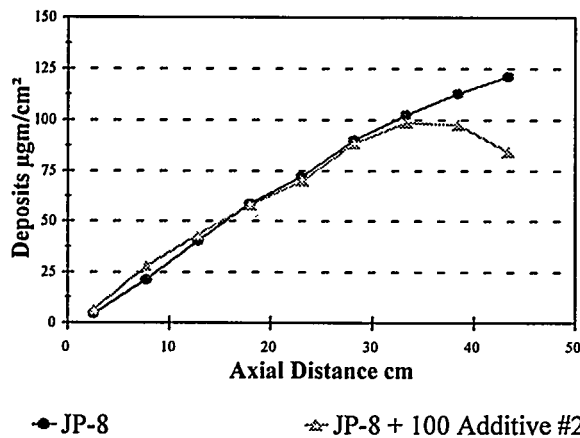


Fig. 8: JP-8+100 Additive Effects in POSF-2827 at 270°C Block Temperature

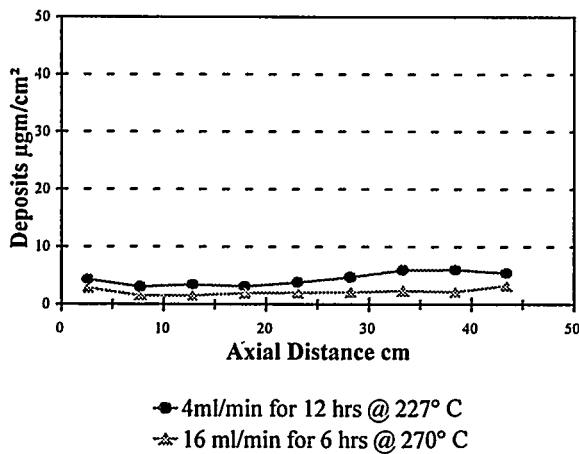


Fig. 9: Effects of POSF-2976 (JPTS) at 227°C and 270°C Block Temperatures

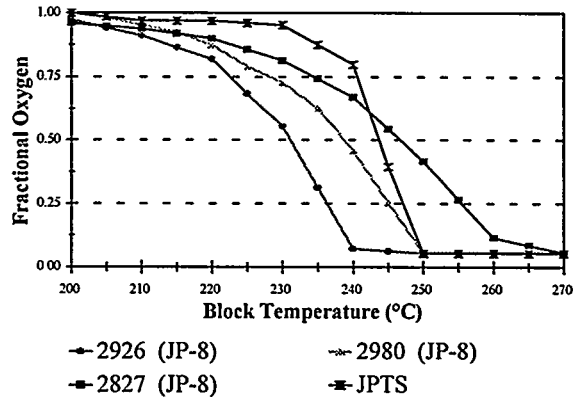


Fig. 10: Oxygen Consumption versus Temperature for Baseline Fuel

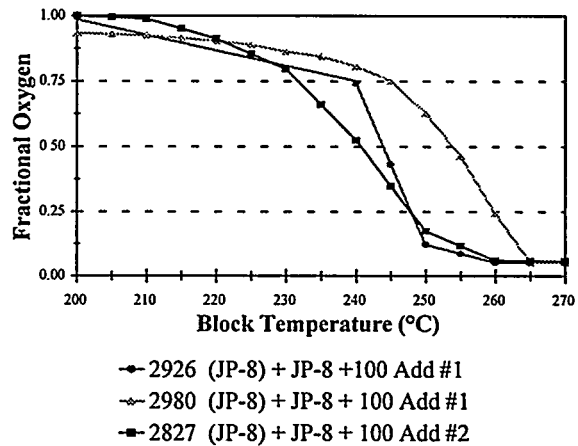


Fig. 11: Oxygen Consumption versus Temperature for Baseline Fuel With JP-8+100 Additives

