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3rd International Conference on Stability and Handling of Liquid Fuels, London, England, September 13-16, 1988. Proceedings published by the Institute of Petroleum (London), R. W. Hiley, R. E. Penfold, and J. F. Pedley, editors; London, England, November 1988.

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Preface

The association's international conferences continue to be the premier forum for papers on stability and handling of liquid fuels, and attract the world's leading authorities on these topics. The 170 delegates from 24 countries on all five continents who attended IASH '97, the 6th of these conferences, attest to their importance.

Within the North America and much of Europe, legislative initiatives and an enlightened environmental awareness have resulted in stringent product specifications and stricter practices at fuel handling and storage facilities. In the U. S., for example, gasoline marketed in certain ozone nonattainment areas is required to contain at least 2 percent oxygen, and less benzene and other aromatics than previously allowed. By the year 2000, the entire U.S. gasoline pool may be reformulated. In many countries, diesel fuel must have an ultra-low sulfur content, and it is possible that even home heating oil may eventually have to conform to this new standard. Stringent product specifications and environmental and statutory requirements are compelling refineries to upgrade their processes to produce cleaner burner fuels.

In the U.S., some refineries have been shutdown rather than investment made in their upgrading. Although reformulated fuels have been in the marketplace for several years now, we still do not fully know how some of them will withstand the rigors of handling and storage, or stand up to microbial attack. Complicating the need to produce cleaner fuels, the world crude oil stream is getting heavier and higher in sulfur. More severe processing is necessary, therefore, to obtain specification products. Moreover, there is a greater tendency to upgrade the bottom of the barrel to provide more transportation fuels in response to rapid growth in demand. These trends are exacerbating problems with product quality and stability.

Despite the dramatic changes in the composition of the gasoline and diesel fuel pools and the relative sparsity of data on their stability, papers on aviation fuels dominated this conference as they did at the 5th conference in Rotterdam. Hopefully, the 7th conference in the year 2000 will have more papers on handling and environmentally-friendly fuels.

I thank the following companies and organizations that provided generous financial support for this conference: Angus Chemical Co.; the Arabian Fuels Center; BDM Oklahoma; BetzDearborn Hydrocarbon Process Group; BP/Plasmos; Chevron Products Co.; Emcee Electronics, Inc.; Ethyl Petroleum Additives; the FQS Group, Inc.; ITS-Caleb Brett; Nalco/Exxon Energy Chemicals, L.P.; Octel America; Oiltanking Houston, Inc.; Saybolt Nederland BV; SGS Canada; Varlen Instruments, Inc.; and the U. S. Air Force Wright Laboratory.

I am also grateful to the many people and organizations that assisted me in organizing this conference. Among them are Ms. Tamika Green of the U. S. Department of Energy, Mrs. Shirley Bradicich and Mrs. Jan Tucker of the Coordinating Research Council, Dr. Edmund W. White, consultant, and Ms. Erna J. Beal of the Naval Research Laboratory. The Canadian Embassy in Washington, DC and Tourism *Vancouver* provided support and assistance in bringing this conference to Vancouver. Finally, I thank everyone that attended the conference. Their interest and support ultimately make these conferences successful.

In opening the 4th conference in Orlando, FL, I reminded the delegates of the words of Francis Bacon, founder of the scientific method, that "science makes books, not books science." I have noted that Powertech Labs. Inc., employer of one of the opening keynote speakers, includes another quote from Bacon in its literature, namely "knowledge is power." I am confident the knowledge gained at the 6th conference will help power our quest for a better understanding of fuel instability and improved handling practices.

Harry N. Giles
Conference Chairman

*IASH '97, the 6th International Conference
on Stability and Handling of Liquid Fuels*

Vancouver, B. C., Canada
October 13-17, 1997

OPENING ADDRESS - I

Dr. Alan King

B. C. Hydro, P. O. Box 8910, Vancouver, B.C. V6B 4X3, CANADA

Good morning ladies and gentlemen. It is my pleasure and honour to welcome you to Canada, to British Columbia and particularly to Vancouver. I am delighted that your committee has chosen Vancouver as the host city for your conference. I hope that you will be able to take the opportunity to explore and enjoy a little of British Columbia and Vancouver during your stay.

You are in good company, in recent years the City has hosted the leaders of the G7 nations, a Clinton - Yeltsin summit, and next month will be hosting the leaders of the eighteen countries that constitute the Asia Pacific Economic Cooperation Trade Group. This latter is an organization that includes the majority of the Pacific Rim Countries including Canada, the U.S. and Japan.

For those of you who are unfamiliar with this part of the world, I would like to give a brief introduction. Forgive me if I brag a little. Canada, as you no doubt know is physically the second largest country in the world, second only to Russia. It spans six time zones and stretches north to the high arctic, and south, surprisingly, to the latitude of northern California. Canada is blessed with abundant natural resources and is a major producer of natural gas and oil, with the tar sands of Alberta holding potential petroleum reserves that rival the Middle East.

British Columbia has the greatest geographical diversity of any part of the country, ranging from a deeply indented and island studded mainland coast line, to the heights of the Rocky Mountains. With coastal rain forests contrasting with inland deserts and mountain ice fields. The Province is home to three and a half million people, a population growing with a steady influx of newcomers from other parts of Canada and around the world, attracted by the Province's prosperous economy and respect for its cultural diversity.

Vancouver is, certainly by world standard, a new city. It was incorporated on April 6th 1886 and was burned to the ground on June 13th 1886; a process that took all of twenty minutes, which says something of the size of the place at that time. Not a very auspicious start. However, we have grown a little since then and are proud to have been recently ranked by the Corporate Resources Group of Geneva as the second most livable city in the world and the top ranked city in North America for public service, efficiency and infrastructure.

Vancouver's strategic location has helped it to take a leading position in trade. It is near the midpoint on the west coast of North America and equidistant by air between London and Tokyo. Vancouver boasts a major port and is the top exporting port to foreign countries in North America. Seventy-two million metric tonnes of cargo are handled annually and seven hundred thousand cruise ship passengers pass through the city each year. It is not, however, a major handler of petroleum products, two million metric tonnes compared with twenty three million metric tonnes of coal and twelve million metric tonnes of grain.

Our focus is primarily on the Pacific Rim with nearly a third of the city's residents able to trace their origins to other Pacific Rim countries. Moreover, Vancouver is a city of immigrants with a population in which over thirty distinct ethnic origins are represented by a significant number of people and incidentally, each of these groups is served by at least half a dozen restaurants. No matter where you come from in the world it is probable that you will be able to find some home cooking somewhere in the city.

My work at B.C. Hydro, the electrical utility that supplies power to most of British Columbia, involves me in the generation of power in the more remote parts of the Province. Power to communities that are not integrated with the power grid. These communities are typically served by diesel engine powered generating stations.

Similarly, seven Provincial and Territorial utilities serve approximately one hundred and fifty communities across northern Canada and face formidable logistical problems, particularly in the handling and stability of fuel. Probably the best example is that of the Northwest Territories Power Corporation. The NWTPC operates forty-nine diesel stations, many of which are in the High Arctic. None of the stations are interconnected and all operate on a continuous basis throughout the year in

temperatures that range from plus thirty to minus fifty Celsius. The stations burn eighty-five million litres of fuel annually. Fuel costs anywhere from twenty-three cents to seventy-three cents a litre depending on the location of the respective power stations. Ensuring a reliable supply of appropriate fuel is the main concern. Delivery is either by truck over winter roads (ice roads) during the coldest months of the year, or by barge and ship during the short summer period when the rivers and sea are relatively ice free. Given the extremes of weather, the emphasis on environmental protection of very sensitive ecosystems, and the absolute criticality of electrical supply to the communities involved, it can be seen that the logistics of fuel supply to the arctic can be quite a challenge.

While B.C. Hydro does not face such severe fuel supply logistical problems as some of the other utilities across the country we do have our own set of concerns, particularly those of fuel stability. We operate a network of micro wave repeater stations. Information carried on the microwave system is vital to the protection and control of the electrical transmission system and associated generating stations located throughout the province. Most of the microwave stations are located on mountain tops and are not easily accessible. Each has an associated small diesel generation station, a few for prime power but most on standby to back up supply by cable up the mountain. The fuel can be in storage for many years and presents potential stability concerns.

B.C. Hydro is encouraging the use of independent power producers in some of our remote areas that historically have been supplied with diesel generation. Typically these are small hydro electric operators. Because of the lack of water storage in these small plants we have to maintain a back up diesel station to ensure continuity of supply to our customers. Again the need to keep fuel on hand for several years presents stability concerns. We operate two relatively large gas turbine powered generating stations, each of which is on standby duty to protect communities fed by a single radial transmission line. The stations maintain approximately two million and four million litres of middle distillate fuel respectively in single tanks. The fuel had been in storage at both sites for over twenty years and during this time it began to give indications of loss of stability and we become concerned that we would run into filter plugging and nozzle varnishing problems, which of course would show up just when we needed power. We have since replaced the fuel at both stations to facilitate tank inspection.

Our operating requirements and the use of middle distillate fuels have presented us with two basic concerns.

- I. How to maintain and ensure the continuing stability of fuel in long term storage and, in particular, what commercially available fuel stabilizing product was most effective for the particular fuel in question; and
- II. How to determine what fuel would be most stable over long storage periods before the fuel was purchased.

For answers to these problems I turned to the research arm of B.C. Hydro, Powertech and, in particular, to my colleague here this morning Hans Schellhase. We have taken the liberty of sharing this welcoming address between us. The user with his problems and the research chemist, the supplier of solutions. An illustration of both sides of the fuel stability coin.

*IASH '97, the 6th International Conference on
Stability and Handling of Liquid Fuels*

Vancouver, B.C., Canada

October 12-17, 1997

OPENING ADDRESS - II

Hans U. Schellhase

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Ladies and Gentlemen, Mesdames et Messieurs. It gives me great pleasure and honor to follow my partner, Dr. Alan King, in welcoming all of you to the Pacific Rim City, Vancouver, and to British Columbia and Canada.

By Way of Introduction:

A highly interesting week is ahead of us, and I consider it fair game to muse in my welcoming address about the topic or, at least, some aspects of the topic that this conference, which was founded by Nahum Por in Tel Aviv, Israel in 1983, will address.

I had the pleasure of attending the 2nd International Conference on Long-Term Storage Stabilities of Liquid Fuels in San Antonio, Texas in July/August of 1986, and I remember with fondness both the excellent presentations and the hospitality of the chairman at that time, Leo L. Stavinoha, of Southwest Research Institute.

But, I am getting ahead of myself and had better start at the beginning.

Using a historical example, let me demonstrate to you how we dealt here in British Columbia with a severe problem of storage stability in the eighties.

Dr. Alan King initiated a project on fuel stability in 1982 which he alluded to a few minutes ago. Not long after the project had been undertaken, a middle distillate fuel (diesel) in one of the storage tanks at B.C. Hydro's Keogh Station started to foul in a bad way. A large amount of fuel (about 1 million imperial gallons, six years in storage) was rapidly turning sludgy and endangering emergency power generation at the associated power plant. Alan called upon us, at what came to be called Powertech Labs Inc., to participate in the clean-up and stabilization of the fuel. Our first line of defense was filtration; our final goal was stabilization of the stored fossil fuel.

We reinvented the wheel and duplicated work that had been done by D. Milson, A.R. Rescorla et al. from "Cities Service Research and Development Company", New York, N.Y. in 1952 to 1956 (1).

At that time, an ASTM method to measure the storage stability of middle distillates did not exist, and whatever one intended to do had to be validated. This study equipped us with the tools to evaluate

systematically storage stability of fuels before and after stabilization, and it resulted, for the fuel in question, in a recommendation to Dr. King to use a commercial multifunctional additive package at a concentration of about 100ppm.

During our work it became clear that not all commercial additives were equally successful in stabilizing a given fuel. The additive package that we recommended was composed of an antioxidant, a color stabilizer, a detergent and a metal deactivator. Sediments that formed initially at a rate of 45mg/L (43.3°C, 12 weeks) were reduced to less than 0.5mg/L annually and maintained at that level without further re-inhibition for at least three years.

Personal computers and Internet were still a few years off, and what had to be done in our research was done on the main frame. The outcome of our work was presented at a meeting of the Society of Automotive Engineers (S.A.E.) as a technical paper in 1983 (2), a fitting year in retrospect. It was the founding year of this association.

At about this time of our investigation, Leo L. Stavinoha, Steven R. Westbrook et al. were in the midst of comprehensive reviews and studies of middle distillate fuels. For example, they published jointly with D.W. Brinkman: "Accelerated Stability Test Techniques for Diesel Fuels" (3). This was and, perhaps, still is the most comprehensive work of this nature to date and had been commissioned by the U.S. Department of Energy (DOE).

Sludge deposition (generalist's view)

Why are straight-run fuels generally of greater stability than those of synthetic, cracked and blended nature? This question plagued some of us, especially petroleum processing engineers. I think, and believe, what I have to say is true for most conventional crude oils. During the geological creation of these fossil fuels the most stable organic compounds survived the numerous reactions under the changing chemical and physical environment of the petroleum reservoir. It is estimated that this lasted millions of years, and resulted in an increase of the carbon/hydrogen ratio, especially in the case of the sludge (asphaltenes). The sludge became more graphite-like, while the crude as a whole assumed the state of a stable, partially colloidal solution. From this point of view, the conventional crude oil is in a stable equilibrium, chemically as well as physically; one might call it cured and well-aged. In addition, it frequently contains compounds that act as natural inhibitors to fuel degradation.

Atmospheric distillation of these conventional crude oils followed by traditional refining techniques results in so-called straight-runs, which frequently show better storage stability than the equivalent cracked or synthetic fractions. In my view, the fast processes of the modern and sophisticated refining techniques that are applied to non-conventional crude oils and heavy feed stocks freeze multicomponent systems in equilibria that have not maximized the entropy of the reaction mixture. They are, as the American physicist Gibbs might have said more than a hundred years ago, in a state of labile thermodynamic equilibrium. Not only that, catalytic cracking, hydrotreating and all the other applied process chemistries reduce the chances of natural inhibitors surviving the chemical onslaught.

I would apply similar reasoning to the blending of fuels of different origins; the resulting blend is not necessarily in thermodynamic equilibrium and may result in storage and thermal instability.

Peroxides and free radicals are formed in petroleum products, once the same are exposed to air, water, catalytic metals and light. They complicate the chemistry of petroleum-based fuels. I am not addressing the issue of which come first, the peroxides or the free radicals? Nor am I exploring whether both are independently active.

What do Middle Distillate Fuels have in Common?

Strictly speaking, the name! The performance characteristics such as cetane number, density, flash point, distillation performance etc.. define the product.

What I said is especially interesting in view of the fact that the United States Department of Energy (DOE), Office of Heavy Vehicle Technologies is developing a vision for the heavy vehicle industry of the future (4). This future is to be based on “diesel fuels”:

Diversity of Feedstocks	→	A Common Diesel Fuel Specification	→	One Energy Conversion System
● Petroleum		Cetane Number		Diesel Cycle Engine
● Natural Gas		Energy Density		
● Coal		Emissions Characteristics		
● Biomass		Cost Competitive etc.		

Here, one of the driving forces is the fact that the diesel engine is the highest efficiency engine today (44% versus 24 % for the gasoline engine). The hopes are to raise this efficiency to 55% or, perhaps, to 63%!

As we can all see, there is going to be lots of work for the respective industries and R&D centers.

An Unorthodox Approach to Correlate Middle Distillate Fuel Properties, Statistics of Populations.

Having introduced middle distillate fuels thus, I would like to share with you a brief reflection. Let me explain.

I used the approach of a generalist in an older study, which came about due to an unsolicited proposal to the Canadian Electrical Association (CEA) in 1984. It resulted in a two-year study into the fuel stability and storage life of middle distillate fuels. Based on the work that had been done for B.C. Hydro, specifically Dr. Alan King, we investigated middle distillates, “Canadian Middle Distillate Fuels” (5), if there is such a thing.

As you can see from Figures 1 and 2, we collected from coast to Canadian coast (about six to seven thousand km apart) 64 middle distillate fuels (14 from the Atlantic Region, 19 from Central Canada, 16 from the Prairie Regions, 14 from the Pacific Region and eight from the Northwest Territories). Oil companies as well as utilities cooperated generously and delivered gallon amounts of fuels that went into cold storage at our place. Yes, in those years common sense prevailed; only one company

inquired if, aside from providing the sample containers, we would also reimburse handling and freight charges.

We assessed their qualities, including long-term storage stability. I failed, like many other investigators before me, in correlating single parameters and stability. The best correlation R^2 I was able to come up with equaled 0.25, but in attempting to do the impossible, we learned a lot. If one sorted the database according to increasing total insolubles (43.3°C, 12 weeks), and divided these into six sub-ranges of about ten fuels each, the correlations for the six mean values improved. Case in point: the R^2 equaled 0.94 for the relationship of sulfur to total insolubles. I hear the argument (from my alter ego), that this is bad science! If I plot the non-manipulated data, I will get the true answer, there is no correlation ($R^2 = 0.25$). I refute this argument by stating that my alter ego is neglecting the fact that I sorted the data first! We are dealing with a population. If I were to investigate the distribution of false teeth in the Canadian Society, I would set up age groups first and then develop correlations between false teeth and these age groups. (Of course I could widen the scope and investigate false teeth, eating habits and ethnic groups!).

It became evident that these 64 fuels formed, just like our Canadian Society, a rather heterogeneous population. The Canadian cross section of middle distillate fuels that we had assembled had not much in common except certain performance characteristics. As a generalist I sorted my database (Lotus 1-2-3) for hours looking for common factors to appear encouraged by the success of this view.

Let me explain to you what I found in this matrix of data which was about 64 lines by 32 columns. Classifying the 64 investigated fuels, 15 fuels (24%) had both a sulfur content greater than 0.15% and a final boiling point greater than 340°C. Eleven of these fifteen fuels were classified as of low stability. The total insolubles were greater than 9mg/L by the accepted storage test of 12 weeks and 43.3°C (110°F). Only one fuel did not fit these criteria and was unstable. We had by our definition a total of 12 severely unstable fuels.

Thus, 92% of the unstable fuels (11 fuels) belonged to the sub-set just described, while 8% (one fuel) of the unstable fuels did not belong. The latter had a significant copper content (catalyst) of 1.5ppm instead. (Also nine of the unstable fuels belonged to a sub-set of 14 fuels of high aromaticity). Seven of the 11 unstable fuels contained synthetic or cracked components, while the other four were of unknown Eastern Canadian feedstock and treatment.

Encouraged by these findings, the data were statistically evaluated by a professional statistician (K. Wensauer, now of B.C. Hydro) using the SAS (Statistical Analysis Software) standard regression package. We reached the conclusion that this is a viable method of combining laboratory tests of some variables with statistical regression theory to arrive at a practical tool that estimates insolubles within a certain acceptance/rejection region.