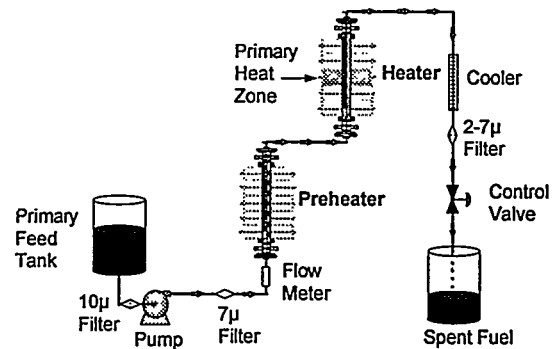


Fig. 12: Schematic of EDTST

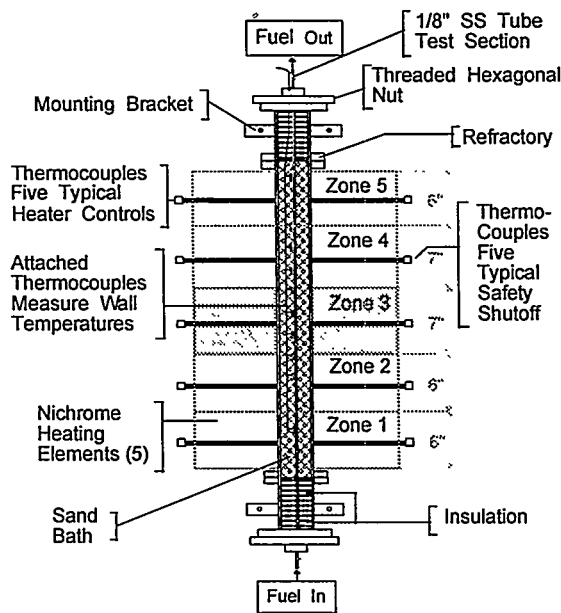


Fig. 13: EDTST Heater Diagram

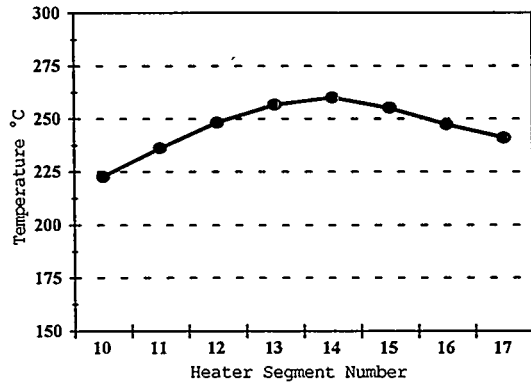


Fig. 14: Temperature Profile of Main Heater (260°C WWT)

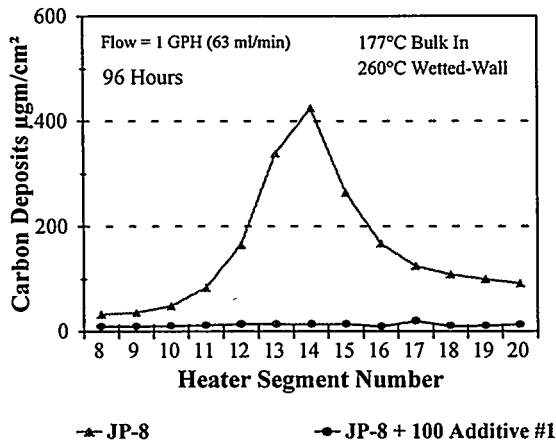


Fig. 15: Carbon Deposits for POSF-2926 with and without the JP-8+100 Additive Package

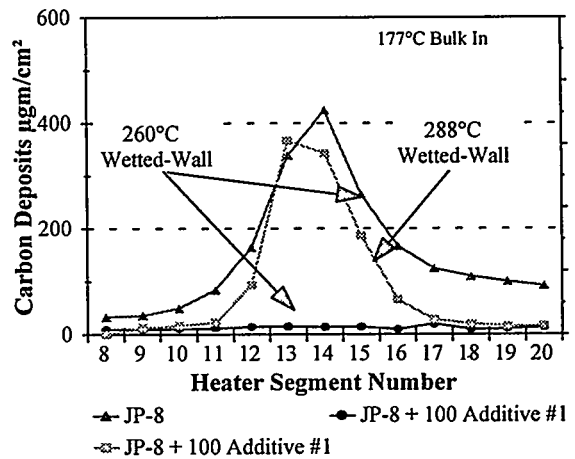


Fig. 16: Carbon Deposits of JP-8+100 Additive #1 Compared to JP-8 at Various Temperatures