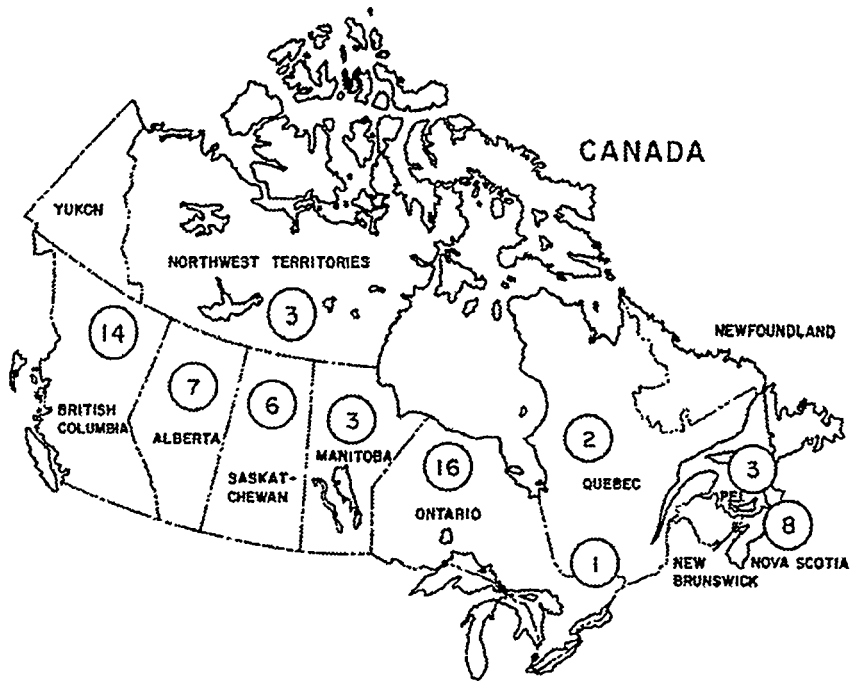


FIGURE 1
NUMBER OF FUELS ACCORDING TO PROVINCE OR TERRITORY

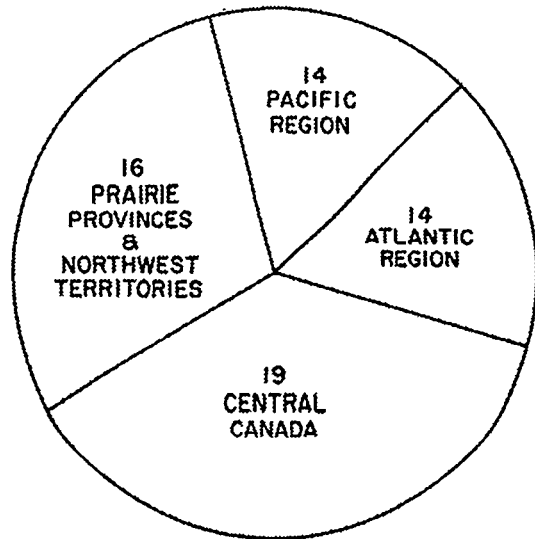


FIGURE 2
NUMBER OF FUELS ACCORDING TO REGIONS

Detailed characterization of 14 test fuels resulted in 63 variables (including NMR - data). We attempted to improve upon the prediction of the storage stability of a fuel beyond the prediction by a single test using regression models with up to three variables. We proved it is possible to assemble:

- improved statistical models from two or three variables (which included a newly developed, accelerated stability test)
- a less satisfactory but still reasonable model from ASTM D2274 and one of the other commonly used, accelerated stability tests (example: 16 hrs/100°C)

Points of Interest

I mentioned the previous findings for high sulfur and total insoluble to staff of the Lawrence-Livermore Laboratories at SAE's International Fuel and Lubricants Meeting and Exposition in Toronto, 1987. I was told that a similar correlation exists between particulate emission and kinetic combustion parameters. From this eagle's view, the restrictions in sulfur content and high boilers for middle distillates became even more meaningful. Our R&D findings were implemented early on in the purchase specifications of middle distillates at B.C. Hydro. These specified a low sulfur content.

It is hoped that the new initiative by the DOE's 'Dieselization' strategy will lead to programs that are similar to the Auto/Oil Air Quality Improvement Research Program (AQUIRP) in the United States (6) which investigated gasolines in great detail. We hope that diesel engine manufacturers, oil companies and government agencies will cooperate in increasing and deepening the knowledge about diesel fuels, diesel composition, engine performance and engine emissions as it has been done by IASH in the areas of stability and the handling of liquid fuels during these past sixteen years.

Where do we go from here?

I hope that it will be possible to establish an international database on distillate fuels into which all recognized laboratories can compile middle distillate fuel data. These databases, if accessible to appropriate research teams, would permit the development of algorithms and expert systems by industrial R&D and academia. The rational upgrading of liquid fuels, equipment and the development of predictive software is in the interest of the public and all parties concerned.

Conclusion and Welcome

If we had the genius of Josiah Willard Gibbs and could apply all thermodynamic principles to chemical equilibria and solutions par excellence; and if we had the gift of an idiot savant, we could evaluate hundreds of thermodynamic data, equilibria and phase relationships in our heads. Indeed, we would not only be able to predict storage stability, thermal stability, and combustion processes but could select the correct additive package as well as many other neat things. Nicole Tesla, a Serbian-American genius and inventor was, reputedly, the only person who was capable of doing things of that nature!

Following far-out thoughts of this kind, we should be able to look at the most up-to-date GC/MS chromatograms as well as the identification and quantitative evaluation of the respective compounds for fuel-x, and voila, we know!

What I try to allude to is this: in my opinion, the time has come to establish national and/or international databases for different liquid fuels. In the case of middle distillate fuels, these databases will combine detailed fuel description and data from gas chromatography, mass spectrometry, ASTM tests etc. and will be available to qualified software teams to develop effective algorithms and expert systems.

This is the reason why I chanced to bore you, the experts, with work that was completed ten years ago. I was not trying to sneak an old paper into this conference and to misuse this platform as invited speaker. I believe the time has come to design expert systems in these fields of study.

The know-how is there or under development and so is the idiot savant (the computer)!

As a postscript (P.S.): You should accept into your association researchers in the field of insulating oils. These oils are chemically similar to middle distillate fuels and many areas of study are useful to both investigating groups.

Thank you for your attention!

Ladies and Gentlemen. Welcome to Vancouver, to British Columbia and the 6th conference -IASH '97' - which is about to begin!

References:

- (1) Daniel Milsom and A.R. Rescorla "Determination of Fuel Oil Stability", Cities Service Research and Development Co., New York, N.Y.; presented before the Division of Petroleum Chemistry, American Chemical Society, Atlantic City Meeting, 17-21 September 1956.
- (2) J.R. Bentley and H.-U. Schellhase "Fuel Stability and Storage Life of Middle Distillate Fuels", B.C. Hydro R&D Centre, Surrey, B.C.; SAE Technical Paper Series No. 831205; Reprinted from SP-548-Fuel Alternatives for Spark Ignition and Diesel Engines, Vancouver, August 1983.
- (3) Stavinoha, L.L., Westbrook, S.R., Southwest Research Institute, San Antonio, Texas. Brinkmann, D.W., Bartlesville Energy Technology Center, Bartlesville, OK. "Accelerated Stability Test Techniques for Diesel Fuels", DOE/BC/10043-12. Prepared for the Department of Energy, under Contract No. DE-AC19-79BC10043, October 1980.
- (4) The CLEAN FUELS and Electric Vehicles REPORT, Comprehensive Coverage of Business, Government and Technology Issues for Transportation Fuels and Electric Vehicles; J.E. Sinor Consultants Inc.; Volume 9, No. 3, June 1997
- (5) H.U. Schellhase "Storage Stability of Middle Distillate Fuels", B.C. Hydro and Power Authority, Surrey, B.C.; Report for the Canadian Electrical Association, Montreal, Quebec; CEA No. 341 G 469, Volume I & II; August 1988.
- (6) Auto/Oil Air Quality Improvement Research Program; Published by: Society of Automotive Engineers, Inc.; SAE SP-920; February 1992.



*6TH International Conference
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**REMOVAL OF COPPER FROM FUEL BY IMMOBILIZED
HETEROGENOUS CHELATING AGENTS**

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ABSTRACT

As a potential alternative to the addition of metal deactivating additives to jet fuels, the removal of dissolved copper by passing fuel over a solid surface functionalized with an optimized chelant structure has been investigated. This approach allows for the use of optimized insoluble chelants with very high binding constants. Since nothing is added to the fuel, the impact of the resulting complex on fuel thermal stability is not a concern. A direct benefit of solid-supported heterogeneous chelant technology is that copper removal is achieved without introducing surface-modifying soluble chelants which can affect the outcome of thermal stability qualification tests that employ heated metal surfaces. Several different substrates have been functionalized with polyamine ligands. Copper extraction from JP-5 and dodecane with surfaces functionalized with a macrocyclic ligand, 1,4,7,11-tetraazacyclotetradecane, and an acyclic ligand, N-3-trimethoxysilylpropyl diethylenetriamine, are reported in this paper. Initial uses are targeted towards cleanup of contaminated fuel stores, with the ultimate goal of applying this technology to perform in-line copper removal at aircraft fueling points. The performance of these chelant systems in both static and flow tests demonstrates the potential of immobilized chelants to accomplish these goals.

INTRODUCTION

Jet fuel undergoes autoxidative degradation at elevated temperatures in the presence of oxygen. Sub-part per million levels of dissolved copper can promote this process, resulting in the formation of insoluble gums and/or sediments. Since copper bearing alloys are used in

components of fuel handling systems, there are ample opportunities for the introduction of copper into aircraft fuel. There is also evidence that dissolved copper can promote certain prerequisite chemical reactions in jet fuel during storage which enhance the autoxidation process and result in thermal degradation¹. The addition of soluble metal chelants has been the basis for present measures in counteracting the catalytic effects of dissolved copper in fuels. This approach is based upon the assumption that the copper is effectively tied up in a soluble catalytically-inactive complex. Copper catalyzes autoxidation through an electron transfer mechanism², although the influence of coordination on the redox potential of the copper atom is not explicitly known in organic media. It is been proposed³ that catalytic deactivation of the copper may be a consequence of the increased energy of activation for the change in valency. Therefore, the conversion of copper(II) disalicylidene to copper(I) disalicylidene would be unfavored, due to the difficulty of undergoing the change in geometry within the complex, thus rendering the copper catalytically inactive.

Findings from long-term high temperature turbulent rig studies^{4,5} have indicated that these metal deactivating additives are not effective under flow and temperature conditions that exist in certain regions of a typical military aircraft fuel system. Other reports have indicated that the effectiveness of a soluble copper chelant at the elevated temperatures reached in jet engines is limited by the thermal stability of the complex^{6,7}. Thus, there are many advantages to eliminating the reliance on soluble copper chelators to provide acceptable levels of thermal stability of jet fuels in the presence of copper.

The approach investigated in this study involves the removal of copper from jet fuel without otherwise changing the fuel constituency. We have examined the feasibility of immobilizing metal chelators on a solid substrate and passing fuel over the surface-modified solids to remove complexed copper from hydrocarbon liquids and jet fuel. The chelators are actually composed of three sections, the chelating group itself, a linker arm, and an attachment site for binding to a solid support. Each of these aspects can be optimized for a particular application or environment. The chelating groups we report here are polyamines, both acyclic and macrocyclic with a linker chain that varies from three to sixteen carbons long, with a variety of substrate linkages.

Polyamine chelators, particularly the macrocyclic forms, are among the strongest metal chelators known⁸. While the acyclic polyamines have an enhanced stability for complexing metal ions through the "chelator effect", azamacrocyclic molecules have additional thermodynamic stabilization attributable to the "macrocyclic effect", as first described by Cabbiness and Margerum⁹. The high metal affinity and selectivity of the polyamines make them attractive as systems for metal sensors⁹, redox systems¹¹, or for water remediation as in ionflotation collectors¹². Adsorption or chemical attachment of chelators to solid supports have been reported previously for chromatography¹³⁻¹⁵ and for removal of metal ions from aqueous waste streams¹⁶⁻²⁰.

The advantages of this approach are that the chelators are highly specific for only transition metal ions, that the copper ions are directly removed from the fuel, that no metal ions need to be exchanged for binding copper, that no chemicals need to be added to fuel, and that the copper may be recovered after treatment of the fuel. In designing this alternative cleanup method, we have tried to consider carefully both the chemistry of the process and the economics of implementing such a technology. The positive results obtained from these studies are encouraging and demonstrate the potential of this approach as a plausible alternative to present methods.

EXPERIMENTAL

Materials

Technical grade DETA -silane, N-3-trimethoxysilylpropyl diethylenetriamine was purchased from Aldrich (Milwaukee, WI). All other standard chemicals and materials were purchased from commercial chemical providers including Aldrich, Fluka, Pierce, Sigma, Polychem and Kodak and were used as obtained without further purification, unless otherwise stated.

A copper-bearing JP-5 fuel used in flow testing was prepared by introducing copper by long-term immersion with copper plates until a copper concentration of 368 ppb was reached. Static tests were conducted with n-dodecane and a copper-free JP-5 doped with 20 ppm copper from copper(II) ethylacetoacetate (Eastman).

Procedures

Static exposure tests. In a typical procedure, a sample of the functionalized polymer was combined with the test solution, either dodecane or JP-5 that was doped with up to 20 ppm copper from the addition of copper acetoacetate. After stirring for a predetermined time, the liquid was recovered by filtration through glass wool and a 0.45 micron microporous nylon filter. The resulting filtrate was analyzed for copper content by graphite furnace atomic absorption.

Dynamic flow tests:

Aqueous tests: Initial flow tests were conducted in the laboratory using 250mm x 10mm tempered borosilicate Omnifit glass LC columns (Supelco, Bellefont, PA) packed 8.5g of the modified or unmodified silica. A variable peristaltic pump was calibrated for each mesh silica and used to pass known copper solutions through packed modified-silica gel. Eluates were taken periodically and copper concentrations measured using the above described method.

JP-5 tests: An Isco model 2350 HPLC pump was used to pass the copper-bearing JP-5 fuel through polyethylene drying tubes packed with approximately 30g of silica or modified silica at a flow rate of 20 ml/min at typically 20 - 30 psi. Samples were taken periodically and analyzed for copper content by graphite furnace atomic absorption.

Large scale JP-5 flow tests: Approximately 30 g of modified silica was packed into drying tubes closed off at each end by glass wool. JP-5 was pumped at the rate of 10 mL/min for 8 hours. Mixtures of modified silica used were: 70-230 mesh DETA-silica, 70-230 mesh DETA-silica/30-60 mesh DETA-silica (1:1), 70-230 mesh DETA-silica/30-60 mesh DETA-silica (1:1), aminopropylsilica, aminopropylsilica/70-230 mesh DETA-silica (1:1), aminopropylsilica/30-60 mesh DETA-silica (1:1) and 70-230 mesh unmodified silica.

Determination of binding capacities for DETA-modified silica in aqueous media. The general procedure was to mix a sample of DETA-modified silica, typically 0.5 g, with 15 mL of 3000 ppm Cu(II) and let stand overnight. The supernatant was then assayed for copper content spectrophotometrically as described below.

Spectrophotometric copper assay method

Aqueous media. The bathocuproine disulfonic acid (disodium salt) complex with Cu(I) is a yellow colored, water-soluble complex used for one-phase aqueous assays of copper. This method gives very sensitive and reliable results. Standard curves had least-squares regression factors of up to 0.999+ for the range of 40 ppb to 5 ppm Cu(I). The assays were verified by comparison with ICP-furnace.

Hydroxylamine hydrochloride was used as a reductant for Cu(II). Since the pH affects the stability of Cu(I)-bathocuproine complex, ammonium acetate was used as a buffer. Absorption measurements were obtained at 480nm. A typical procedure for 10 mL samples was as follows: a 1 ml sample was transferred into a test tube and the following aliquots added sequentially to the tube, mixing well after each addition: 1 ml 10% hydroxylamine hydrochloride solution, 1 ml 0.1 % bathocuproine solution, 1 ml 10 % ammonium acetate solution, and 6 ml of water for a 1:10 dilution. The solution was mixed and the absorption measured at 480-483 nm. Reagent blanks were prepared by substituting 1 ml water for the sample.

The sample results were compared to a linear standard curve. From the difference between the initial and measured Cu(II) concentrations, the total amount of copper absorbed and the mass of copper absorbed per gram of modified silica were obtained.

Organic media. A bathocuproine solution consisting of 225 ppm bathocuproine in ethanol and a 10% hydroxylamine solution were mixed in a 7:3 ratio, respectively. To a 16 ml portion of the copper-bearing hydrocarbon sample, 1 ml of the bathocuproine solution was added and mixed vigorously for 5-10 min. After standing for 24 h at room temperature, absorbance was measured at 475 nm. Copper content was calculated by comparison with a standard curve.

Aqueous formation constants. Formation constants in aqueous media were obtained²¹ by titration and analysis of the titration data with HYPERQUAD²², a suite of programs designed for analyzing chemical equilibria. Briefly, 1.0 mM of the fully protonated chelator was titrated with sodium hydroxide to obtain metal-free titration curves. These curves were analyzed by HYPERQUAD to obtain the protonation constants for the polyamines. Subsequent titration of

the chelator-metal complex with sodium hydroxide and application of HYPERQUAD yielded the formation constants.

RESULTS AND DISCUSSION

Copper extraction from JP-5 and a model fuel with surfaces functionalized with a macrocyclic ligand, 1,4,7,11-tetraazacyclotetradecane (cyclam) and an acyclic ligand, N-3-trimethoxysilylpropyl diethylenetriamine (DETA-silica) were examined. The structures of these compounds are shown in Figure 1. They were attached to a silica via a hydrocarbon bridging group, as shown schematically in Figure 2 for the acyclic ligand, DETA. The bonding model shown is one of several possible mechanisms where the vacant coordination site could be filled with an ion or an organic fuel constituent. If the DETA density were sufficient, participation by adjacent DETA molecules is also feasible.

Cyclic Polyamines (cyclam)

The results of the slurry (static) tests with different cyclam-attached materials are shown in Table 1. Tests were carried out with n-dodecane and JP-5 doped with copper from copper ethylacetoacetate. In tests with soluble cyclam which was not immobilized to a solid substrate, significant amounts of copper remained after filtering, particularly in the JP-5. This is probably due to the inability of filtration to remove all the unimmobilized chelator-metal complex from the liquid

All the materials modified with cyclam performed well. The agarose control appeared to be efficient in adsorbing copper from dodecane, but was not as effective in JP-5, where the copper was more tightly bound. One of the variables examined was the length of the hydrocarbon linker arm that connects the ligand molecule to the surface. This was examined by correlating the copper removal efficiency with the length of the linker arm. The link has to be sufficiently long to provide adequate exposure of the chelant to the soluble copper in the fuel, but not so long as to impair the mechanical stability of the linkage. The length of the linker arm, as varied in the acrylate polymer series, did not appear to make a great deal of difference within the $n = 2$ to 8 range. However, the presence of a long linker versus the absence of any linker arm may account for much of the differences observed in the results between cyclam and cyclam-C₁₆.

Generally, the silanized silica showed the lowest levels of copper, although the agarose-coupled material was comparable, especially when one takes into consideration that there was a higher ratio of doped copper to agarose for the 0.1 g samples of agarose.

The survey results from the slurry tests demonstrated the feasibility of this approach for removal of copper from non-aqueous liquids. It is interesting to note that significant amounts of copper were still left in JP-5 fuel after treatment with free hexadecylcyclam, where less copper was left in solution when treated with free underivatized cyclam. This can be attributed to the higher affinity of cyclam, than its modified analogs, for copper²¹. However, given that several of the immobilized cyclam results are even lower, another likely factor may be the greater degree of solubilization of the free alkylated cyclam, with its long hydrophobic chain, and the consequent difficulty of removing the soluble complex by filtration.

Acyclic Polyamines

Subsequent studies have been focused on the acyclic ligands, triethylenetetramine (TETA), diethylenetriamine (DETA), and silica modified with DETA. The structures of the acyclic ligands are shown in Figure 1. There are several advantages to the use of these acyclic polyamines: TETA and DETA have very high formation constants for Cu(II), both chemicals were available commercially in large quantities, and, in particular, trimethoxysilylpropyl-DETA, which is the chelator with a trimethoxypropyl linker arm, is also available commercially. The last point is important from a cost-effectiveness point of view because it decreases the number of steps in the immobilization chemistry.

We first sought to ascertain whether derivatization at the amine nitrogen atoms of the DETA and TETA with an alkyl group would significantly reduce the required high stability of their respective copper complexes. The tests were conducted in aqueous solutions by titration as described above. The results from Table 2 show that while both DETA and TETA have significantly lower copper formation constants than cyclam, although the mono-alkylated forms of cyclam (HDC), DETA (HDDETA), and TETA (HDTETA) were much closer together in their binding constants. Since it is the alkylated analogs of the chelators that are relevant, we felt that the DETA and TETA would make good alternates to cyclam. The selectivity of HDDETA for copper versus that of Mg(II) or Ca(II) is also included in Table 2. While the Ca(II) value is

surprisingly high, it is still four orders of magnitude lower than that for Cu(II). The affinity of HDDETA for Mg(II) is negligible. As far as we are aware, these are the first measurements for the formation constants of Mg(II) and Ca(II) with a polyamine.

Static Tests

Trimethoxysilylpropyl-DETA was chemically immobilized to silica as described above. A slurry test in tetradecane, similar to the cyclam tests, was performed for the modified DETA-silica, varying the amount of time for mixing the slurry and standing time (Table 3). As was observed with the cyclam, decolorization of the copper ethylacetoacetate in the tetradecane occurred almost immediately. This was confirmed by undetectable amounts of copper even after only 150 seconds of exposure. These results indicated that DETA-modified silica was a suitable candidate for further flow studies.

Aqueous Flow Tests

Initially, 30-60 mesh silica was used to maximize the flow rate and keep the backpressure as low as possible, but we found that modified 70-230 mesh silica performed much more effectively in removing copper. Therefore, most of the subsequent flow tests were done using the finer mesh silica. We have also examined other parameters, such as choice of solvent, silane to silica ratio, baking time, temperature, and other factors to optimize for the capacity of the modified materials. For the flow tests reported here, we used DETA-silica with a capacity of 50 mg Cu/g modified silica.

Flow tests were done with aqueous copper solutions and with copper-bearing JP-5. The aqueous flow rates were kept between 4-5 ml/min through tempered borosilicate Omnifit glass LC columns packed with approximately 8.5 g modified DETA-silica. Figure 3a shows the breakthrough point at 590 ml for a 527 ppm Cu solution corresponding to a capacity under flow of 36 mg Cu/g of modified silica. A test performed with a 1:1 mixture of DETA-silica and aminopropyl-silica (Figure 3b) showed similar results: 580 mL breakthrough with a 520 ppm Cu solution, indicating a flow capacity of 36 mg Cu/g of modified silica.