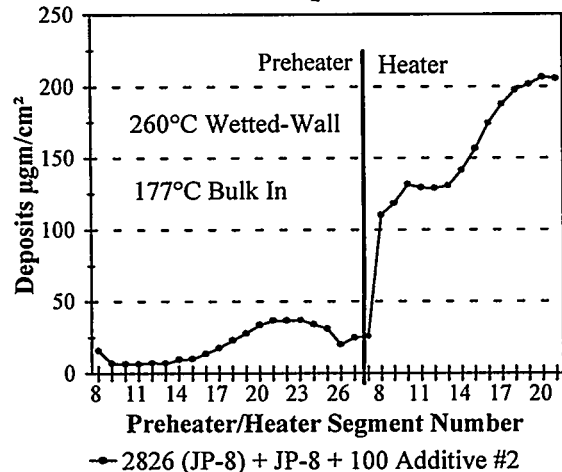


Fig. 17: Carbon Deposits with JP-8+100 Additive #2 in POSF-2926

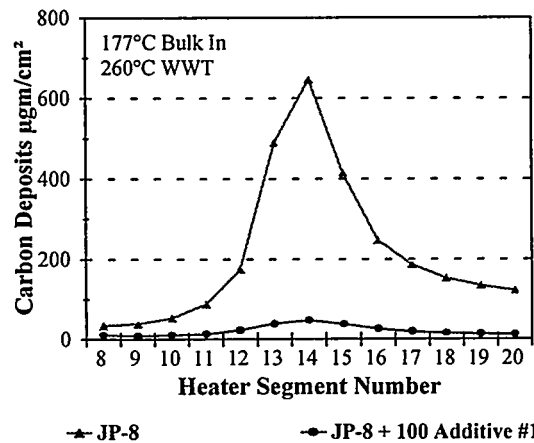


Fig. 18: Carbon Deposits for POSF-2980 with and without the JP-8+100 Additives

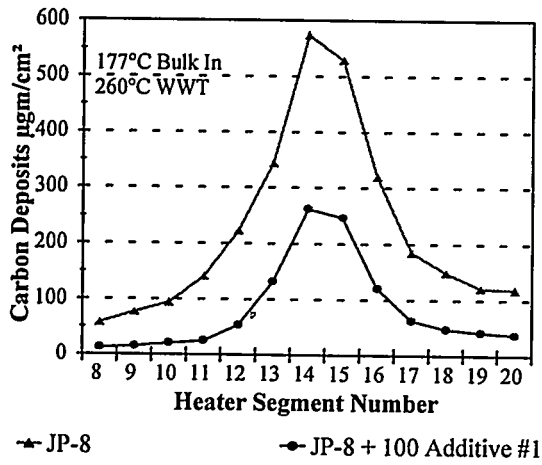


Fig. 19: Carbon Deposits for POSF-2827 with and without JP-8+100 Additives

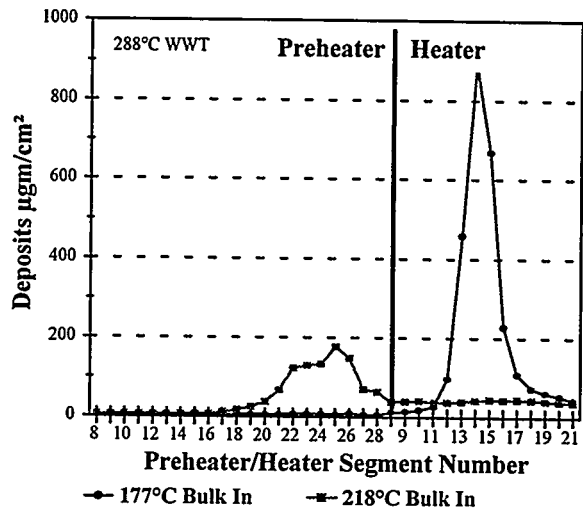


Fig. 22: Carbon Deposits for POSF-2980 with JP-8+100 Additives at Different Bulk Inlet Temperatures

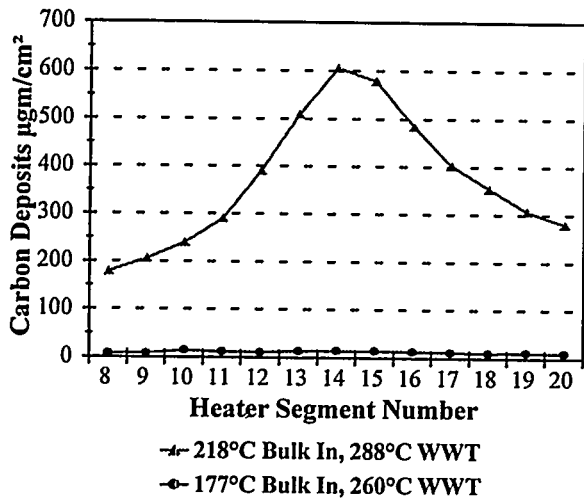


Fig. 20: Carbon Deposits for JPTS Fuels

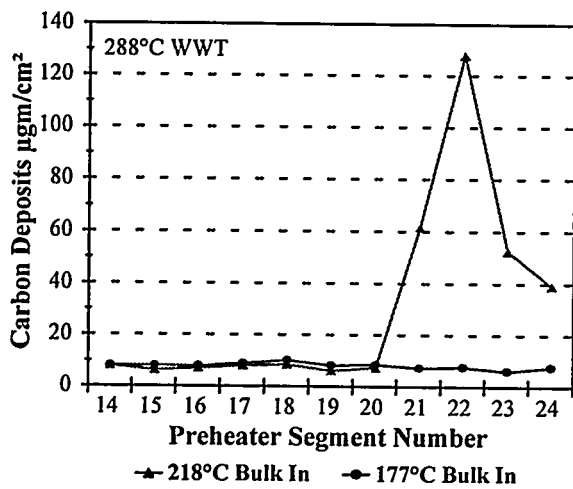


Fig. 21: Carbon Deposits for JPTS Fuels



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**IMPROVEMENT OF TEST METHODOLOGY FOR EVALUATING
DIESEL FUEL STABILITY**

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The storage stability of diesel fuel has been extensively investigated for many years under laboratory conditions. Although continuous efforts have been made to improve testing techniques, there does not yet exist a generally accepted correlation between laboratory methods (such as chemical analysis of the fuel) and actual diesel engine tests. A testing method was developed by the Technion Internal Combustion Engines Laboratory (TICEL), in order to address this problem. The test procedure was designed to simulate diesel engine operation under field conditions. It is based on running a laboratory-modified single cylinder diesel engine for 50 h under cycling operating conditions. The overall rating of each test is based on individual evaluation of the deposits and residue formation in the fuel filter, nozzle body and needle, piston head, piston rings, exhaust valve, and combustion chamber (six parameters). Two methods for analyzing the test results were used: objective, based on measured data, and subjective, based on visual evaluation results of these deposits by a group of experts. Only the residual level in the fuel filter was evaluated quantitatively by measured results. In order to achieve higher accuracy of the method, the test procedure was improved by introducing the measured results of nozzle fouling as an additional objective evaluating (seventh) parameter. This factor is evaluated on the basis of the change in the air flow rate through the nozzle before and after the complete engine test. Other improvements in the method include the use of the nozzle assembly photograph in the test evaluation, and representation of all seven parameters on a continuous scale instead of the discrete scale used anteriorly, in order to achieve higher accuracy. This paper also contains the results obtained by application of this improved fuel stability test for a diesel fuel stored for a five-year period.