The column flow tests were performed using aqueous 500 ppm CuSO₄ solutions. The high copper concentration was chosen to keep the volume of solution down to a reasonable

amount. At this concentration, one could see a deep blue band move down the column as the DETA-silica became saturated with copper ions. The column capacity for the 70-230 mesh modified silica was lower than the slurry capacity due to the more limited contact time of the solution with the silica.

JP-5 Flow Tests

Flow tests were conducted with the JP-5, containing initially 368 ppb copper, over DETA and aminopropyl chelants on 30-60, 70-230 mesh silica at 10 ml/min for 8 hours. The copper contents of the effluents, shown in Table 4, illustrate the loss in column efficiency when the larger 30-60 mesh silica was used. By mixing equal parts of the two mesh sizes, the copper content went from 0.1 to 1.3 ppb with DETA. The results also show that the aminopropyl silica was generally not as effective as DETA and this difference was also larger when the 30-60 mesh silica substrate was used. Moreover, most of the column efficiency of the aminopropyl silica columns was lost after allowing to sit in contact with the fuel for two days; whereas the DETA surfaces retained their copper specificity.

Thermal Stability Testing

The benefits of copper removal on the quality of the JP-5 test fuel were demonstrated by evaluating the thermal stability of the effluent after passing through the modified silica columns. This fuel had contained soluble copper for approximately nine months and at the time of the test contained 317 ppb copper. The fuel was passed through column containing the 70-230 mesh DETA-silica and unmodified silica gel. A total of four liters of fuel was passed through each column and each liter of sample was collected and tested for thermal stability by the Gravimetric JFTOT apparatus, described elsewhere²³, at a flow rate of 3 ml/min at 260°C (500°F) for 2.5 hours. The fuel was passed through at a rate of 20 ml/min, with each column containing approximately 30 grams of the silica or DETA-silica. The results are shown in Table 5, for the filterable, adherant and total insoluble products for each fraction of fuel that passed thorough the column. From Table 5 the benefit of DETA-silica treatment of this fuel is clearly shown, with a decrease from an initial total insoluble content of 3.4 mg/L in the untreated copper-doped fuel to less than 1 mg/L. While initial reductions in thermal oxidation products were obtained with the

unmodified silica, stability began to increase as the copper passed through the column when the capacity was exceeded. It is interesting that, although there were undetectable levels of copper in all fuel samples after passing through the DETA-SiO₂ column, higher amounts of insolubles were formed from the first 2 liters of fuel. Comparison with the thermal products formed in the effluent from the unmodified silica column suggests that this is not a consequence of interactions with underivatized silica surface sites. This will be further investigated as we continue to characterize the relationship of ligand surface density and column efficiency.

CONCLUSIONS

We have studied the potential of polyamines chemically immobilized on solid supports to remove copper from both aqueous and non-aqueous solutions, particularly from jet fuel. In the process, we have examined a number of chelator-modified materials for their ability to bind copper in solution and found that they were all effective, to varying degrees, in extracting the soluble copper. While cyclam showed great promise, the high cost of the starting materials required that we focus on DETA, a more cost-effective acyclic polyamine. We found the DETA-silica system to be suitable for adsorbing copper from jet fuel, potentially at just pennies per gallon. It is envisioned that these types of functionalized surfaces will be employed as column packings.

There are still a number of remaining issues to be addressed. Underivatized silica will remove polar constituents, including stabilizing additives, along with natural and added lubricity enhancers from jet fuel. To minimize the contact of fuel with silica sites, synthetic procedures will be investigated to maximize the density of chelator linkages on the surface. It may also be possible to chemically block, or end-cap remaining free silica surface sites. A possible added advantage to end-capping would be the freeing up of some amines that could form hydrogen bonds to silanol functionalities on the surface²⁴. While silica has some obvious advantages as a solid support, a polymerized chelator may have an edge in other areas. In order to be practical for field use, flow rates on the order of tens of gallons per minute must be achieved. Efforts are currently underway to determine how to increase the flowrate through the relatively small-sized 70-230 mesh silica. In order to reach the flow rates required to utilize such a column packing for field

use, a balance must be reached between column efficiency and throughput. However, these are considered engineering issues and beyond the scope of this preliminary study.

In terms of cost-effectiveness of this approach, the material cost of the modified silica is approximately \$0.09 per gram of modified silica, with the most expensive material being the silane. If one were to use the breakthrough data at 500 ppm Cu(II) to extrapolate the cost for removing 1000 ppb of copper from jet fuel, it is estimated that the cost would be about \$0.01 per gallon, depending on the exact flowrate.

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REFERENCES

- (1) Pande, S. G. and Hardy, D. R. *Energy & Fuels*, **1997**, 11, 1019.
- (2) Scott, G. "Atmospheric Oxidation and Antioxidants"; Elsevier Publishing Company, Amsterdam, 1965; p.179-80.
- (3) Chalk, A. J. and Smith, J. F. *Nature*, **174**, **1954**, 802.
- (4) Kendall, D. R.; Houlbrook, et al., Presented at the 1987 Tokyo International Gas Turbine Congress, October 26-31, Tokyo, Japan, 1987.
- (5) Moses, C. A. Southwest Research Institute report No. 281, contract DAAK70-92-C-0059, August 1992.
- (6) Morris, R. E. and N. H. Turner. *Fuel and Science Technology Int.* **1990** 8(4), 327-350.
- (7) Morris, R. E.; Hasan, M. T.; et al., submitted for publication in *Energy & Fuels*.
- (8) Kodama, M. and E. Kimura. *J. Chem Soc. Dalton* **1978**, 1081-85.
- (9) Cabiness, D. K. and D. W. Margerum. *J. Am. Chem. Soc.* **1969**, 91, 6540-1.
- (10) Singh, A., L.-I. Tsao, et al. *Langmuir* **1992**, 8, 1570-7.
- (11) De Santis, G., M. Di Casa, et al. *J. Am. Chem. Soc.* **1989**, 111, 2422-7.
- (12) Yamada, K., Y. Koide, et al.. *Bull. Chem Soc. Jpn.* **1989**, 62, 2867-74.
- (13) Zhou, X. C., C. Y. Wu, et al. *J. Chromatography* **1994**, 662, 203-18.
- (14) Lamb, J. D. and R. G. Smith *J. Chromatography* **1991**, 546, 73-88.
- (15) Blain, S., P. Appriou, et al. *Analytica Chim. Acta* **1990**, 232, 331-6.
- (16) Izatt, R. M., J. S. Bradshaw, et al. *Pure & Appl. Chem.* **1995**, 67(7), 1069-74.
- (17) Tuncay, M., S. D. Christian, et al.. *Langmuir* **1994**, 10, 4688-92.
- (18) Izatt, R. M., R. L. Bruening, et al.. *Pure & Appl. Chem.* **1990**, 62(6), 1115-18.
- (19) Schlapfer, C. W. U.S Patent 5 102 640, 1992.
- (20) Macedo, P. B. and A. Barkatt U.S. Patent 4 659 512, 1987.

- (21) Puranik, D. B., A. N. Singh, et al. *J. Coord. Chemistry*, in press.
- (22) P.Gans; A.Vacca and A.Sabatini, *J.Chem.Soc., Dalton Trans.*, 1196, 1985.
- (23) Beal, E. J.; Hardy, D. R.; Burnett, J. C. *Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels*, Orlando, FL, Nov 1991, pp 245-59. *Aviation Fuel: Thermal Stability Requirements*, ASTM STP 1138; Kirklin, P. W. and David, P., Eds.; American Society for Testing and Materials, Philadelphia, PA, 1992, pp. 138 - 50.
- (24) Kahn, F. J. *Appl. Phys. Lett.* 1973, 22, 386-8.

Table 1. Summary of Slurry Tests with Cyclam-Modified Substrates

Chelant	Substrate ¹	Chain Length ²	Chelant derivative, grams ³	Dodecane Cu, ppb ⁴	JP-5 Cu, ppb ⁴
CYCLAM	polystyrene	16	--	8	--
CYCLAM	[none]	[none]	--	1	52
CYCLAM	[none]	16	--	16	319
[none]	Epoxy-activated aragose	[none]	0.2	1	45
CYCLAM	Epoxy-activated aragose	16	0.1	0	6
CYCLAM	Epoxy-activated aragose	16	0.1	0	17
CYCLAM	Epoxy-activated aragose	16	0.2	0	5
CYCLAM	Silica	8	0.4	0	1
CYCLAM	Silica	8	0.4	0	0
CYCLAM	Silica	8	0.4	0	1
CYCLAM	methacrylate polymer	2	0.8	2	--
CYCLAM	methacrylate polymer	8	0.8	2	9
CYCLAM	methacrylate polymer	6	1.1	3	6

¹All initial copper concentrations were 20 ppm and volumes of dodecane and JP-5 were 5.0g, except for aragose samples which used 3.5g. ² Length of hydrocarbon chelant-substrate bridging group in number of methylene groups. ³ Grams of immobilized chelant treated with 20 ppm copper solutions. ⁴ Typical errors are ± 5 ppb.

Table 2. Comparison of Formation Constants for Cyclic and Acyclic Chelators in Aqueous Media

Chleator	Log $K_{Cu(II)}$	Log $K_{Mg(II)}$	Log $K_{Ca(II)}$
Cyclam*	27.0		
TETA	20.0		
DETA	16.0		
HDC**	20.0		
HDTETA	16.0		
HDDETA	14.0	3.0	10.0

TETA=triethylenetetramine, DETA=diethylenetriamine, HDC=hexadecylcyclam
HDTETA=hexadecyl triethylenetetramine, HDDETA=hexadecyldiethylenetriamine *Cyclam value from Bianchi^x, *et al.* (1991). **HDC value from Puranik, *et al.*²¹

Table 3. Copper Content of 10 ml Solutions of Copper in Tetradecane after Static Exposure to 2 g DETA-Silica

Mixing time	Standing time	Initial [Cu] = 5 ppm	Initial [Cu] = 20 ppm
30 s	2 min	0 ± 2 ppb	0 ± 2ppb
5 min	10 min	0 ± 2ppb	0 ± 2ppb
5 h	overnight	0 ± 2ppb	0 ± 2ppb

Control (neat tetradecane)= 1 ± 2 ppb. Samples filtered through Magna nylon filter.

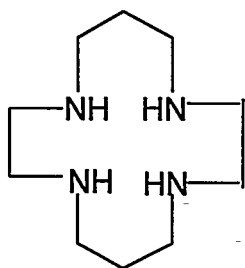
Table 4. Copper Remaining in JP-5 after Passing Through Columns Packed with Various Modified Silica Surfaces*.

Liters	F1	F2	F3	F4	F5	F6
0.0	1	1	2	2	6	3
0.6	1	1	2	3	8	41
1.2	1	1	2	3	9	183
1.8	1	1	1	3	11	229
2.4	1	1	2	3	11	325
3.0	0	2	1	3	12	283
3.6	0	2	1	3	12	256
4.2	0	2	1	3	16	238
4.8	0	2	1	3	18	234
After 48 hour soak						
10.8	0	0	60	129	--	--
20.4	0	2	233	137	--	--
30.0	0	17	258	140	--	--
36.0	0	15	271	129	--	--

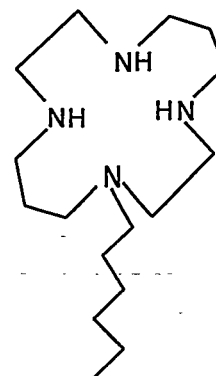
*Flow rate was 10 ml/min for 8 hours, total volume = 4.8 L. Initial [Cu] = 368 ppb.
 F1 = 70-230 mesh DETA-silica; F2 = (1:1) 70-230 + 30-60 mesh DETA-silica;
 F3 = aminopropyl silane; F4 = (1:1) 70-230 mesh DETA-silica + aminopropyl silane;
 F5 = (1:1) 30-60 mesh DETA-silica + aminopropyl silane; F7 = unmodified silica.

Table 5. Insoluble Products Formed in GravJFTOT Testing of JP-5 after Passing Through Columns Packed with DETA-Modified and Unmodified Silica

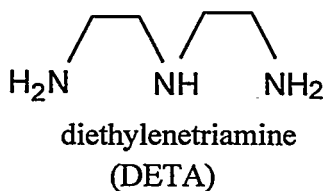
Treatment	Volume	Cu, ppb	Insoluble Products, mg/L		
			Filterable	Gum	Total
before copper exposure	--	<2	0.26	0.01	0.27
after copper exposure	--	177	3.39		3.41
SiO ₂	0 - 1 liters	2	0.15	0.55	0.70
SiO ₂	1 - 2 liters	57	0.97	<0.01	0.97
SiO ₂	2 - 3 liters	26	2.62	0.02	2.64
SiO ₂	3 - 4 liters	20	2.51	<0.01	2.51
DETA-SiO ₂	0 - 1 liters	<2	1.94	0.19	2.13
DETA-SiO ₂	1 - 2 liters	<2	1.16	0.21	1.37
DETA-SiO ₂	2 - 3 liters	<2	0.64	0.23	0.87
DETA-SiO ₂	3 - 4 liters	<2	0.87	0.12	0.99



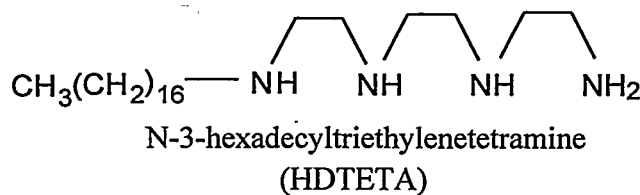
1,4,7,11-tetraazacyclotetradecane
(CYCLAM)



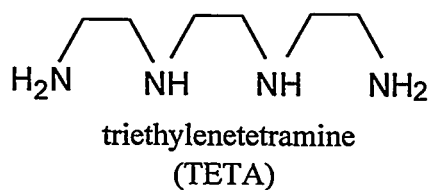
N-1-hexyl-1,4,7,11-tetraazacyclotetradecane



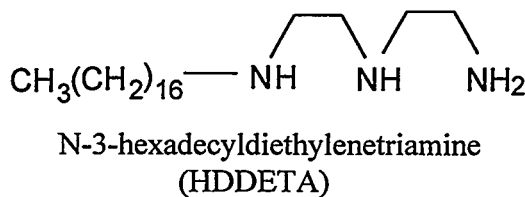
diethylenetriamine
(DETA)



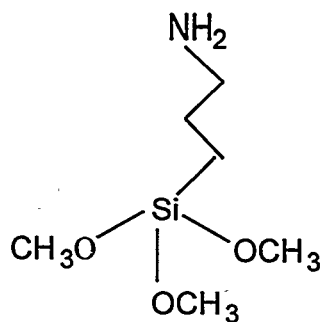
N-3-hexadecyltriethylenetetramine
(HDTETA)



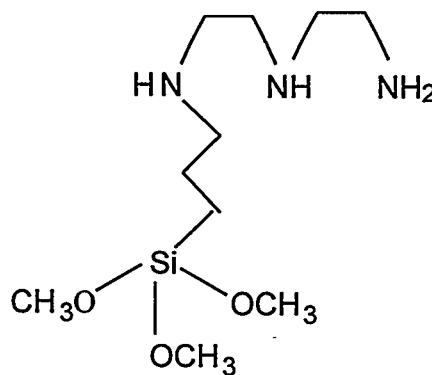
triethylenetetramine
(TETA)



N-3-hexadecyldiethylenetriamine
(HDDETA)



N-trimethoxysilylpropylamine
(aminopropyl silica)



N-3-trimethoxysilylpropyl diethylenetriamine
(DETA-silane)

Figure 1. Cyclic and acyclic chelants used in this study.

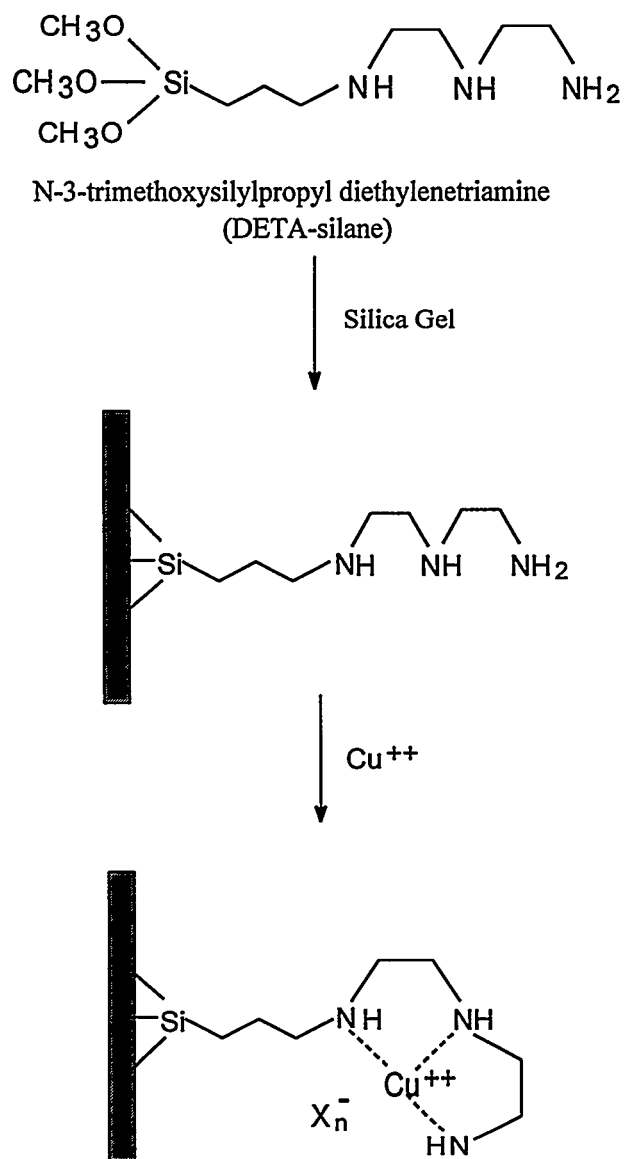


Figure 2. Schematic representation of the DETA-silica surface. X = a charged species, which forms an ion-pair or an organic species which can coordinate with the copper.

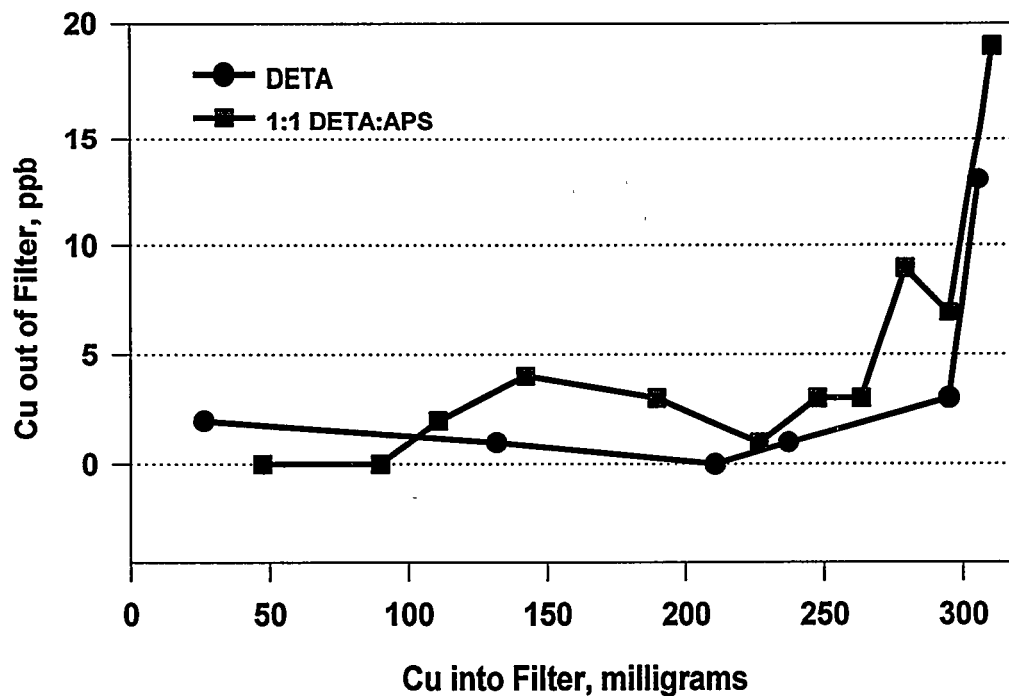


Figure 3. Copper breakthrough in effluent from 4 - 5 ml/min flow of aqueous 500 ppm CuSO_4 through 250 mm x 10 mm columns packed with modified silica. Breakthrough patterns shown for 70-230 mesh DETA-silica and a 1:1 mixture of 70-230 mesh DETA-silica and aminopropyl-silica.