Introduction

A number of stability tests have been suggested for the evaluation of long-term storage of gas oil. Most of these tests are conventional, and can be performed in a reasonable time. It seems that the most important accelerated aging test is the ASTM-D-2274 Stability of distillate fuel oil by an accelerated oxidation test. This technique is also currently specified in the VV-F800C specification¹ for gas oil, and in the MIL-F-16884G specification². Another alternative method used for diesel fuel stability testing during a prolonged storage period is ASTM-D-4625.

Stavinoha et al.³ reported field problems caused by unstable diesel fuels in military applications. Some of the reported problems were: fuel injection pump seizure, filter plugging, corrosion of vehicle fuel tanks, fuel tank sludge, and accumulation of fuel deterioration by microbial contamination.

Despite the intensive work devoted to the improvement of storage stability tests, little has been achieved to establish correlations between the above-mentioned tests and actual diesel engine field tests. For this reason, a testing method was developed by the Technion Internal Combustion Engines Laboratory (TICEL)⁴. The test procedure was designed to simulate diesel engine operation under field conditions. It is

based on running a single cylinder diesel engine for 50 h at 1500 rpm, under cycling operating conditions. The method has been implemented successfully to test diesel fuel stability after long-term storage.

In order to improve the method's accuracy, some modifications have been made, including the additional objective measurement of the injector nozzle fouling. This paper describes the modified method, and presents the results of its application for testing the stability of diesel fuel after five years of storage.

Original Test Method

The test method developed by TICEL⁴, to evaluate diesel fuel stability, is based on running a laboratory-modified Petter AV-1 single cylinder diesel engine with the tested fuel 50 hours at engine constant speed (1500 rpm), completing three full cycles (45 h) at three different loads, according to the following schedule:

| Cycle Mode | Time (h) | Engine Power (kw) |
|------------|----------|-------------------|
| a | 5 | 2.22 |
| b | 5 | 2.95 |
| c | 5 | 3.69 |

and an additional short cycle 1 2/3 h at each of these loads.

An engine running-in before every test has to be performed for 8 hours with the tested fuel, as specified by IP standards⁵. The test (including the engine running-in), is carried out during a 6-day period, and the daily fuel tank temperature is maintained constant for the length of this period.

The lubricating oil used was MIL-L-21040, and the fuel filter was the conventional type in the Petter AV-1 diesel engine tests employed.

The overall rating of each test is based on the individual evaluation of the deposits in residual formation in the following engine components: fuel filter, nozzle body and injection needle, piston head, rings (ring sticking), exhaust valve and combustion chamber. Our previous paper⁴ outlined the procedure for evaluating the amount of residue in the fuel filter. The codes of the final evaluation are given at the bottom of Table III

Two methods for analyzing the test results were used: objective, based on measured data, and subjective, based on visual evaluation results of these deposits by a group of experts. Most of the fuel stability evaluations have been performed so far by using the subjective method. Only the residue level in the fuel filter was evaluated quantitatively by measured results.

Improved Methodology

In order to achieve higher accuracy of the method, the test procedure was modified by introducing the test results of checking the nozzle fouling, as an additional objective evaluating factor. This measurement is performed in an air-flow test bench, designed specifically for this purpose, according to ISO standard 4010 (see Appendix A). The nozzle fouling level is evaluated on the basis of the change in the air flow rate through the nozzle before and after the complete engine test. This supplementary information enables the consideration of additional quantitative data regarding the influence of fuel aging on deposit formation in the injector.

During the tests performed since introducing the method for evaluating diesel fuel stability, it has been observed that when the needle was removed from the nozzle body to obtain the photograph in Fig. 1, some parts of the deposit were detached. Therefore, the photograph of nozzle assembly was added, in order to permit a better visual evaluation of deposit formation on the nozzle frontal surface.