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**EFFECTIVENESS OF MDA ON JET FUEL THERMAL STABILITY AS DETERMINED
USING THE GRAVIMETRIC JFTOT: *EFFECTS OF EXTENDED DURATION
TESTING AND TIME OF ADDITION OF MDA***

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Abstract

Two studies were conducted on the effects of the metal deactivator, N,N'-disalicylidene-1,2-propane diamine (MDA) on jet fuel thermal stability. Study 1 focused on the effects of MDA on extended duration thermal stability testings ranging from 120 to 152 hours. The test fuel was a Jet A, and the effects of MDA were examined with and without the addition of the antioxidant, BHT (2,6-di-*tert*-butyl-4-methyl-phenol) as well as with and without added copper. For study 2, the thermal stability test duration was 2.5 hours, and the effect of time of addition of MDA, which was also investigated in study 1, was further examined in a test matrix that comprised two JP-5 fuels, two sources of copper and three concentrations of MDA. Thermal stability was determined using the gravimetric JFTOT. The results of the extended duration testings indicate that even at the relatively high MDA concentrations examined (15 and 35 ppm), MDA exhibited a beneficial effect in the non copper doped commercial (Jet A) and Navy type fuel (Jet A +BHT). The results of the time of MDA addition studies indicate that early addition of MDA is more effective than late addition for copper-contaminated stored jet fuels.

Introduction

The beneficial effects of the metal deactivator additive, N,N'-disalicylidene-1,2-propane diamine, commonly known as MDA, in counteracting the detrimental effects of copper on fuel thermal stability are well recognized.¹ However, on extended duration thermal stability tests of a non copper doped jet A-1 fuel, MDA was interpreted as having no effect after 30 hrs,² and, for a non copper doped JP-5 fuel, as having a potentially detrimental effect after 120 hrs.³ These findings are based on injector feed-arm rig (IFAR) studies,² and on flow reduction studies of two atomizers,³ respectively.

Because of the possible impact of these results on the use of MDA - which is both an optional military specification (MIL-T-5624) thermal stability additive, and an optional commercial fuel additive (ASTM D1655) - the effect of MDA on extended duration testing was reinvestigated (study 1). In the re-investigative study, we revised the protocol used in the initial extended duration

testings.^{2,3} These revisions, which include storage of the test fuels prior to determining their thermal stabilities, the time of addition of MDA, and its concentration are subsequently described.

Revision 1 involved storing the test fuels in the presence of the test additive(s) prior to determining their thermal stabilities. The objective of this revision was to decrease the neat fuels' inherent thermal stabilities, such that the effects of the test additives could be better differentiated. This approach is based on the results of an earlier study,⁴ which indicated that precursors that lead to thermal instability are predominantly formed during long term storage of the fuel in the presence of copper, and not during the thermal stability test itself.

Revision 2 involved the early addition of MDA and hence the use of a freshly refined jet fuel. This adoption is also based on the results obtained from the earlier study⁴ wherein we found that the early addition of MDA to be especially important for fuels that are stored in the presence of copper. The early addition of MDA is consistent with Pedersen's recommendation⁵ for gasolines, viz., MDA should be added at the earliest possible moment. The late addition of MDA, i.e., after storage, was examined to determine the effect of time of addition of MDA to non copper doped fuels.

Revision 3 was the addition of MDA at higher concentrations (~35 ppm) compared to the military specification⁶ level of 5.8 mg /L. High concentrations of MDA were used for the following reasons: (a) To compensate for possible depletion on the long term storage conducted, e.g., losses of MDA may occur due to adherence on the walls of the samples' containers. And (b), to ensure that the amounts of MDA added, will be in excess of the concentration of solubilized copper in the copper dissolution studies.

Experimental Section

Test Matrices for studies 1 and 2. Common to the test matrices for studies 1 and 2, are the following: (a) the use of jet fuels that were freshly refined, where the term freshly refined refers to an interim period of 0-4 weeks after refining; (b) the early addition of the test additives, i.e., prior to storage unless otherwise stated; (c) the addition of MDA at relatively high concentrations ranging from 15-40 ppm: 15 ppm were used only for those studies involving the late addition of MDA, i.e., after storage, since compensation for possible losses due to depletion on storage was not relevant; and (d) storage of the test fuels at room temperature conditions for a period of approximately 13-16 months prior to determining their thermal stabilities. In study 1, storage of the additized test fuels extended over an interim period of a few months due to the length of time taken to complete the extended testings of the neat and doped fuels in the test matrix. The overall test matrices for both studies, 1 and 2 are summarized in Table 1.

Gravimetric JFTOT. Fuel thermal stability was determined using the gravimetric JFTOT. The method is based on the weight of the total thermal deposits (mg/L) formed when the filtered fuel flowing at 3 mL/min, under a back pressure of 500 psi, is heated at 260°C for 2.5 hours. This was the test duration used in study 2 (see below for the extended duration testing). Further details of the method are described elsewhere.^{4,7}

Extended duration testing using the gravimetric JFTOT (study 1). For the extended duration testings, at the start of each gravimetric JFTOT test, and after each subsequent start-up, we employed a warm-up period of approximately 15 minutes during which the effluent was not collected. Extended gravimetric JFTOT testing was conducted for a duration period of 120 hours for the neat fuel, which was the first fuel examined. Subsequent testings were extended to a maximum of 152 hours, in the effort to monitor MDA's performance on further increasing the test duration (see Figures 2-5). To monitor the trend in deposit formation, with time, for each test fuel after known time intervals, the thermal deposits formed on the strip, and the filterables collected in the effluent were determined. To simulate continuity of the test, the same strip was reused until the test duration was completed. A new/clean strip was used per test fuel.

Copper analyses (studies 1 and 2). The concentrations of fuel solubilized copper from the copper doped/storage studies, with and without MDA present, were determined at periodic intervals (see Figure 1). Copper analyses were performed using graphite furnace atomic absorption spectroscopy at the Naval Air Warfare Center, Aircraft Division, in Trenton, NJ.

Results and Discussion

Study 1. Extended Duration Thermal Stability of a Stored Jet A Fuel: With and without the Presence of the Test Additives

Data presentation. To better understand the effects of the additives on increasing test duration, the cumulated strip and filterable deposits formed, in mg/L (i.e., total weight of deposits ÷ total volume of fuel used), were plotted versus the test duration (see Figures 2 and 3, respectively). As shown in these plots, after approximately 96 hours test duration, the rate of thermal deposition appears to level off for all the tests conducted, indicating a constant rate of deposit formation. Consequently, the test durations, including the 120 hours minimum, were more than adequate to study the effects of the additives on extended testings. From a maintenance perspective, the weights in milligrams of the cumulated strip and filterable deposits were also plotted versus the test duration (Figures 4 and 5, respectively).

General evaluation. As illustrated in the thermal deposit profiles versus time, for plots based either on mg/L (Figures 2 and 3), or from a maintenance standpoint, on milligrams (Figures 4 and 5), except for "BHT alone", most of the remaining test additives/additive combinations decreased both the strip and filterable thermal deposits of the reference fuel (see below). The extent of the decrease varied with the test additive/additive combination. Furthermore, the consistency in the trend of the extended duration test profiles, i.e., an apparent lack of scatter in the data (Figures 2-5), suggests that the apparent decreases are likely real. Moreover, what is significant is that MDA was neither detrimental nor innocuous in any of the cases examined. Instead, MDA was found to be beneficial.

Evaluation of the test additives by ranking. The relative effectiveness of the various test additives, individual and combined - on extended duration thermal stability testings - were evaluated by ranking their cumulated total thermal deposits formed for similar test durations (Table 3). Listed in order of decreasing fuel thermal stability, from best to worst, the test additives are ranked as follows:

1. Early addition of MDA alone \approx BHT/late addition of MDA
2. BHT/early addition of MDA
3. BHT/MDA \sim 2500ppb Cu \approx BHT alone \approx None: neat fuel

Note: Based on the repeatability of the gravimetric JFTOT ($\pm 15\%$), we have ranked the neat fuel similar to that of BHT/MDA/Cu and BHT alone.

Based on the extended gravimetric JFTOT tests conducted on the stored doped test fuels examined, the above rankings indicate the following: For the *non copper doped* Jet A fuel, the two most effective additive/additive combination were: (1) the early addition of MDA alone, and (2) the combination of BHT/late addition of MDA. Both these additive/additive combination further decreased the thermal deposits of an inherently stable non copper doped Jet A fuel by approximately 60-70% (Table 3). Furthermore, the similarity in their effectiveness indicates that the observed efficacy is attributable to MDA. This premise is supported by the lesser performance of BHT alone (see Figures 2-5).

Pertinent to the above discussion are the results of a preliminary investigation (Table 4) that was also conducted on the thermal stabilities of the same Jet A fuel, but which was copper doped and stored using accelerated conditions that simulate ambient storage for approximately one year (*viz.*, 90°C/50 psig air for 48 hrs). Accelerated storage was conducted in the presence of 400 ppb copper from CuEA in conjunction with each of the following additive/additive combination, *viz.*, BHT, MDA, and BHT/MDA. The thermal stability test duration was 2.5 hours. As shown in Table 4, MDA appears to be the operative additive in significantly decreasing the thermal deposits of the copper/BHT doped stored fuel. However, these findings need to be confirmed in future studies using an ambient mode of storage.

The effects of the remaining additives are subsequently addressed with respect to the roles of MDA and the effects of BHT. However, the effect of early versus late addition of MDA is discussed later in conjunction with the results from study 2, because of the common link between the two studies.

Roles of MDA.

Copper doped fuel/chelation mechanism. On extended duration thermal stability testings, similar thermal stabilities were observed between the Jet A fuel that was stored in the joint presence of BHT, MDA, and copper (approximately 4000 ppb measured after 13 months storage), and that stored in the presence of BHT alone. Since MDA was present in an excess molar ratio relative to copper (based on a copper concentration of 4000 ppb and 35 ppm added MDA, the mole ratio of MDA:Cu is 1.96:1), these results suggest that MDA was effective in chelating the copper such that the net result was similar to that of BHT alone. Such an explanation is consistent with MDA's well known copper chelation mechanism,^{1,4,5,8} in the autoxidation of fuels. Note, extended duration testing of the copper-doped stored fuel, with no MDA present, would have been useful for reference purposes. This test was not done, along with other pertinent studies, because of the time constraints in conducting the extended duration tests of an already large matrix, and because the primary objective was to investigate whether MDA would be detrimental on long term testing as was reported.³

Non copper doped test fuels/alternative mechanisms of MDA. The role of MDA in increasing thermal stability is not limited to a metal chelation mechanism. Supporting this position are the results from independent studies which demonstrate the effectiveness of MDA in fuels that contain negligibly low levels of copper. Examples include the following: (a) our current findings, wherein MDA improved the thermal stability of a Jet A, and JP-5 type fuel (Jet A+BHT) by as much as 60-70% (Table 3); the copper content of the Jet A fuel was 3 ppb; (b) the substantial decrease in thermal deposits due to the addition of MDA at 5.8 ppm, in a JP-5 fuel with a copper content of <1ppb, as reported by Morris *et al.*,⁹ and (c), MDA's concentration effect identified by Clark.⁸ In the latter case, when MDA was added at 0.3 and 5.7 ppm to a Jet A-1 fuel that contained no added catalytic metals (inherent copper content was <2 ppb), relative to the neat fuel, the 5.7 ppm-MDA doped fuel was found to exhibit a fivefold benefit in the Single Tube Heat Transfer Rig across all temperatures. No improvement was observed when the MDA concentration level was 0.3 ppm.

The mechanism whereby MDA is effective in fuels that contain negligibly low levels of copper, has not been elucidated, to date. Possible suggestions include interactions in the liquid phase,¹⁰ e.g., that of an antioxidant,⁹ though this effect appears to be fuel dependent;¹¹ and surface effects,¹² such as passivation.^{8,13,14}

Effects of BHT. Of the test additives examined, BHT was the least effective and its decreased performance is particularly apparent from the extended duration test profiles of the strip deposit (see Figures 2 and 4). These results suggest that BHT is not an effective antioxidant at the 260°C test temperature. Thus, whereas BHT's hindered phenol structure serves well as an antioxidant for fuel storage stability, it may not be effective for thermal stability. In fact, Heneghan and Zabarnick's¹⁵ proposed mechanistic pathways indicate that BHT may contribute to thermal deposits. Nevertheless, it is difficult to explain why the combination of BHT/addition of MDA after storage, is more beneficial than the combination of BHT/early addition of MDA, since BHT was present in both cases. Further discussion on the effects of BHT is beyond the scope of this study.

Significance of the results of MDA addition to non copper doped fuels on extended duration testing in the gravimetric JFTOT. As discussed earlier, consistent with other findings, MDA significantly decreased the thermal deposits of a typical thermally stable non copper doped Jet A fuel, by as much as 64% (Table 3), in the extended duration tests conducted. These results are significant from the following two aspects:

(a) The beneficial effects of MDA that were obtained, even on extended duration testings, the maximum being 152 hr. Since the operating conditions in the gravimetric JFTOT are similar to the JFTOT's (ASTM D3241), our results do not support the previously held interpretation⁸ that the beneficial effects of MDA, observed in the JFTOT, is due to the JFTOT's short test duration of 2.5 hr. Specifically, the JFTOT (D3241) has been characterized as being over responsive to MDA (i.e., it supposedly gives false passes for MDA additized fuels) due to its short test duration. Furthermore, as indicated in the profiles of the test plots of the filterable deposits, which comprise the bulk of the

total deposits, based on mg/L (Figure 3), the MDA additized fuels depict either a decrease or nochange in the filterables with increasing test duration. These results are significant for they substantiate the beneficial effects of MDA observed in the JFTOT at the test temperatures employed.

(b) The applicability of MDA. This includes its future use in commercial jet fuels, where neither copper nor storage is of concern, and its ongoing use in Navy fuels at higher concentrations, where copper and storage are. The potential economic advantage in the use of MDA is well illustrated in the plots, based on milligrams, of the cumulated strip and filterable deposits, which represent the surface and bulk fuel deposits, respectively (Figures 4 and 5). The impact of such decreases in the thermal deposits of an inherently stable fuel includes decreased maintenance requirements, hence decreased downtime and, decreased maintenance costs for both commercial and Navy fuels.

Study 2. Effect of Early versus Late Addition of MDA on Jet Fuel Thermal Stability with and without the Presence of the Test Additives

Fuel solubilization of copper from 90:10 Cu-Ni alloy for two JP-5 test fuels. The solubilized copper concentrations of the Cu-Ni doped JP-5 test fuels, with and without MDA present, on long term storage are shown in Table 5. The results indicate that, in general, during the first six months of storage in the presence of six and eighteen Cu-Ni rods, the copper content of both test fuels did not increase significantly, with time. However, on extended storage (from approximately 6-12 months), the copper content did increase significantly for the TX test fuels that contained MDA, and for the LA test fuels that did *not* contain MDA. On further storage (13-16 months), the copper content of most of the test fuels exhibited some decrease. For fuels that *did not* contain MDA, copper absorption was greater in the LA fuel than in the TX fuel.

In general, copper solubilization appears to be dependent on the fuel (e.g., possibly, on the amount and type of organic acids present in the fuel), as well as on the amount of copper to which the fuel is exposed, the presence/absence of MDA, the MDA concentration when present, and the storage period. The difference in copper solubilization between the two fuels, when MDA was present focuses on possible fuel compositional differences. However, the similarity in total acid content of the two fuels (see Table 2) suggests that this parameter was not a contributing factor. Losses/decreases in the concentration of solubilized copper with time are likely due to adherence on the walls of the container as well as incorporation in the insolubles formed on storage.

Time of addition of MDA: studies 1 and 2. To facilitate the analysis of the overall results obtained from early versus late addition of MDA, the pertinent results from study 1 will be discussed jointly with those from study 2. Based on the collective results from studies 1 and 2, the time of MDA addition appears to be related to the presence/absence of copper. And, for the non copper doped fuels, which were thermally stable, on the presence/absence of an antioxidant and the test duration. The impacts of these factors on the time of addition of MDA for both non copper and copper doped fuels are discussed subsequently.

Non copper doped Jet A fuel/no antioxidant present (study 1). For fuels that do not contain an antioxidant (e.g., Jet A fuels), and provided they are storage stable, the overall extended duration test results suggest that the time of addition of MDA would not be critical. This interpretation is based on the following considerations: (a) high thermal stability effectiveness on the early addition of MDA alone; and (b) a similar effectiveness on the late addition of MDA (i.e., after storage). In the latter case, the Jet A fuel was stored in the presence of BHT, prior to the addition of MDA, but as discussed earlier, the observed beneficial effect is attributable to MDA. Also, the unchanged BHT concentration after long term ambient storage of the test fuel indicates that this fuel exhibited high storage stability. Consequently, BHT, which is used as an antioxidant for storage stability, is unnecessary for storage-stable fuels.

Non copper doped fuels/antioxidant present (studies 1 and 2). In the extended duration thermal stability study (study 1), late addition of MDA to the non copper doped Jet A fuel stored in the presence of BHT was more effective than early addition of MDA and BHT. But in study 2 (Table 6), the effect of the time of addition of MDA was not definitive for the non copper doped JP-5 fuels. This evaluation is based on the rationale that large percentage decreases/increases of small amount of deposits are not meaningful. Nonetheless, the disparity in the results between the two studies on the time of MDA addition may be related to the short test duration of study 2 *in conjunction with* the high thermal stabilities of the non copper doped JP-5 test fuels. Consequently, from a practical standpoint, based on the extended duration test results, for *non copper doped fuels that contain a hindered phenol antioxidant*, late addition of MDA appears more beneficial than early addition.

Copper doped fuels (study 2 only). For the TX and LA test fuels that were doped with copper either from CuEA or 90:10 Cu-Ni alloy, in general, the *early* addition of MDA was *consistently more* effective than the addition of MDA after storage in decreasing the total thermal deposits. Because of the inherent thermal stabilities of both the TX and LA fuels, the beneficial effect of early addition of MDA was generally not dramatic. A noted exception, however, was the 98% decrease in total thermal deposits (i.e., from 21.1 to 0.5 mg/L, see Table 6, cf., tests #14 vs #16) on *early* MDA addition to the TX fuel that was doped at an initial concentration of 2000 ppb copper from CuEA. In contrast, on MDA addition *after* storage, a small increase or, based on the $\pm 15\%$ repeatability of the gravimetric JFTOT, no change in the total thermal deposits was obtained relative to the reference copper doped fuel (Table 6, cf., tests #14 vs #15).

Comparison of the time of addition effect versus the MDA:Cu mole ratio effect. As discussed earlier, for copper doped fuels, the beneficial effect of MDA is attributable to its chelation of copper. Consequently, a minimum 1:1 mole ratio of MDA:Cu is required. As shown in Table 6, the molar ratios of MDA:Cu were in excess in all cases. However, although the extent of the excess varied, for both TX and LA copper doped fuels, the beneficial effect of MDA is consistently attributable to its early time of addition rather than to the extent of the mole ratio excess of MDA:Cu. Examples, include all the TX fuels' tests for which the MDA:Cu mole ratios were significantly higher for MDA addition after storage versus its addition before storage. For the LA fuel, in certain cases, although the MDA:Cu mole ratios were lower for MDA addition after storage versus its addition before storage (e.g., see Table 6: tests# 9 and 10, also #12 and 13), in other cases the corresponding mole ratios were fairly similar (Table 6: tests #6 and 7, also #15 and 16).

Significance of the results on the time of MDA addition to copper containing JP-5 fuels. The improved thermal stabilities on early versus late addition of MDA to copper doped JP-5 fuels further support our premise^{4,16} that for copper containing fuels, the precursors that lead to thermal deposits are formed primarily during long term ambient storage; i.e., the copper promoted/catalyzed autoxidation reactions, whence the precursors are formed, occur primarily during storage. Thus, on *early* MDA addition such reactions are arrested due to copper chelation, thereby subsequently effecting improved thermal stabilities. These results are also particularly meaningful, since in the current investigations, storage was conducted using field conditions, viz., room temperature storage in the presence of 90:10 Cu-Ni alloy, whereas in our original study,⁴ storage was conducted using laboratory test conditions, viz., accelerated storage in the presence of CuEA.

Impact of the Results Obtained on Traditionally Held Viewpoints

Areas of concerns that have in the past diminished/discounted the merits of MDA include: (a) increased copper solubilization in fuels due to MDA; and (b) the use of laminar flow test methods for determining thermal stability (e.g., the JFTOT: ASTM D3241, and the gravimetric JFTOT), whereas the fuel flow in jet engines is turbulent. Both these concerns are addressed below.

MDA/copper solubilization effect. The favorable results obtained at high MDA concentrations, even for non copper doped fuels, indicate that MDA is beneficial at concentrations well in excess of the current 5.8 ppm MDA military specification⁶ level. Increasing the current military specification is particularly pertinent to US Navy fuels, for which, copper contamination is of concern. Nevertheless, anticipated opposition to such a revision may stem from the tendency of MDA to increase copper solubilization in fuels. However, the results in Table 5 indicate a fuel dependency. For example, whereas copper solubilization increased with time on storage in the presence of MDA for the TX fuel, a corresponding decrease was observed for the LA fuel. Nevertheless, as Pedersen has reported,⁵ and our results attest to, despite the increased copper solubilization, MDA decreased the thermal deposits of the copper/MDA stored fuels.

Laminar versus Turbulent Flow Devices for Measuring Thermal Stabilities

The effects of flow velocity on heat transfer and deposition rates reviewed by Hazlett¹⁷ indicate varying results. Nonetheless, it has been suggested¹⁸ in the recent past that turbulent flow has some effect on the chemistry of fuel thermal instability deposition. This suggestion may be due to a temperature effect attributable to the mode of operation of the turbulent flow test devices, which tend to run at much hotter metal surface temperatures than laminar flow devices. For example, turbulent flow devices are designed to more closely simulate actual airframe and engine conditions from the standpoint of flow and the actual *initial* hot metal surface temperatures. However, as the test time progresses, these turbulent flow devices usually deviate to much higher than realistic metal surface temperatures. Consequently, the hidden variable between turbulent and laminar flow test devices is likely a temperature effect and it is this effect that may be the cause of the differences in thermal deposition between turbulent and laminar flow. In the gravimetric JFTOT, based on *the combination of*: 260°C wall temperature (the fuel temperature is approximately 250 °C for about 75% of the heated zone), six seconds residence time, 19 cm⁻¹ surface/volume ratio, and the laminar flow, in general, the conditions employed are more severe than the initial conditions in the turbulent flow devices.

Conclusions

Based on the extended duration gravimetric JFTOT tests conducted, which ranged from a minimum of 120 hours for the stored neat Jet A fuel, and a maximum of 152 hours for most other tests, MDA, at the high concentration used (15-35 ppm), was not detrimental. Instead, MDA improved the thermal stability of a typical non copper doped commercial jet fuel by approximately 64%, based on the total deposits accumulated during a 125-hr test duration period. And, based on the individual and combined effects of MDA and BHT examined, the effectiveness observed appears to be attributable to MDA. Furthermore, based on the plots of mg/L versus time, after 96 hours, the rate of thermal deposition appears to level off. Consequently, the extended test durations employed, including the minimum of 120 hours, were more than adequate.

Since the operating conditions of the gravimetric JFTOT are similar to the JFTOT's (ASTM D3241), the beneficial effects of MDA observed in the extended duration gravimetric JFTOT tests do not support the interpretation that the JFTOT (D3241) is over responsive to MDA, due to its short duration test time of 2.5 hr. In addition, because the conditions employed in the gravimetric JFTOT are more severe than the initial conditions in the turbulent flow devices (viz., the combination of high fuel temperature, long residence time, surface/volume ratio, and laminar flow), the overall results obtained have even greater significance.

The apparent beneficial effect of MDA alone/early addition exhibited in the extended duration tests of a typical commercial jet fuel (Jet A: no antioxidant added) containing negligibly low copper content, appears promising with respect to decreasing maintenance costs and needs to be explored further. Although the effect of late addition of MDA (i.e., addition after storage) to the Jet A test fuel (no BHT present) was not examined, the overall data suggest that for storage stable Jet A fuels, the time of MDA addition would not be critical. For non-copper doped thermally stable JP-5 or JP-5 type fuels (BHT present), the effect of time of addition of MDA appears to be dependent on the test duration.

For *copper doped* JP-5 fuels, using copper derived from either copper II ethyl acetoacetate or 90:10 Cu-Ni alloy, the *early* addition of MDA appears to be more effective than late addition. These latter results are particularly significant because they further validate our premise that for copper contaminated fuels, the precursors that lead to thermal stability are formed primarily during storage. Finally, the overall thermal stability results obtained when BHT was present/absent focus on reassessing the use of BHT for storage stability. MDA may be a viable replacement in serving not only as a thermal stability enhancer, but as a storage stability additive. However, MDA's role in controlling peroxidation, on long term storage, needs to be established.

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Literature Cited

1. Hazlett, R.N. *Thermal Oxidation Stability of Aviation Turbine Fuels*; ASTM Mongraph 1, American Society of Testing and Materials: Philadelphia, 1991, chapter 1X.
2. Kendall, D.R.; Houlbrook, G.; Clark, R.H.; Bullock, S.P.; Lewis, C. Thermal Degradation of Aviation Fuels in Jet Engine Injector Feed Arms. Part I - Results from a Full-Scale Rig. Paper 87-IGTC-49 presented at the *International Gas Turbine Congress*, Tokyo, October 1987.
3. Moses, C.A. Effect of a Metal Deactivator Fuel Additive on Fuel Deposition in Fuel Atomizers at High Temperature. Interim Report 281, Belvoir Fuels and Lubricants Research Facility (SwRI) Southwest Research Institute, San Antonio, TX, August 1992.
4. Pande, S.G.; Hardy, D.R. Effect of Copper, MDA, and Accelerated Aging on Jet Fuel Thermal Stability as Measured by the Gravimetric JFTOT. *Energy and Fuels* 1995, 9, 177-182.
5. Pedersen, C.J. Inhibition of Deterioration of Cracked Gasoline During Storage. *Ind. Eng. Chem.* 1949, 41, 924.
6. Military specification, MIL-T-5624.
7. Beal, E.J.; Hardy, D.R.; Burnett, J.C. In (a) *Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels*: Orlando, FL, Nov. 1991, pp245-259. (b) *Aviation Fuels Thermal Stability Requirements*, ASTM STP 1138; Kirklin, P.W.; David, P., Eds; American Society for Testing and Materials: Philadelphia, PA, 1992, pp. 138-150.
8. Clark, R.H. The Role of a Metal Deactivator in Improving the Thermal Stability of Aviation Kerosines. Presented at the *3rd International Conference on the Stability and Handling of Liquid Fuels*: London, September 1988, Paper No. 47, p.283, Institute of Petroleum, 1989.
9. Morris, R.E.; Hazlett, R.N.; McIlvaine, C.L. *Ind. Eng. Chem. Res.* 1988, 27, (8), 1524.
10. Schreifels, J.A.; Morris, R.E.; Turner, N.H.; Mowery, R.L. *Prepr.-Am.Chem. Soc., Div. Fuel Chem.* 1990, 35, (2), 555.
11. Morris, R.E.; Turner, N.H. *Fuel Science and Technology*, 1990, 8(4), 327.
12. Schreifels, J.A.; Gwynn, L.; Morris, R.E.; Interactions of a Metal Deactivator with Metal Surfaces at Elevated Temperatures. Presented at the *4th International Conference on the Stability and Handling of Liquid Fuels*: Orlando, FL., November 19-22, 1991.

13. Kendall, D.R.; Houlbrook, G.; Clark, R.H.; Bullock, S.P.; Lewis, C. Presented at the Tokyo International Gas Turbine Congress, October, 26-31, Tokyo, Japan, 1987, Paper 87-IGTC-49.
14. Clark, R.H.; Delargy, K.M.; Heins, R.J. *Prepr.-Am.Chem. Soc., Div. Fuel Chem.* **1990**, *35*, (4), 1223.
15. Heneghan, S.P.; Zabarnick, S. *Fuel* **1994**, *73*, (1), 35.
16. Pande, S.G.; Hardy, D.R. Comparison of the Effects of Storage in the Presence of Copper Using Laboratory versus Field Conditions on Jet Fuel Thermal Stability As Measured by the Gravimetric JFTOT. *Energy and Fuels* **1997**, *11*, 1019.
17. Hazlett, R.N. *Thermal Oxidation Stability of Aviation Turbine Fuels, American Society of Testing and Materials*, ASTM Mongraph 1, American Society of Testing and Materials: Philadelphia, 1991, chapter V.
18. Clark, R.H.; Stevenson, P.A. *Prepr.-Am. Chem. Soc., Div. of Fuel Chem.* **1990**, *35*, 1302.

Table 1. Overall Test Matrix for the Two Studies Conducted

test matrix	extended duration testing (study 1)	early vs. late MDA addition follow-up study (study 2)
no. and type of fuel: id	1 freshly refined Jet A: Jet A	2 freshly refined JP-5s: TX, LA
room temp storage period:	13-16 months	14-15 months
<u>non copper doped stored fuels:</u>		
neat fuel	✓	✓
test additives*	✓	✓
antioxidant (AO)	BHT added in lab at 24mg/L	AO added at refinery at 17mg/L
MDA: no AO	at 35 ppm	na**: JP-5s contain an AO
AO +: MDA before storage	MDA at 35 ppm	MDA at 20 ppm
AO +: MDA after storage	MDA at 15 ppm	MDA at 15 ppm
<u>copper doped stored fuels:</u>		
	Cu as copper wires	Cu as CuEA and Cu-Ni rods
Cu +AO +: MDA before storage	MDA at 35 ppm	MDA at 20 ppm +: (a) 400 ppb (CuEA) (b) 6 Cu-Ni rods MDA at 40 ppm+: (a)2000 ppb Cu (CuEA) (b) 18 Cu-Ni rods
Cu +AO: + MDA after storage	nd**	MDA at 15 ppm in all cases
grav. JFTOT test duration	min: 120 hr max: 152 hr	2.5 hr

* Unless otherwise stated, all additives were added early, i.e., prior to storage. Antioxidants used at concentrations shown in all tests conducted. And, MDA concentrations are, as specified. ** na: not applicable; nd: not determined.
✓: tests conducted as identified.

**Table 2. Available Properties and Compositional Data for the Two JP-5 Fuels Examined
and Specification Limits for Jet A Fuels**

properties/composition (ASTM method, MIL-T- 5624 specification limits for JP-5 fuels)	JetA* ASTM D1655	JP-5 fuels	
		TX	LA
aromatics, vol% (D1319, max: 25)	20 25	19	14.9
olefin, vol% (D1319, max: 5)	not reqd.	0.8	1.1
mercaptan sulfur, wt% (D3227, max: 0.0020)	0.003	0.0001	0.0012
total sulfur, wt% (D4294, max: 0.40)	0.3	0.0069	0.09
total acid, mg KOH/g (D3242, max:0.015)	0.1	0.003	0.002
density, g/mL (D4052, min-max: 0.788 - 0.845)	0.775-0.840	0.816	0.819
flash point, °C (D93, min: 60)	37.8	62.2	64
freeze point, °C (D2386, max: - 46)	-40	- 50.5	- 48.5
peroxide content, ppm (D3703, max: 8)	not reqd.	<0.001	<0.001
antioxidant	option	✓	✓
corrosion inhibitor	agreement	✓	✓
fuel system icing inhibitor, vol% (0.15-0.20)	agreement	0.13	not stated
copper content, ppb	3	4	2

* specification values only: actual values not available.

Table 3. Cumulated Deposits Formed after 120-128 Hours Extended Duration Thermal Stability Testings of the Specified Additives in the Jet A Test Fuel*

Thermal Stabilities Ranked from best to worst

additive/additive combination	cumulated deposits,** mg			% -decrease*** in total deposits
	strip	filterables	total	
BHT/MDA after storage	0.2	11.2	11.4	68
MDA	0.1	12.5	12.6	64
BHT/MDA before storage	0.1	23.3	23.4	34
BHT/MDA/~4000 ppb Cu	0.3	30.8	31.1	12
BHT	0.9	30.8	31.7	11
none (neat)	0.9	34.6	35.5	reference

* The test fuels were stored for approximately 13-16 months in the presence of the specified test additives prior to the extended duration thermal stability testings.

** For the neat fuel, the deposits shown are for a test duration of 120 hours. For the test additives/additive combinations, the deposits shown are for a test duration of 128 hours.

*** Relative to the reference neat fuel, i.e., $[(\text{wt of total deposits of neat fuel}) \text{ minus } (\text{wt of total deposits of additized fuel}) \times 100] \div (\text{wt of total deposits of neat fuel})$.

Table 4. Thermal Stability of the Jet A Test Fuel That Was Stored under Accelerated Conditions*in the Presence of the Specified Additives

test description**	grav. JFTOT deposits, mg/L		
	strip	filter	total
Cu/BHT	0.06	5.80	5.86
Cu/MDA	0.00	0.13	0.13
Cu/BHT/MDA	0.01	0.15	0.16

* The accelerated storage conditions are: 90°C/50 psig air/48 hrs.

** The respective concentrations of the additives are: Cu at 400 ppb derived from copper II ethyl acetoacetate; MDA at 5.8 mg/L; and BHT at 24 mg/L.

Table 5. Copper Levels on Storage at Room Temperature with and without MDA for Two Typical JP-5 Fuels

JP-5 fuel	description	copper concentration in ppb, at storage times shown:													
		1 mth	2 mth	4 mth	5 mth	6.3 mth	8.4 mth	9.5 mth	11.5 mth	13 mth	16 mth				
TX	neat				4										3
	+ 6 Cu-Ni rods	37	45	54	75	70	97	96	99	75					38
	+ 6 Cu-Ni rods + 20 ppm MDA	55	56	74	86	98	200	340	631	477					401
	+ CuEA (400ppb Cu)	nd*	nd	nd	320	nd	nd	153	174	92					44
	+ CuEA (400ppb Cu) + 20 ppm MDA	nd	nd	nd	298	nd	nd	325	448	368					339
	+ 18 Cu-Ni rods	99	133	152	128	108	183	201	260	210					95
LA	+ 18 Cu-Ni rods + 40 ppm MDA	146	164	215	283	318	770	1382	2559	2093					2127
	+ CuEA (2000ppb Cu)	nd	nd	nd	1698	nd	nd	1462	665	226					9
	+ CuEA (2000ppb Cu) + 40 ppm MDA	nd	nd	nd	1464	nd	nd	1966	2290	1892					nd
	neat				2										3
	+ 6 Cu-Ni rods	92	111	117	155	169	562	831	1689	2172					1591
	+ 6 Cu-Ni rods + 20 ppm MDA	60	63	66	67	76	125	197	279	254					243
TX	+ CuEA (400ppb Cu)	nd	nd	nd	491	nd	nd	417	432	398					388
	+ CuEA (400ppb Cu) + 20 ppm MDA	nd	nd	nd	341	nd	nd	340	399	386					nd
	+ 18 Cu-Ni rods	256	305	342	425	455	1664	3058	3570	2731					2253
	+ 18 Cu-Ni rods + 40 ppm MDA	134	124	152	196	211	566	981	1467	1539					1390
	+ CuEA (2000ppb Cu)	nd	nd	nd	2173	nd	nd	1289	1411	763					763
	+ CuEA (2000ppb Cu) + 40 ppm MDA	nd	nd	nd	1871	nd	nd	2242	2257	2081					nd

* not determined

**Table 6. Summary of the Total Thermal Deposits Formed for Two Stored JP-5 Fuels
Storage conducted for 14-15 months with and without the Test Additives as Stated
Effect of Early versus Late Addition of MDA***

test no.	test description ***	mole ratio**		tot. deposit wt, mg/L	
		TX	LA	TX	LA
1	neat (reference): no additives/no storage	na ****	na	0.3	0.3
<u>Fuels stored in presence of test additives unless otherwise stated</u>					
2	neat: storage without additives	na	na	0.2	0.4
3	15 ppm MDA added after storage	na	na	0.2	0.2
4	20 ppm MDA added before storage	na	na	0.3	0.1
<u>For fuels doped originally at 400 ppb Cu (CuEA)</u>					
5	400 ppb Cu (CuEA): original Cu concentration added	na	na	0.6	2.3
6	92 and 398 ppb Cu (CuEA):+ 15.2 ppm MDA added after storage	37.2	8.8	0.4	1.2
7	400 ppb Cu (CuEA)+ 20 ppm MDA added before storage	11.2	11.3	0.1	0.5
<u>Cu concentration from Cu-Ni at the time of grav. JFTOT</u>					
8	75 and 2170 ppb Cu (6 Cu-Ni rods)	na	na	0.7	2.8
9	75 and 2170 ppb Cu (6 Cu-Ni rods): +15.5 ppm MDA added after storage	46.6	1.6	0.7	2.9
10	480 and 260 ppb Cu (6 Cu-Ni rods) + 20 ppm MDA added before storage	9.4	17.7	0.2	0.6
11	210 and 2730 ppb Cu (18 Cu-Ni rods)	na	na	0.5	5.3
12	210 and 2730 ppb Cu (18 Cu-Ni rods): +15.4 ppm MDA added after storage	16.5	1.7	0.5	3.1
13	2090 and 1540 ppb Cu (18 Cu-Ni rods) + 40 ppm MDA added before storage	4.3	5.8	0.3	1.1
<u>For fuels doped originally at 2000 ppb Cu (CuEA)</u>					
14	2000 ppb Cu (CuEA): original Cu concentration added	na	na	21.1	3.5
15	230 and 760 ppb Cu (CuEA): + 15.1 ppm MDA added after storage	14.8	4.6	22.3	2.2
16	2000 ppb Cu (CuEA) +40 ppm MDA added before storage	4.5	4.5	0.5	0.9

* Early addition of MDA refers to its addition before storage; late addition, to its addition after storage.

**mole ratios are based on the MDA and Cu copper concentrations, at the time of addition of MDA.

*** For the sole purpose of calculating the mole ratios of MDA:Cu, for the CuEA doped fuels, the quoted copper levels are based on the time of addition of MDA. When MDA is added early, the quoted copper level is the original concentration added. When MDA is added late to the CuEA doped fuels, and for all cases of the Cu-Ni doped fuels, the quoted copper levels refer to the copper concentration at the time the grav. JFTOT tests were conducted. In cases where two copper concentrations are given, the first value pertains to the TX fuel, and the second, to the LA fuel.

**** na: not applicable

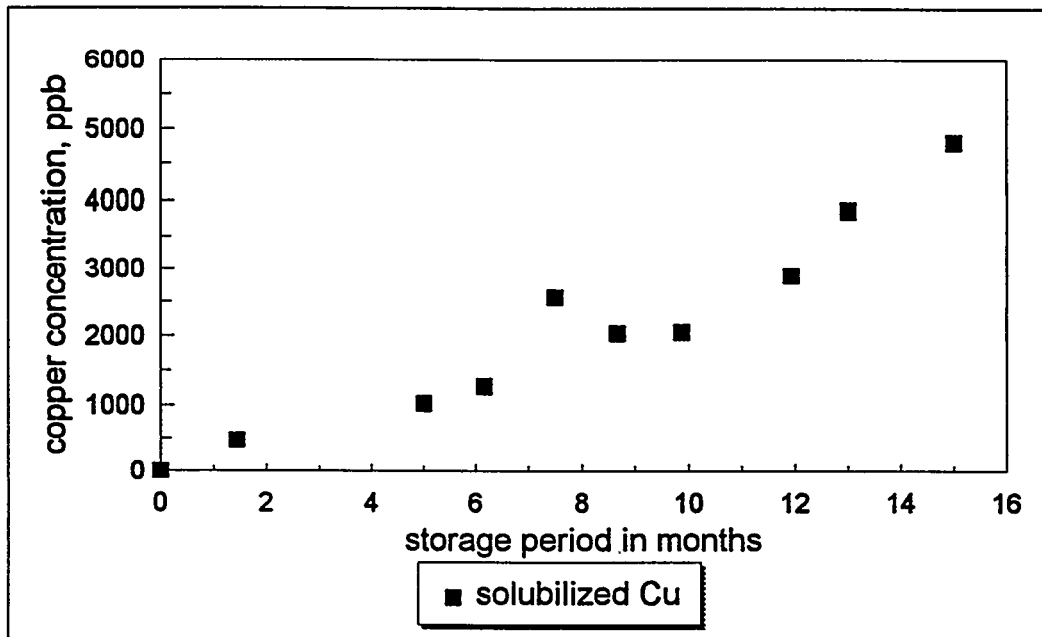


Figure 1. Fuel absorption of copper on storage. The Jet A test fuel was stored in the presence of copper as copper wires, BHT at 24 mg/L, and MDA at 30-35 ppm.