Another improvement of the methodology is the evaluation on the basis of a continuous scale. Originally, five of the first six parameters in Table III (column 2), were marked on a discrete basis, while only the residue in the fuel filter was the result of a

measured quantity. Since the objective measurement of the nozzle fouling (by air flow) has been added, it was decided to represent all seven parameters on a continuous basis. Linear scales were chosen, as shown at the bottom of Table III. The scale for the fuel filter residue was determined such that it agrees with the previous discrete scale. The one for the nozzle air flow is based on a perfect mark (10) for a new injector, and zero for a totally clogged nozzle. The Total Achievement is calculated, as previously, by summing the average marks given by the experts and the two objective ones. The Relative Achievement is then obtained by dividing this value by the maximum possible score of 70.

Application of the Improved Method: Evaluation of Diesel-Fuel Stability After Long-Term Storage

Fuel. The diesel fuel tested in this work by TICEL was military gas-oil, with pour point - 15°C. The fuel was stored for five years in a tank without any additives.

Test Procedure. The present test was carried out according to the above procedure, including the nozzle air flow test.

Test Results. Figures 1 - 3 represent the nozzle body and injection needle, nozzle assembly and piston head,

respectively, and Tables I and II present the results of the fuel filter weighing and the nozzle air-flow test, respectively.

Analysis of the Results. In order to compare the present findings with those obtained with the original test procedure⁴, on the same basis, columns 2 and 3 in Table III do not contain the evaluation of the nozzle fouling, but only of the six parameters used before. A group of experts graded each parameter. Column 2 in this Table includes grades on a discrete level basis determined unanimously by the group. Column 3 in Table III contains averages of grades given individually by the experts on the basis of a continuous scale (except for the residue in fuel filter, see code at the bottom of the Table). In both columns (2 and 3), the grades are summed to yield the Total Achievement, and the Relative Achievement is calculated as percent of the maximum (60 points).

Column 4 in Table III includes the evaluation based on seven parameters: the previous six and the nozzle air flow test as explained above. This evaluation is new, and is introduced here for the first time as an improvement of the method developed earlier to check diesel fuel stability.

The Relative Achievement of the tested fuel was found to be 70%, as can be seen in Table III. This result is compared to the Relative Achievement of 80% obtained⁶ for the same fuel,

stored four years with stabilizer and biocide additives.

Conclusions

The method developed earlier by TICEL to test the stability of diesel fuel was modified to include evaluation of injector fouling by measuring the air flow through it. These objective quantitative data improve the accuracy of the method.

The modified method has been used to test the stability of non-additized diesel fuel after five-year storage⁵, and of the same fuel after four-year storage with stabilizer and biocide additives⁶. The Relative Achievement was found to be higher in the latter case (80%, compared to 70% in the former case).

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- (3) Stavinoha, L.L; Westbrook, S.R; Le Pera, M.E. Army Need for Diesel Fuel Stability and Cleanliness. ASTM STP 751, 1981; pp. 103-126.
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Acknowledgment

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Figure 1: Nozzle body and injection needle