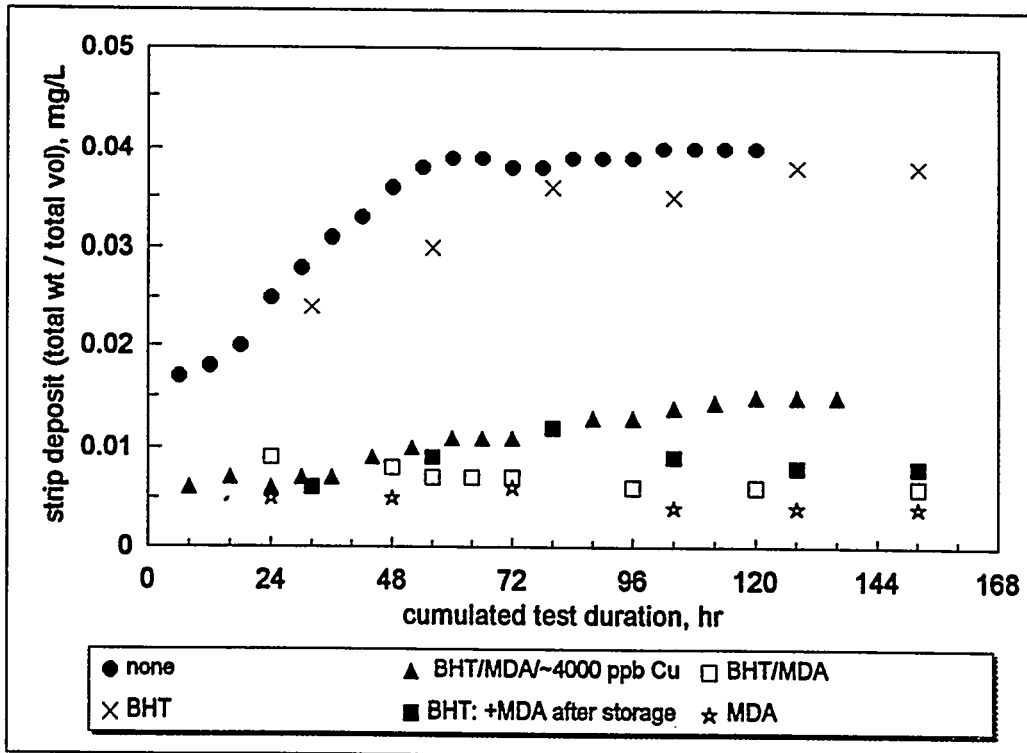


Figure 2. Cumulated strip deposits in mg/L. Effect of the test additives on the strip deposits formed on extended duration testings of the stored neat and doped Jet A test fuel.

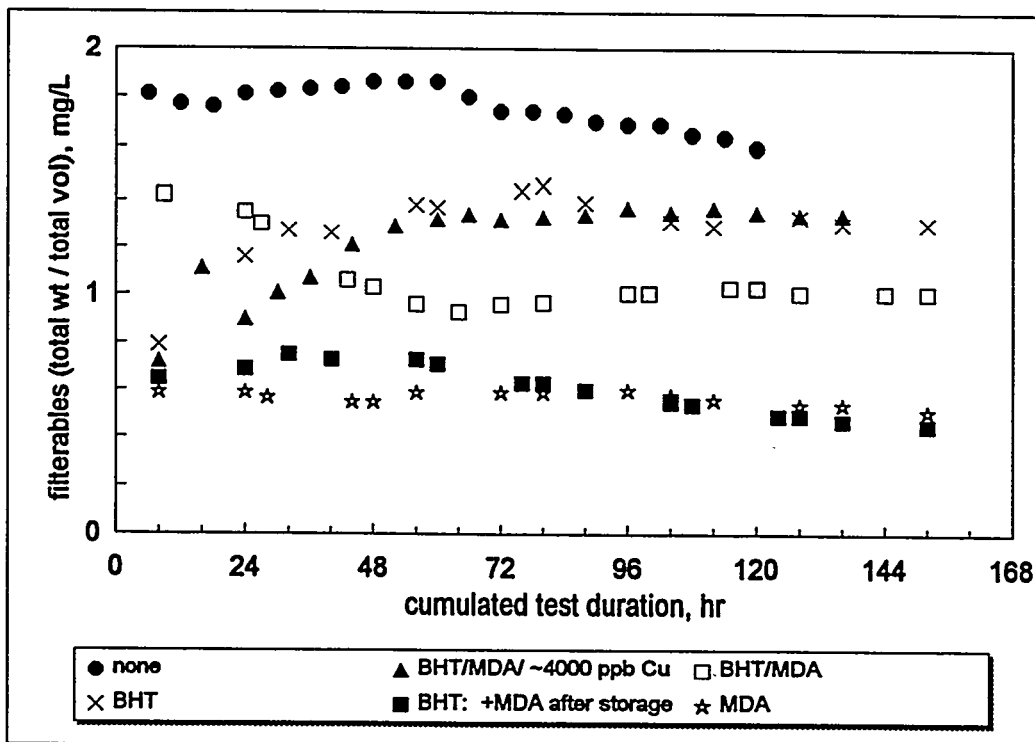


Figure 3. Cumulated filterable deposits in mg/L. Effect of the test additives on the filterable deposits formed on extended duration testings of the stored neat and doped Jet A test fuel.

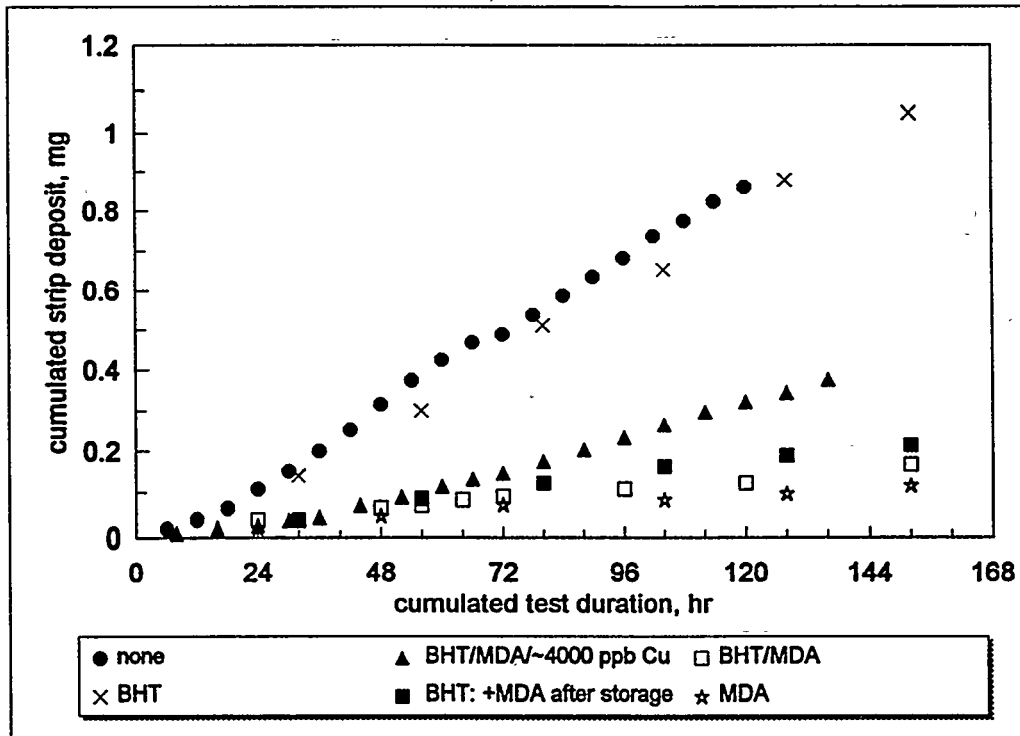


Figure 4. Cumulated strip deposits in mg: Effect of the test additives on the strip deposits formed on extended duration testings of the stored neat and doped Jet A test fuel.

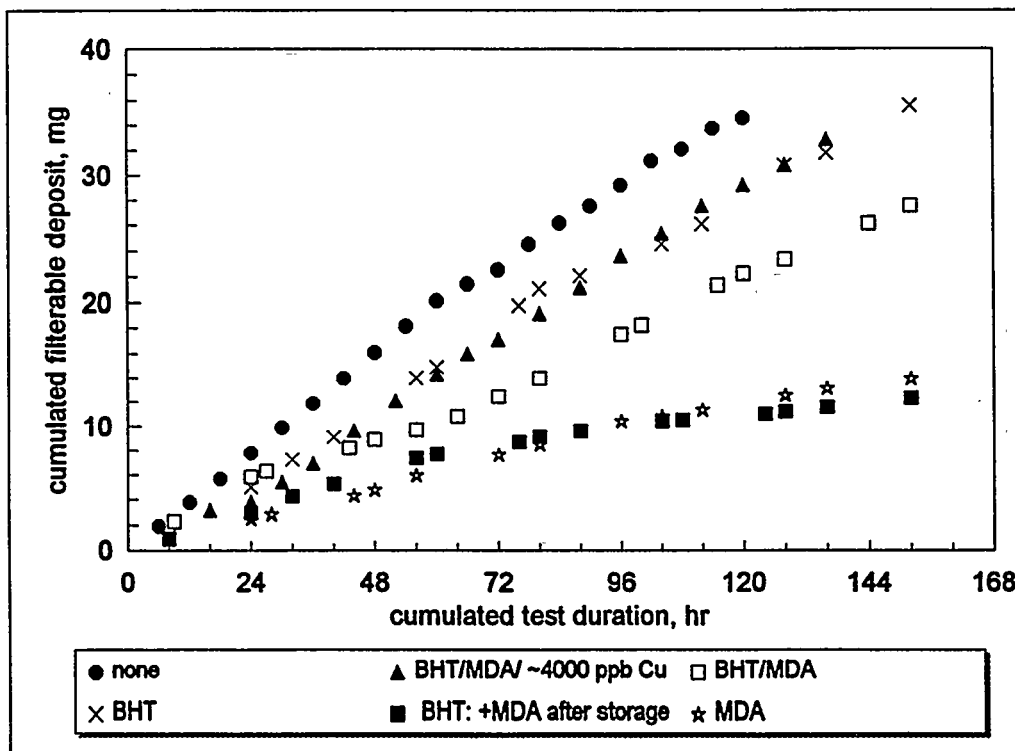


Figure 5. Cumulated filterable deposits in mg: Effect of the test additives on the filterable deposits formed on extended duration testings of the stored neat and doped Jet A test fuel.

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RETENTION OF METAL DEACTIVATOR ADDITIVE PERFORMANCE DURING STORAGE OF AVIATION TURBINE FUELS

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The use of Metal Deactivator Additive (MDA) in aviation turbine fuels has continued to be controversial following the publication of Shell Thornton Research Centre data, which were presented in a paper at the 3rd International Congress. While benefits from MDA may be overstated in fuels with undetectable dissolved metal content in the ASTM D 3241 JFTOT test, there is also no question that use is fully merited when dissolved copper is present. Arguments have been presented that the allowed level in jet fuel should be significantly reduced, because the potential for copper contamination is lessened by the virtual disappearance of copper sweetening processes. There were concerns, however, about the possible loss of the additive during fuel storage, such that re-doping may be appropriate but not accommodated by reduced maximum use levels. To address that concern, samples of jet fuel containing MDA were stored and then challenged by the addition of soluble copper, followed by ASTM D 3241 JFTOT testing to determine whether the additive is still active.

INTRODUCTION

Use of up to 5.7 mg/L of Metal Deactivator Additive (MDA) has been permitted by most major civil aviation turbine fuel specifications for many years. Its primary purpose is to eliminate oxidation catalysis by dissolved metals, especially copper. Of the various metallic ions which might be dissolved in fuel, copper is generally regarded as the most potent oxidation catalyst. MDA is an extremely efficient chelating agent for copper, and for many years it has been used at low concentrations in aviation turbine fuel, motor gasolines, and other middle distillate fuels for that purpose. The MDA copper chelate is essentially inactive as an oxidation catalyst. In addition, copper sweetening processes were commonly used to reduce the odor of aviation kerosine; these fuels frequently contained traces of dissolved copper and effects were conveniently negated by addition of MDA. This practice was routinely followed for many years without controversy¹.

During the last twenty years, a chain of events has led to considerable debate about use of MDA in aviation fuels. In the mid 1970's, the D 3241 JFTOT thermal stability test method² was

accepted in aviation turbine fuel specifications as a suitable means to show that jet fuel has adequate thermal stability, and it is now the only method cited, except for Russian GOST specifications and those based on them. Copper sweetening processes have nearly disappeared and thus dissolved copper levels are lower; however, some fuels are still known to contain dissolved copper, primarily due to exposure to copper alloy heat exchangers or flow through copper alloy piping. Then during the 1980's, it became generally known that addition of MDA to aviation fuels could give a dramatic improvement in the thermal stability as determined by the D 3241 JFTOT test method, and its use as a "quick fix" became common when fuels failed to meet the specification requirements – even though dissolved copper content was frequently not determined by analysis. At that time, most specifications allowing MDA permitted its use at the discretion of the supplier, requiring only that its presence be declared on quality certificates. Growing use of MDA prompted the MOD (United Kingdom) to fund a project at Shells' Thornton Research Centre, to determine whether the apparent benefits of MDA as observed in the JFTOT test method were mirrored when fuel was then used in aviation turbines. A landmark presentation ³ of those results in 1988 suggested that benefits of MDA are overstated in the JFTOT test method.

As a consequence, a number of papers presented in this forum and elsewhere ^{4,5} have reported work on the use of MDA in aviation fuels, and some specifications have been altered to require permission for use ⁶ or reporting of test results before and after addition ⁷. Studies previously reported by the author discussed results from eight jet fuels (three without measurable copper content) from field sources which all gave failing JFTOT test results at a test temperature of 260°C. All gave passing results when a small fraction of the allowed MDA concentration was added ⁸. We also suggested that, while the apparatus no longer exists for direct comparison, old D 1660 ⁹ Coker thermal stability test data show much less effect from MDA.

While much has been learned, a fundamental conundrum remains: how should the use of MDA be limited to allow appropriate use when trace levels of dissolved copper are present, but avoiding indiscriminate use to satisfy a requirement for fuel quality – when it is known that the test method result might be unduly enhanced by the additive? Further complicating this question is the lack of adequate test methods (especially for field use) to determine parts-per-billion concentrations of copper or of MDA at use concentrations in fuel.

Finally, at the 1997 meeting of the MOD-UK Aviation Fuel Committee a proposal was advanced to limit the initial MDA concentration in aviation fuels to 2.0 mg/L, but allowing further re-doping up a cumulative maximum concentration of 5.7 mg/L. Since further addition of MDA is generally inconvenient, this action would generally result in a nearly 2/3 reduction in the typical concentration of MDA when used. We have recommended that a concentration of 2mg/L MDA is generally adequate in aviation turbine fuel for some time ¹⁰. A question raised in response to this proposal was, however – will this concentration be maintained during storage of fuel or will loss of MDA due to degradation result in failing JFTOT test results after some period of time? We were aware that Hardy et al were also addressing this question and planned to discuss findings at this Symposium ¹¹, but their work was not aimed at the suitability of this proposal.

EXPERIMENTAL

We were aware of early efforts by Hardy in which retention of metal deactivator was determined by an HPLC technique, and showed MDA disappeared over time ¹². However, there were concerns about the methodology. Instead, we focused on the performance of the additive over time. With rare exceptions, the concentration of copper in jet fuel samples from field sources is in the range < 5 – 100 parts per billion (higher levels are anticipated for JP-5 on board carriers, and might also be possible from extended exposure to copper alloy heat exchangers on board tankers). For many years, the concentration of copper in Jet A-1 fuels was limited to 150 parts per billion (ppb) in DERD 2494, United Kingdom Jet A-1 Specification which preceded the current Def Stan 91-91 Specification for Jet A-1 ¹. That requirement has been dropped from the current specification ⁷, because copper sweetening is very little practiced today, and to improve commonality between turbine fuel specifications. The amount of dissolved copper used to challenge MDA was therefore set at 80 and 160 ppb for this work on the basis that 80 ppb was in the upper range of typical copper contamination, and 160 ppb is the maximum concentration normally expected.

Fuels were aged under D 4625 ¹³ conditions in borosilicate glass containers, except one liter containers were used. Fuel samples were stored for 13 weeks at 43°C, conditions which are generally regarded equivalent to storage for one year at ambient temperature ¹³. Since 2 mg MDA /L (active ingredient) is the proposed maximum concentration, all work was done using this amount. Tests were carried out where both MDA and 80 ppb dissolved copper (as copper

naphthenate) were added before storage, and in a second set of tests, an additional 80 ppb copper was also added so that a total of 160 mg/L soluble copper was used. These amounts were in addition to any adventitious copper already present in the base fuels.

D 3241 JFTOT tests were performed on un-aged fuels and on base fuels with added copper. In a second round of testing, samples with added copper and MDA were also tested prior to aging. For the second data set, the JFTOT apparatus being used malfunctioned, and the testing on aged samples was done at another site.

RESULTS AND DISCUSSION

A first set of preliminary data gave results shown in Table 1. The fuels used in these studies were three Jet A and Jet A-1 fuels available in our laboratory. These fuels had been in our hands for some time, and gave fair to poor results when tested without added copper or MDA. Addition of 80 ppb copper in the form of copper naphthenate to these fuels gave significantly poorer tube ratings, and in one case a failing ΔP result. When both copper and MDA were added to the fresh fuels, results were improved in terms of tube rating, but were still failing because of abnormally colored deposits. We have previously seen the high incidence of abnormally colored deposits from addition of copper naphthenate, and are puzzled these results which indicate inability of MDA to overcome the effects of dissolved copper.

Nonetheless, results showed that MDA was in fact retained after storage and in the case of Fuel B, the JFTOT rating was improved to a passing result (less than code 3 visual rating and not greater than 25 mm Hg pressure differential across the filter). In the case of Fuel B, abnormal tube deposits (and therefore a failing result) was obtained when fuel was aged with MDA and later copper addition, but passing results were obtained when the fuel was aged with both 80 ppb copper and MDA. Similarly, Fuel A gave better post-aging results when copper was added before aging, but Fuel C gave the reverse result.

We wanted to carry out additional tests in more fuels to supplement these data, and requested fuels from Steve Anderson, USAF for that purpose. He provided seven Jet A and Jet A-1 kerosines from a suite of fuels being used on the JP-8+100 program at Wright Patterson AFB which were then used for similar studies.

Table 1. Preliminary Data – Effect of Storing Fuel containing MDA and Dissolved Copper

Fuel Batch	Additive Treatment	Rating ASTM code	ΔP	
			Time	ΔP
A1	as is	< 2	150	2
A2	80 ppb Cu	< 4	125	123
A3 aged	80 ppb Cu + 2 ppm MDA	A, < 2	150	2
A4 aged	80 ppb Cu + 2 ppm MDA	< 2	150	2
B1	as is	< 4	150	2
B2	80 ppb Cu	A, heavy deposit	150	2
B3 aged	80 ppb Cu + 2 ppm MDA	A, < 3	150	3
B4 aged	80 ppb Cu + 2 ppm MDA	< 2	150	4
C1	as is	< 2	150	1
C2	80 ppb Cu	A, < 2	150	0
C3 aged	80 ppb Cu + 2 ppm MDA	< 1	150	2
C4 aged	80 ppb Cu + 2 ppm MDA	< 2	150	0

A3, B3, C3 – Aged with MDA, copper naphthenate addition after aging

A4, B4, C4 – Aged with MDA and copper naphthenate added before aging

These were tested as received, with 80 ppb copper as copper naphthenate, and with 80 ppb of copper and 2 mg/L of MDA before aging. Results from this testing is shown in Table 2, and also shows some unusual aspects – addition of excess MDA did not completely overcome the effect of added copper. As in the case of the first set of tests reported in Table 1, the fuels used for this study were not freshly produced, and had generally been stored under ambient conditions for some time. All seven fuels had satisfactory JFTOT results tested at 260°C before addition of copper or MDA; two failed on pressure drop after copper addition and six of the seven fuels failed due to pressure drop or abnormal deposits after copper addition.

Table 2. JFTOT Results on POSF As-received Base Fuels Before Aging of Samples

Fuel Batch (ppb Cu)	Additive Treatment	Rating ASTM code	ΔP	
			Time	ΔP
2827 (10)	as is	1	150	1
	80 ppb Cu	3 A	150	69
	80 ppb Cu + 2 ppm MDA	< 3 A	150	3
3219 (<5)	as is	1	150	3
	80 ppb Cu	1A	150	1
	80 ppb Cu + 2 ppm MDA	1	150	4
2926 (<5)	as is	1	150	1
	80 ppb Cu	1	61	125
	80 ppb Cu + 2 ppm MDA	< 2	150	2
3084 (6)	as is	< 2	150	0
	80 ppb Cu	3 A	150	4
	80 ppb Cu + 2 ppm MDA	< 2	150	0
3166 (5)	as is	< 2	150	0
	80 ppb Cu	3A	150	10
	80 ppb Cu + 2 ppm MDA	< 2	150	2
3305 (34)	as is	< 2	150	0
	80 ppb Cu	3 A	150	3
	80 ppb Cu + 2 ppm MDA	< 3	141	125
3119 (<5)	as is	2	150	1
	80 ppb Cu	< 3	150	1
	80 ppb Cu + 2 ppm MDA	---	---	---

Copper content of the as-received fuels was determined by ICP analysis and is shown with the fuel identification in Table 2.

Samples of these fuels, containing both 2 mg/L MDA (2 ppm) and 80 ppb dissolved copper, were aged as previously for 13 weeks at 43°C, and were again tested; however, the testing was done in another laboratory because our JFTOT apparatus had failed. The results of that testing are shown below in Table 3. Data are somewhat disconcerting, because the results

were generally better than that from un-aged fuels shown in Table 2. Although not shown, TDR data did not indicate that better results were due to differences between visual raters.

Table 3. JFTOT Results on POSF Aged Fuels

Fuel Batch	Additive Treatment	Rating ASTM code	ΔP	
			Time	ΔP
2827	Aged with 80 ppb Cu + 2 ppm MDA	< 2	150	0
	Aged with 80 ppb Cu + 2 ppm MDA; + additional 80 ppb copper	< 1	150	0
3219	Aged with 80 ppb Cu + 2 ppm MDA	< 1	150	0
	Aged with 80 ppb Cu + 2 ppm MDA; + additional 80 ppb copper	< 1	150	0
2926	Aged with 80 ppb Cu + 2 ppm MDA	< 1	150	0
	Aged with 80 ppb Cu + 2 ppm MDA; + additional 80 ppb copper	< 1	150	0
3084	Aged with 80 ppb Cu + 2 ppm MDA	< 1	150	0
	Aged with 80 ppb Cu + 2 ppm MDA; + additional 80 ppb copper	< 1	150	0
3166	Aged with 80 ppb Cu + 2 ppm MDA	< 1	150	0
	Aged with 80 ppb Cu + 2 ppm MDA; + additional 80 ppb copper	< 1	150	0
3305	Aged with 80 ppb Cu + 2 ppm MDA	1A	150	157
	Aged with 80 ppb Cu + 2 ppm MDA; + additional 80 ppb copper	< 2A	150	175
3119	Aged with 80 ppb Cu + 2 ppm MDA	< 1	150	1
	Aged with 80 ppb Cu + 2 ppm MDA; + additional 80 ppb copper	< 1	150	0

CONCLUSIONS

The data which were obtained with 10 jet fuels demonstrates that in general, fuels containing 2 mg/L of MDA can be stored for prolonged periods without loss in the ability of the MDA to chelate amounts of dissolved copper which can reasonably be expected in today's fuels. We therefore believe a limitation to allow 2 mg MDA/L for initial treatment of jet fuel is reasonable.

Several disturbing phenomena were encountered. We were mildly surprised that data obtained on a different instrument showed a systematic bias toward a milder result. The more disturbing JFTOT results were from treatment of fuel with a small amount of soluble copper and excess MDA – then finding that the resulting thermal stability was not as good as before either was added. This deserves further exploration; it may be due in part to use of older fuels for the study and formation of strongly acidic or other interfering species during aging.

ACKNOWLEDGEMENTS

Alan Garcia, Octel America, Inc. carried out all the experimental work on this project; his efforts are gratefully acknowledged.

REFERENCES

1. Smith, M., *Aviation Fuels*, G.T. Foulis & Co., Ltd., Cambridge UK 1970, p. 284-287.
2. ASTM D 3241-96a "Standard Test Method for Thermal Oxidation Stability of Aviation Turbine Fuels (JFTOT Procedure), *1997 Annual Book of ASTM Standards, Vol. 5.02*, American Society for Testing and Materials, West Conshohocken PA, 1997.
3. Clark, R.H., In *Proceedings of the 3rd International Conference on Stability and Handling of Liquid Fuels*, London, UK, 13-16 Sept. 1988, p. 283.
4. Baker, C., David, P., Hall, D., and Swatridge, R., In *Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels*, Orlando FL, Nov. 19-22, 1991, p. 316.
5. Schreifels, J.A., Gwynn, L., and Morris, R.E. In *Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels*, Orlando FL, Nov. 19-22, 1991, p. 661.

6. Performance Specification for Turbine Fuel, Aviation, Grades JP-4, JP-5, and JP-5/JP-8 ST, MIL-PRF-5624S, 22 November 1996.
7. Defence Standard 91-91/Issue 2, "Turbine Fuel, Aviation Kerosene Type, Jet A-1", Ministry of Defence Directorate of Standardization, Glasgow, UK, 1996.
8. Henry, C.P., In Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels, Orlando FL, Nov. 19-22, 1991, p. 692.
9. ASTM D 1660, "Method of Test for Thermal Stability of Aviation Turbine Fuels", Discontinued, See *1993 Book of ASTM Standards*, Vol. 5.02, 1993.
10. "Octel Additives for Use In Aviation Fuels", Octel America Tech Memo 10,001-96, Octel America, Inc., Newark DE, 1996.
11. Pande, S.G., and Hardy, D.R., "Effectiveness of MDA on Jet Fuel Thermal Stability as Determined Using the Gravimetric JFTOT", Vancouver BC, Oct. 12-17, 1997.
12. D.R. Hardy, private communication.
13. ASTM D 4625, "Test Method for Distillate Fuel Storage Stability at 43°C (110°F)", *1997 Annual Book of ASTM Standards*, Vol. 5.02, American Society for Testing and Materials, West Conshohocken PA, 1997.



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**THE 'BLACK AVTUR' INCIDENT IN NORTHERN AUSTRALIA (1994/95);
REPORT ON THE AMRL INVESTIGATION (1995/97)**

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ABSTRACT

The 'Black AVTUR' incident that occurred at a northern Australian Air Force base in late 1994 to early 1995, was the first known example in Australia of an aviation fuel throwing a sediment. The fuel was JET A-1 which had been additised to the military specifications of NATO Code F-34. The JET A1 fuel had been refined in Singapore from a Chinese crude oil. The black coloured fuel that formed at low point drains in ten 162,000 litre fuel tanks, after several months of storage, caused significant military logistic problems. From investigations by the above laboratory, it was established that the fuel was storage unstable, a characteristic that was responsible for the black colouration of the fuel. The bulk fuel temperature at the base was 32°C and at this temperature, the sediment particulate matter was apparently being held as a stable colloid that gave the fuel its black appearance. This report describes the investigation of this incident and provides details of work done in an attempt to identify the cause(s) of the 'Black AVTUR' incident. A major finding from this research was that an antioxidant present in the AVTUR fuel lubricity improver additive is strongly implicated as a component involved in the formation of the jet fuel sediment molecules that were responsible for the quarantining of the contaminated fuel for several months, at the military air base.

INTRODUCTION

The 'Black AVTUR' incident that occurred at RAAF Base Townsville in late 1994 to early 1995 was a unique event for the Air Force. The formation in AVTUR (F-34, JP-8) of a black coloured sediment was without precedent in jet fuel supplied to the RAAF. The consignment of fuel involved was an imported JET A-1, having been refined in Singapore from a Chinese crude oil. The fuel supplier additised the JET A1 fuel delivery to NATO F-34 specification requirements. The formation of black coloured fuel, after about five months storage, resulted in ten 162,000 L

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fuel tanks, up to 75% of the total fuel storage capacity at the base, being held in quarantine. This threatened supply of fuel for scheduled joint military exercises. RAAF personnel requested its Quality Assurance organisation and the fuel supply contractors for assistance with the black fuel problem. After no satisfactory resolution could be found from these agencies, the RAAF approached AMRL for assistance in solving and rectifying the black fuel problem.

TECHNICAL RESOLUTION OF THE 'BLACK AVTUR' INCIDENT

Samples of black AVTUR submitted to AMRL for investigation, on arrival, were observed not to be black, but were light straw in colour with a dark sediment at the bottom of the container. Clearly the fuel colour had changed in transit due to settling and/or temperature reductions. When the black fuel at Townsville was cooled in a refrigerator it was reported that the fuel changed from black to clear, indicating the contaminant was in a stable suspension at high ambient temperatures that settled out on cooling. A visit was made to the base to establish the history relating to details of the receipt and handling of the fuel, and to conduct contamination measurements in the field. AMRL was advised that black AVTUR (F-34, JP-8) had been first observed by RAAF personnel during the regular low point drain checks routinely carried out for removal of water from the tanks. This was reported about five months after fuel delivery. The colour intensity resembled an Indian ink black, as shown in the photograph displayed in **Figure 1**.

The extent of particulate matter contamination in the F-34 fuel storage tanks was measured and these ranged from low point drains (42 mgL^{-1}), middle level (1.9 mgL^{-1}) and upper level (1.5 mgL^{-1}). The fuel colour at middle and upper levels varied in colour from orange through to pale to straw-brown, whilst fuel at low point drains was Indian Ink black. It was evident from fuel storage tank inspections and laboratory measurements that a stable colloid of fine black particulate matter was forming in the fuel and settling to the bottom. This was occurring at the low point drains at intervals of 2-3 days, in volumes of about 20 litres.

BLACK AVTUR - RAAF TOWNSVILLE

Bulk fuel storages -

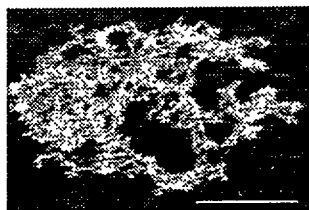
- left - August 94
- middle - December 94
- right - March 95

**75% fuel storage capacity
quarantined in March 1995
- threatened fuel supply to
military exercises**

**Particle clusters 25 micron
wide - rapidly blocked a 5
micron fuel filter coalescer**



**Bulk Fuel Temp: 32°C;
Humidity: 95%**



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Figure 1: Visual examples of the 'Black AVTUR' fuel that was forming at the low point drains in the tanks, and a SEM microphotograph of typical clusters of sediment being thrown by the fuel

As the bulk of the fuel above the low point drains was not black, the RAAF was considering using this fuel in aircraft. To determine whether the fuel could be cleaned up by fine filtration and used before significant quantities of particulate matter re-formed, a coalescer filtration unit was used to transfer 30,000 L of the upper level fuel to a road tanker. The fuel particulate concentration in the bulk fuel was reduced to 0.03 mgL^{-1} . After three days storage, the particulate level in the tanker increased to more than 1 mgL^{-1} , about a thirty-fold increase, indicating that this batch of fuel was extremely unstable in storage.

Although AVTUR with this level of contamination could have been used immediately after filtration, it was concluded that if an aircraft was refuelled with this fuel, and then for some reason was not flown for an extended period, air safety may have been compromised when the aircraft re-entered service, due to accumulation of sediment over time in the aircraft's fuel systems. The particulate level found in the fuel farm tanks at low point drains was about 40 mgL^{-1} . When this is expressed as a total amount of solid in aircraft fuel tanks, of the order of 4,000L volume, accumulation of about 160g of sediment was possible. The possibility of a slug of this sediment entering an aircraft fuel system was of particular concern, because of the very small tolerances in fuel metering systems and nozzle orifices, such as in the F/A-18 F404 engine (diameter $38 \text{ }\mu\text{m}$).

Nozzles orifices of this dimension could have readily been blocked by a surge of fuel possessing such high particulate levels.

This risk was assessed as being potentially dangerous and as a result of the AMRL technical investigation, the RAAF decided that the suspect fuel above the black fuel forming at the low point drains was unusable. The fuel supplier then accepted the AMRL finding that there was a storage stability problem associated with this imported aviation fuel, and that there was a responsibility to take remedial action. The fuel (1.5 million L) was removed by the original fuel supplier.

AMRL Research into the Cause(s) of the 'Black AVTUR' Incident

The black AVTUR sediment was initially analysed by Fourier Transform infrared (FTIR) spectrometry to investigate its chemical composition. The FTIR spectrum (Figure 2) of the Black AVTUR sediment was consistent with sediment from secondary refined diesel fuels [1-3]. The large, broad absorbance centred at about 3400 cm^{-1} has been attributed previously either to stretching vibrations of hydrogen-bonded aromatic hydroxyl or amino groups.

Elemental analysis of the 'Black AVTUR' sediment was carried out for carbon (C), hydrogen (H), nitrogen (N), oxygen (O) and sulphur (S), with the following results:

C = 63.7%; H = 7.6%; N = 3.3%; O = 15.7%; S = 3.1%

These sediment elemental values are generally typical of those from storage unstable diesel fuels that result from unhydrogenated light cycle oil (LCO) blending stocks. In particular, the very high oxygen content of such LCO-derived fuel sediments has been discussed in a publication [1] that involved experimental derivatisation of LCO sediment using the reagents benzoyl chloride and acetic anhydride. The mass of the sediment increased significantly, and the IR spectra of the reaction products indicated conversion of the bulk of the sediment to benzoates and acetates.

Black AVTUR FTIR Spectrum

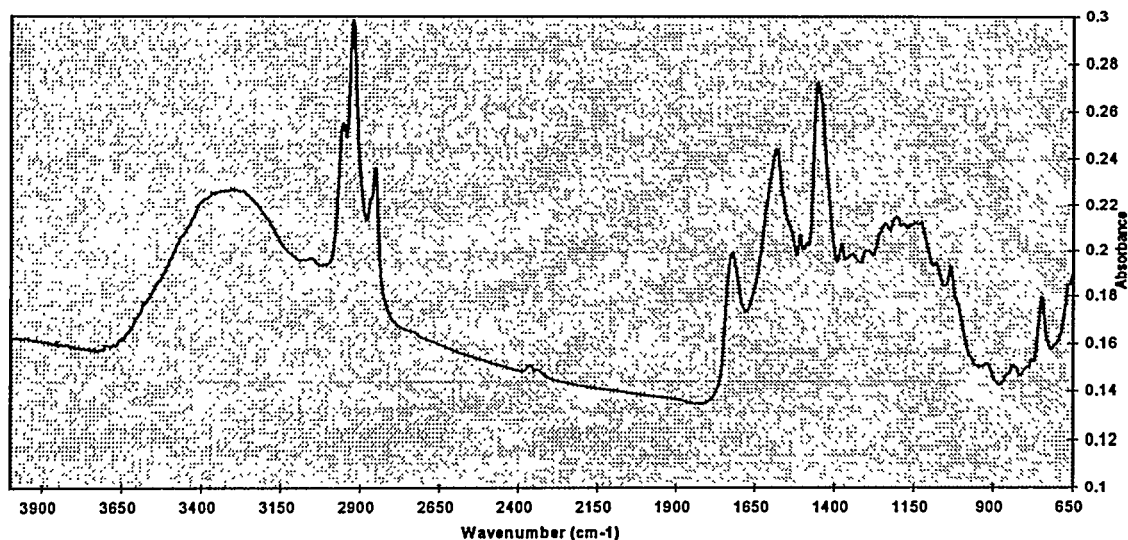


Figure 2. FTIR spectrum of the ‘Black AVTUR’ sediment exhibited IR absorbances that are characteristic of those published for diesel fuel sediments which form from unhydrogenated light cycle oil from the catalytic or thermal refinery cracker [1-3].

Conversion of indole species that may possibly exist in the sediment to amides was not indicated, while synthetic indolylphenalenone acid salt did convert to amide.

Blue-green coloured indolylphenalenone acid salts are very reliable indicators of insufficient hydrogenation of cracked stock in blends of LCO. However, it was concluded in that work that indolylphenalenone acid salts are not principal constituents of the total mass of fuel sediments. It was further concluded in that study that the broad FTIR peak at 3400cm^{-1} was attributable to aromatic hydroxyl groups from the fuel and not to amino species.

In the current study, it was therefore concluded that the chemical nature of the sediment from the black AVTUR was due, at least in part, to the presence in the fuel of unstable products of secondary refinery processing.

AMRL acquired a pyrolysis/gas chromatography/mass spectrometry (PyGCMS) facility to support investigation of the composition of the black fuel sediment. The intractable fuel sediment material that is shown in **Figure 1** is too involatile to be able to be examined by gas

chromatography (GC). To enable GC separation of sediment components, it was initially necessary to pyrolyse the sediment at high temperatures to volatilise the precursor molecules that had reacted in the fuel to form the solid deposit. This procedure could then lead to an attempt to elucidate potential precursor molecules in the fuel that may have been responsible for the 'Black AVTUR' incident.

Figure 3 demonstrates the capability of PyGCMS equipment to identify a candidate chemical participant in the formation of the black fuel sediment. The major component in the pyrogram was identified as an antioxidant from the fuel lubricity improver additive in the fuel. High precision in the spectral library match of the mass spectrum of the 4-amyphenol in the pyrogram was obtained. In **Figure 3**, the lower mass spectrum is from the electronic library. It was concluded that the presence of the 4-amyphenol, as a primary component of the sediment thrown by the 'Black AVTUR' sediment, was of synthetic origin. The smaller peak with an asterisk in **Figure 3** matched exactly with bis-2,4-amyphenol. A diagrammatic representation of chemical structures of the compounds identified is provided in **Figure 4**. It is rare in nature that a substituted alkylphenol derivative would be present, together with its related di-substituted derivative. Catalytic alkylation of phenols usually follows a chemical mechanism that leads to formation of a mono-substituted alkyl derivative, with minor amounts of the di-substituted derivatives being formed. It was on this basis that the 4-amyphenol was concluded to have been of synthetic origin. Several other alkylphenolic components were identified in the pyrogram, but none had related di-substituted homologues present.

In order to identify longer chain molecules in the Py/GC/MS pyrogram, which do not survive severe fragmentation caused by high voltage electron impact in the conventional electron impact (EI) mass spectrometric detector, AMRL has now acquired a soft ionisation source, namely a chemical ionisation (CI) source. This has now been trialed with standard organic chemicals, and has been found to work effectively. It can be seen from **Figure 5** that CI enhances the abundance of the molecular ion, at the expense of fragmentation seen in an EI mass spectrum. An example of the difference between EI and CI is shown in **Figure 5**, where the EI source (bottom picture) almost completely fragmented the decanoic acid methyl ester, giving only a very small molecular

ion at m/z 186, while the CI gave a large molecular ion (+ 1 for a hydrogen ion from the methane gas used in the CI source) at m/z 187.

Using a combination of electron impact and chemical ionisation detectors in the PyGCMS equipment, several longer chain alkylphenols were found in the pyrogram of the sediment. The presence of phthallic anhydride was also identified, indicating that cross-contamination of the fuel with phthallic acid esters, that are widely used as plasticisers of common plastics, may have occurred. At pyrolysis temperatures between 500-650°C, esters of phthallic acid would almost certainly be converted to phthallic anhydride. However, in recent investigations it has been found that phthallic anhydride, along with alkylanthracene and alkylphenanthrene, form the bulk of fuel thermal deposits from fuels that could not have been exposed to plasticisers [4]. The role of unreacted polycyclic fuel components in thermal deposits is being studied.

Treatment of 'Black AVTUR' with AMRL Fuel Stability Foam (FSF)

The 'Black AVTUR' was treated at 32°C (the bulk fuel temperature of the 'Black AVTUR' - refer **Figure 1**) with AMRL Fuel Stability Foam (FSF), to investigate the absorptivity of the foam for the sediment and the possible removal of sediment from the black fuel. The FSF removed the sediment from the fuel sample, indicating that the known benefits of storing diesel fuel in contact with FSF may be applied to aviation fuels such as that involved in the 'Black AVTUR' incident. AMRL is currently studying absorptivity of FSF to F-34 fuel additives to ensure that, should FSF be used to protect AVTUR from build-up of sediment in future, the essential additives would still be present in the fuel. If FSF is found to be compatible with AVTUR, the RAAF will install this material in large fuel storages in northern Australia as additional protection against future potentially storage-unstable fuels.