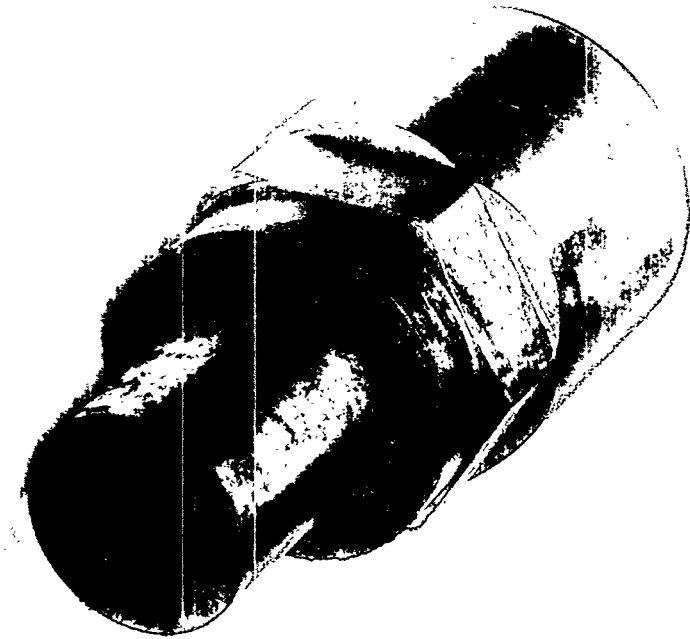


Figure 2: Nozzle assembly

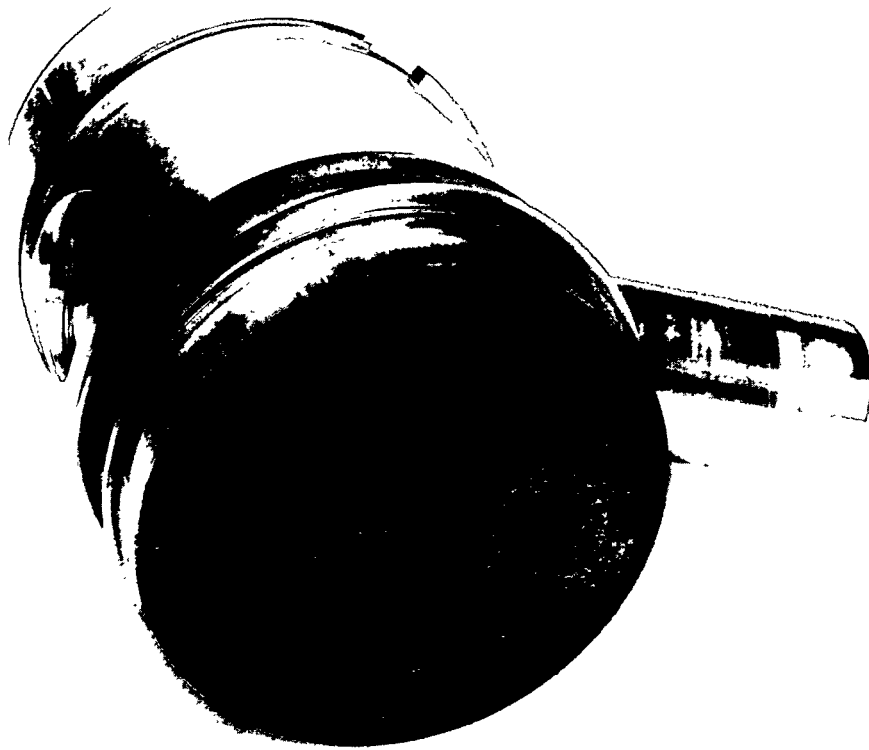


Figure 3. Piston Head

Table I. Results of fuel filter weighing

| Weight of fuel filter, g. | | |
|----------------------------------|---------------------------------|--------------------------|
| Before test, after drying, G_1 | After test, after drying, G_2 | $G_2 - G_1$ (difference) |
| 36.6505 | 38.1014 | 1.4509 |

Table II. Results of nozzle air flow test

| Needle lift, mm. | Flow rate, l/min | | Flow rate change, % |
|------------------|------------------|------------|------------------------|
| | Before test | After test | |
| 0.05 | 0.65 | 0.36 | 45 |
| 0.10 | 1.71 | 1.35 | 21 |
| 0.15 | 1.86 | 1.66 | 11 |
| 0.20 | 1.90 | 1.73 | 9 |

Table III. Achievements Results

| Item | Discrete Basis | Continuous Basis | |
|------------------------|-----------------------|---|--------------|
| | 6 parameters | 6 parameters | 7 parameters |
| | Experts Group Marks * | Average Experts' Marks ** *** | |
| 1 | 2 | 3 | 4 |
| Injector | 5 | 6.6 | 6.6 |
| Piston Head | 5 | 6.5 | 6.5 |
| Ring Sticking | 10 | 10 | 10 |
| Exhaust Valve | 7.5 | 7.6 | 7.6 |
| Combustion Chamber | 7.5 | 7.6 | 7.6 |
| Residue in Fuel Filter | 5 | 5 | 5.2 |
| Nozzle Air Flow Test | - | - | 5.5 |
| Total Achievement | 40 | 43.3 | 49 |
| Relative Achievement | 67% | 72% | 70% |

Discrete Scale

Code 1 - Engine Components:

- good - 10
- good-moderate - 7.5
- moderate - 5
- moderate-poor - 2.5
- poor - 0

Code 2 - Residue in Fuel Filter:

- residue \leq 0.5g - good - 10
- 0.5g \leq residue \leq 1.0g - good-moderate - 7.5
- 1.0g \leq residue \leq 2.0g - moderate - 5
- residue \geq 2.0g - poor - 0

Continuous Scale

Code 1 - Engine Components:

Continuous rating between the grades of Code 1 for the Discrete Scale.

Code 2 - Residue in Filter:

Linear Scale:
0g - 10
 \geq 3g - 0

Code 3 - Nozzle Air Flow Test:

Difference in air flow rate before and after engine test:
Linear Scale:
0% - 10
100% (zero flow) - 0

* According to the discrete scale.

** According to the continuous scale for 5 parameters and the discrete scale for the residue in fuel filter.

*** According to the continuous scale.

Appendix A: Procedure of Nozzle Fouling Evaluation by air-flow test

Purpose

This procedure is for checking the air-flow rate through a nozzle in order to evaluate its fouling grade.

Test System

The test system was designed according to Standard ISO-4010 requirements. A schematic description of the test bench is given in Figure A1.

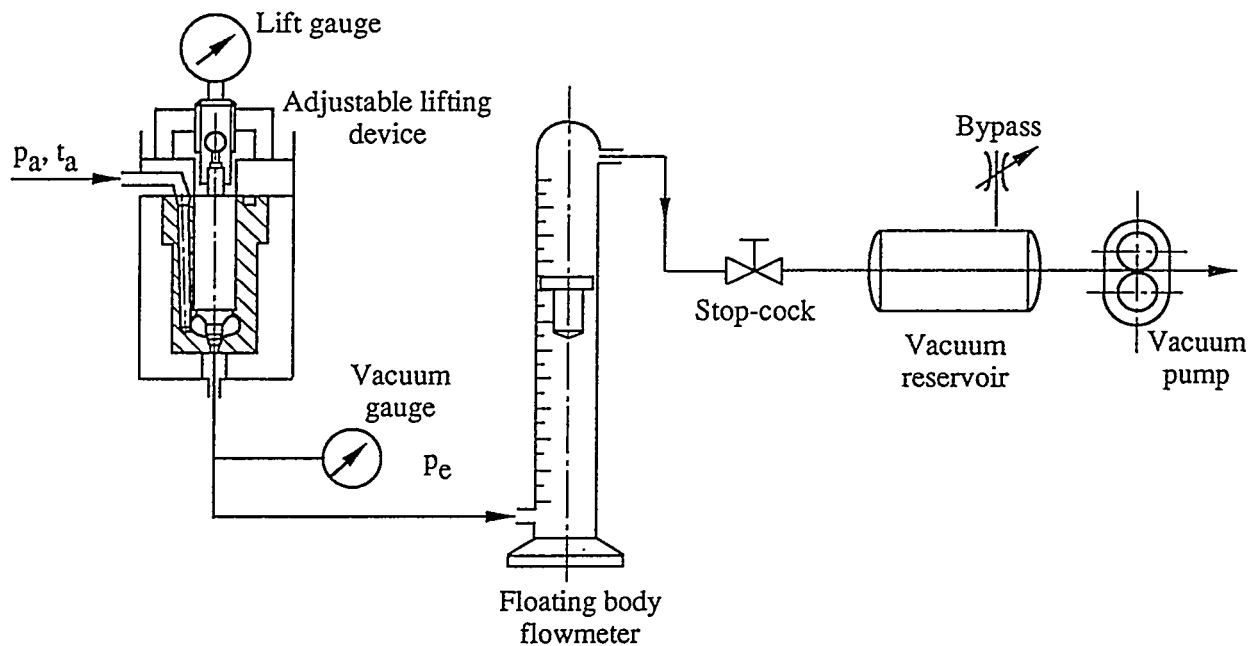


Figure A1: Test bench (schematic) for measuring the air-flow through a fuel injector nozzle.