SUMMARY OF CONCLUSIONS

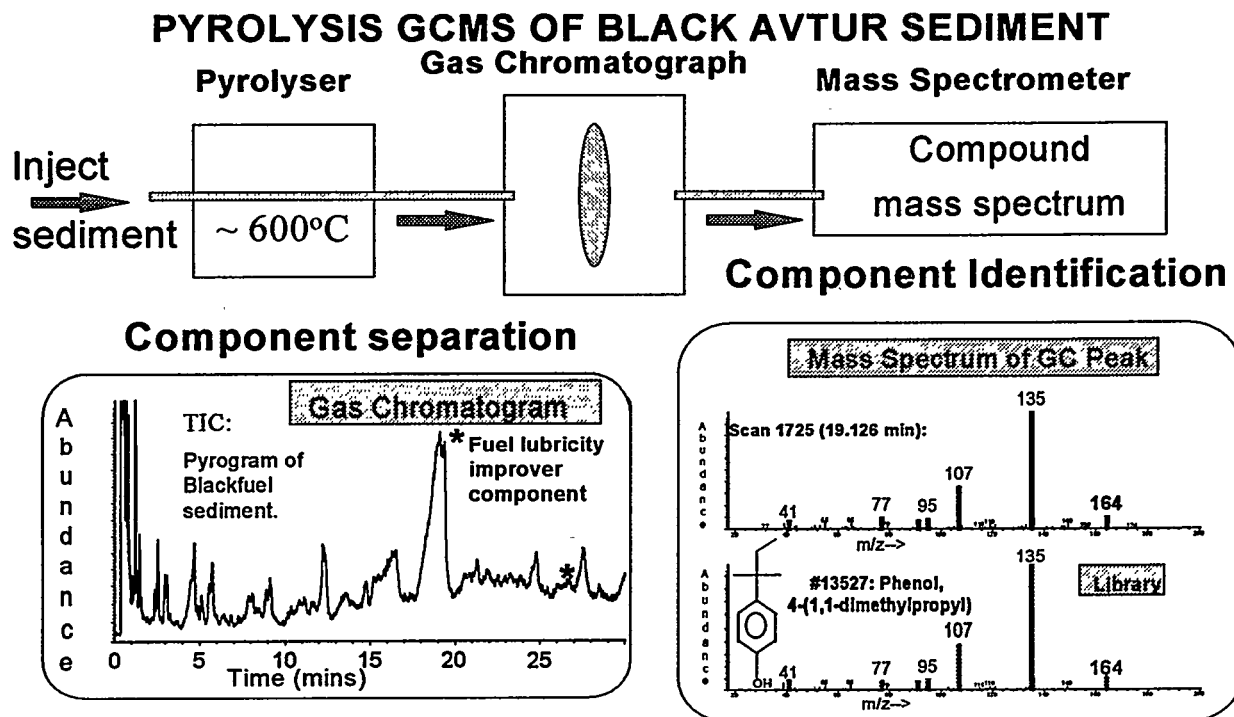
1. The 'Black AVTUR' incident at RAAF Townsville occurred due to storage instability of the F-34 aviation fuel.
2. The chemical nature of the sediment is indicative that at least part of the fuel had been derived through secondary refinery processing, similar to the manufacture of diesel fuel.
3. The elemental analysis and the FTIR spectrum of the fuel sediment were very similar in nature to that which forms in diesel fuel that contains unhydrogenated light cycle oil.
4. The major fuel sediment precursor component in a pyrolysis/gas chromatography/ mass spectrometry pyrogram of the sediment was identified as a phenolic antioxidant from the fuel lubricity improver additive in the fuel.
5. The 'Black AVTUR' fuel that shed sediment can be rejuvenated by contact with FSF.

PRINCIPAL AUTHOR'S COMMENT

It has been suggested by a peer reviewer of this paper that conclusion 4, above, conflicts with conclusions 2-3. Consistent with our previous report [1] that phenolic species are involved in the formation of the bulk of fuel sediments derived from fuel blends that contain partially or fully unhydrogenated, unstable light cycle oil (LCO), it is relevant that the lubricity improver antioxidant identified in the PyGCMS work above is also phenolic. Competition between phenolic molecules derived from the LCO and that from the antioxidant, in the formation of the sediment, has now been found to have been approximately 3:1. This estimate was derived by summation of areas of the phenolic species found in the PyGCMS pyrogram (homologous series of C₁, C₂ and C₃ phenols from the LCO) and comparing the total area of those peaks with the area of the peak identified as 4-amyphenol, the lubricity improver antioxidant. Thus, conclusions 2-3 and 4 are considered to be both internally consistent and synergistic.

REFERENCES

1. Power, A J and Mathys, G I. (1992). "Characterization of Distillate Fuel Sediment Molecules: Functional Group Derivatization", FUEL, 71, 903-908.
2. Green, J B, Stirling, K Q and Ripley, D L, (1991). "Storage Stability and Hydrotreating Chemistry of Phenolic Compounds Present in Mid-Distillate", 4th International Conference on Stability and Handling of Liquid Fuels, Orlando, Florida, USA, November 19-22, Ed H N Giles, Volume 2, 503-517.
3. Power, A J, (1986). "Accelerated Oxidation of Diesel Distillate", FUEL, 65, 133-137.
4. Power, A J, Rawson, P M and O'Connell, M G, unpublished results (draft in preparation).



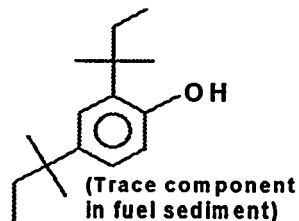
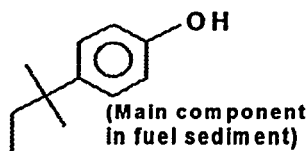
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Figure 3. Pyrogram of the 'Black AVTUR' sediment, in conjunction with GC/MS separation / identification of the volatilised constituents from the sediment, implicate the presence of an antioxidant associated with the fuel lubricity improver.

PYROLYSIS GCMS OF BLACK AVTUR SEDIMENT
SYNTHETIC AMYLPHENOL COMPONENTS IN LUBRICITY
IMPROVER SAME AS THOSE IN BLACK AVTUR SEDIMENT

4-(1,1-dimethylpropyl)phenol



2,4-bis(1,1-dimethylpropyl)phenol

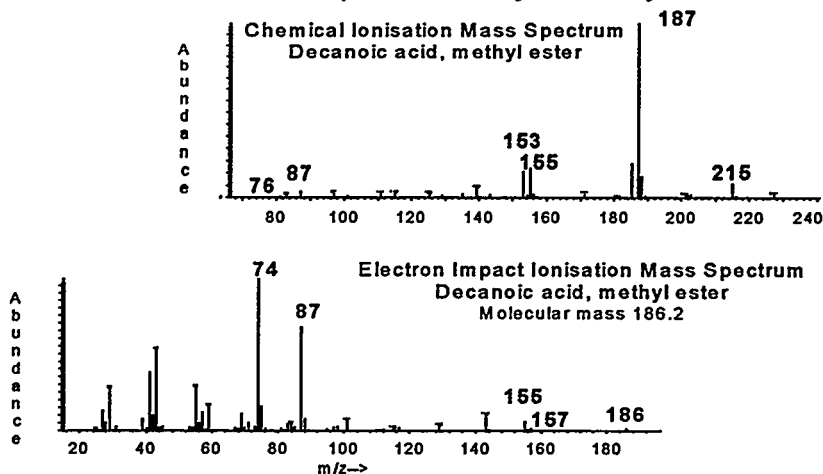
Presence of di-substituted phenol indicates that main component is synthetic

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Figure 4. Identification of the di-substituted derivative of the 4-t-amylphenol shown in Figure 3 indicated that these sediment components were of synthetic origin.

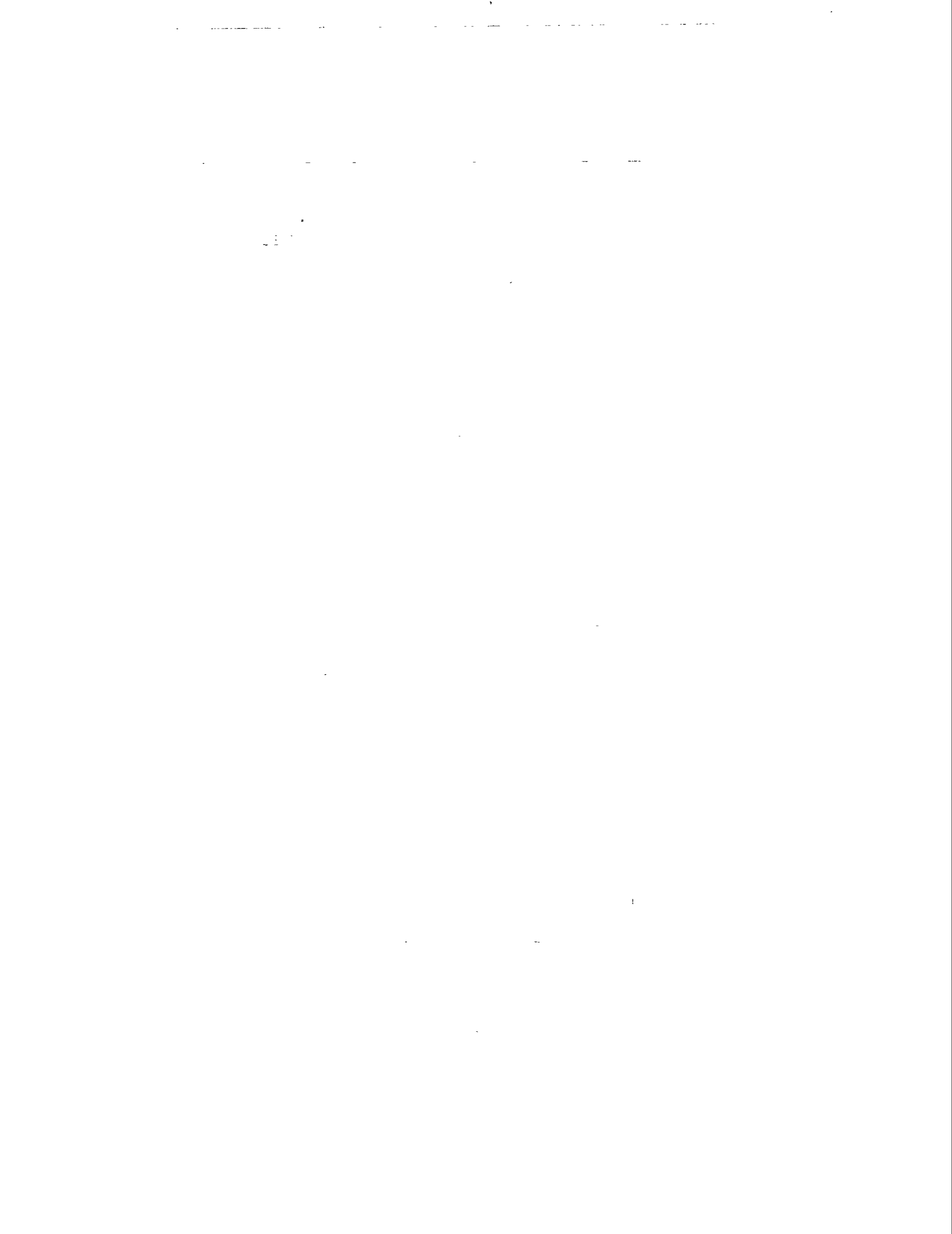
Comparison of Chemical & Electron Impact Ionisation
in the Mass Spectrometry of Fatty Acids



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Figure 5. An example of the facility for correlating long chain chemical components in fuel, as seen by the Electron Impact (EI) detector, compared with the soft ionisation technique using Chemical Ionisation (CI).



*6th International Conference
on Stability and Handling of Liquid Fuels
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JET FUEL CONTAMINATION BY DIESEL FUEL DYE

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An investigation of jet fuel contamination by diesel fuel dye in the USA has been coordinated by the Coordinating Research Council since April 1994. During that time the CRC was instrumental in getting the dye color changed from blue to red to avoid confusion with aviation gasoline. Subsequent to that change laboratory tests were conducted to establish the effect of red dye on specification properties with high temperature stability being the only affected property. Based on these results aircraft operation with dye-containing fuel was severely restricted by airframe manufacturers. The paper reviews the test results and traces the chronology of industry actions to control the problem.

Background

Regulations published by the U. S. Environmental Protection Agency⁽¹⁾ (EPA) on August 21, 1990 required that, beginning on October 1, 1993, on-highway diesel fuel contain no more than 0.05 m% sulfur. Diesel fuel containing more than 0.05% sulfur was to be identified by the visible presence of a blue dye, 1,4-dialkylamino-anthraquinone. Simultaneously the Internal Revenue Service⁽²⁾ (IRS) required the addition of the blue dye into diesel fuel or heating oil not subject to road tax. Following concerns by the aviation community about the possible misidentification of blue-dyed diesel fuel for 100 LL aviation gasoline, which is also dyed blue, both IRS⁽³⁾ and EPA⁽⁴⁾ changed the required dye to the solvent red 164 dye (alkyl derivatives of azobenzene-4-azo-2-naphthol), effective October 1, 1994. Currently EPA requires a "visible" dosage of red dye to be added to high sulfur diesel fuel (or high sulfur No. 2 heating oil), while the IRS minimum reference color strength dosage for color strength is 3.9 pounds per thousand barrels (PTB) of the solvent red 26 dye which is a better defined compound (methyl derivatives of azobenzene-4-azo-2-naphthol). The EPA dye level is to be added at the refinery, while the IRS dosage must be present when tax exempt fuel is delivered to the user at a refinery, at a terminal or at an import point. Although these requirements involve different fuel categories, sulfur levels vs. taxability, in practice

they tend to involve the same fuels in the U.S. Violation of either regulation involves heavy fines.

Neither regulation contains a dye requirement for aviation turbine fuel. Why then is there any concern in the aviation industry? The answer lies in the U. S. distribution system where differing fuels are not always physically separated from each other. Thus in large multi-product pipelines, different products follow each other with no separation. Cuts between products are usually made where there is a 50/50 mix of two products in the interface. The resultant interface is blended back into the product as long as the limited amount of mixed fuel does not drive either product off-specification. Mixing can also occur in manifolds, pumps and other shared components in pipelines as well as marine transports. Transport trucks which are not maintained in a single product can be another source of mixing. Because fuel appearance is a major component of aviation fuel quality control, particularly at airports, any discoloration due to diesel dye raises immediate questions regarding fuel acceptability by airframe manufacturers.

Industry Reactions

Subsequent to the issuance of the Federal regulations, the Boeing Company distributed an advisory letter⁽⁵⁾ to its customers prohibiting the operation of Boeing aircraft on fuel containing the red dye because of the unknown effects of dye on aircraft operation. McDonnell-Douglas⁽⁶⁾ issued similar prohibitions soon thereafter. These actions could result in shutting down an airport fuel system or running an airport out of fuel if any dye was found. For obvious reasons the actions caused major concerns among airlines and their fuel suppliers as no one had any way of forecasting the incidence of such contamination, but all agreed the results of airport shutdowns would be drastic.

Coordinating Research Council Activities

To answer a great variety of questions about dye effects on aviation turbine fuel performance, the Coordinating Research Council (CRC) organized a group to deal with the dye matter in June 1993. The Group membership is shown in Table 1. Among its first efforts⁽⁷⁾ was an objection to the IRS and EPA to the use of blue dye because of possible confusion with 100LL Aviation Gasoline which is the major aviation gasoline in the North American market. Instead the letter suggested the use of red dye and requested a red dye dosage of less than 3 PTB. (Although the 80 grade aviation gasoline is dyed red, there is

little, if any, of this product available in the U. S.) While the two government agencies agreed to the dye color change, the IRS rejected a reduced dosage because of a desire to detect blending of taxable and nontaxable diesel fuels.

The second step was a cooperative program to ascertain the effect of red dye on specification properties. As a point of clarification it should be noted that the IRS dosage is expressed in terms of solid red dye (solvent red 26), a pure material. Commercially red dye is handled as a liquid in a carrier solvent. Both active ingredients and total liquid dye concentrations, therefore, differ from the solid dye concentrations. Equivalent dosages and various concentrations of both dye versions are shown in Table 2. In the program, 12 organizations ran a variety of specification tests, with most participants concentrating on thermal stability. Testing was done on Jet A fuels containing the dye but no diesel fuel. Fuel samples were selected at random but all dye samples came from the same supplier. The program established that the full IRS fuel dye dosage for tax-free diesel fuel affected no commercial specification properties except thermal stability. In addition to the specification requirements, Rolls Royce⁽⁸⁾ and McDonnell-Douglas⁽⁹⁾ tested the effect of dye on engine and airframe elastomers as summarized in Table 3. The Navy⁽¹⁰⁾ found that the full dye dosage level gave higher readings in the Shipboard Contamination test than the neat fuel. (This test depends on light transmission through a wet membrane.) Tests by Boeing⁽¹¹⁾ showed the full IRS dosage to have no effect on freezing point or on turbidity at ambient temperatures.

Thermal stability was measured by conducting a series of Alcor JFTOT tests (ASTM D 3241) in which the control tube temperature was increased in 5°C steps until the test failed by exceeding the specification definition of either tube deposits or filter pressure drop. The minimum failure temperature was designated as the fuel break point. Dye effects were expressed as decreases in breakpoint temperature. Results are detailed in Table 4⁽¹⁰⁾. About 33% showed a breakpoint drop of 10°C or greater with the full dye dosage; a decrease of 5°C was considered within test repeatability. Four samples, which are shown in bold print, failed the specification minimum of 260°C tube temperature but passed the alternative ASTM D 1655 requirement of 245°C. However, two of these samples failed at 260°C without any dye.

The next step was to find the effect of reduced dye dosages. Those laboratories whose product in the first round had the 10°C or higher decrease repeated the testing with a 10% red

dye concentration. (Fuel samples J-7 and K-8 had been depleted in the earlier testing.) Those results are listed in the last column of Table 4. Although a number of fuels now showed no dye effects at the 10% dye level, 4 out of 10 samples still reflected a significant adverse effect of the red dye at this level. In addition, five laboratories ran additional fuels with wider concentrations of dye as shown in Table 5⁽¹²⁾. Here again, the higher dye dosages caused three of the fuels to have break points below 260°C.

At this point some comments on the program are in order. Fuel samples were selected at random. Although none of the fuels failed specification requirements even with the full IRS dosage, none of the fuels were a marginal pass in the absence of dye. Lastly, the testing did not include the effect of diesel fuel addition, although field contamination would normally take place through the inadvertent addition of dyed diesel fuel. The JFTOT results therefore raised a warning flag without answering the question of what was an acceptable industry maximum of dye contamination.

Field Problems

Over the history of red dye addition to specific grades of diesel fuel, quite a number of cases of dye-contaminated jet fuel occurred. Thus for the first half of 1996, one airline reported 22 cases of dye-contaminated product, including 4 cases where such product was received into airport storage. The remaining incidents were detected further upstream in the system. Most incidents involved tank truck deliveries, but several of the larger volumes were pipeline deliveries to an airport. In the last three years one airport in Alaska had to be shut down, but several other airports only avoided closure because not the entire receiving storage was contaminated. These cases included Dulles, LaGuardia and Miami Airports. At Boeing Field, Seattle, eight aircraft were fuelled with dye-contaminated fuel and had to be defuelled, but an alternate fuel system allowed other operations to continue.

Field Detection of Dye

The contamination incidents graphically illustrated differences in detection methods. At refineries and terminals product appearance is normally checked by the Clear and Bright or bottle test (ASTM D 4176), while airport personnel look at product appearance with the White Bucket test⁽¹³⁾, using a white porcelain bucket. In the former color is determined by transmitted light through about 100 mm of product, while in the latter appearance is judged by transmitted and reflected light through about 150 mm of fuel. In addition the white bucket

rating includes a significant surface area integration factor. Comparisons have shown the white bucket to be more sensitive to red dye contamination than the Clear and Bright test, with a lower detectable level in the white bucket being about 1 volume of fuel dyed to the IRS minimum level in 3000 volumes of water-white jet fuel, although some have reported even lower detectable levels with this test⁽¹⁴⁾.

However, both methods are subject to human judgment and an early CRC initiative was to encourage the development of a field meter capable of measuring these low dye levels. Such a meter is now available in the PetroSpec JT 100 and has been submitted to ASTM for standardization.

Industry Remedies

Pipelines and other fuel handling organizations have concentrated on eliminating contamination as much as possible. One major improvement has been a change in the injection points for the IRS dosage. Originally, the full IRS dye dosage was injected at the refinery to minimize the number of injection points. This practice created two problems. When dyed fuel preceded or followed jet fuel, normal cuts could not be made at the middle of the interface but had to be made where the interface mix was almost 100% jet fuel, resulting in a substantial loss of jet fuel. Refinery injection also meant handling a highly dyed fuel which could contaminate jet fuel in manifolds, pumps and other shared parts of the system. As of July 1996, the IRS dosage is now injected at the receiving terminals of two major pipelines. While this has reduced the problem, it does not eliminate it because the EPA dosage (roughly 25% of the IRS requirement) must still be injected at the refinery. Pipeline problems are compounded by the fact that the low sulfur, taxable diesel fuel cannot show any dye either, thereby limiting which products can follow or precede the dyed product.

Almost from the beginning, the airline industry has been searching for ways of avoiding airport shut downs. Early on it was proposed to the engine manufacturers that fuel containing a maximum of 2.5% dye or 0.40 mg liquid dye per liter be acceptable on an emergency basis and that a maximum of 0.5% (0.08 mg/L) be acceptable on a continuous basis. These proposals have not been agreed to at the date of this writing. A partial resolution has been made by a Boeing Service letter ⁽¹⁵⁾ which accepts fuel that does not show color in the White Bucket test. Such fuel is considered equivalent to satisfactory fuel made before the existence of the dye problem. However, the service letter does not answer the airline request

for an acceptable dye level which would avoid airport shutdowns. Being a high temperature problem, that answer has to come from the engine companies.

One engine company, General Electric, has conducted a 12 hour accelerated cycle test program with a CF6-80C2 engine and Jet A fuel containing 5% of the minimum IRS dosage of red dye or 0.80 mg of liquid dye per liter⁽¹⁶⁾. The thermal stability of this fuel by JFTOT exceeded the specification minimum by 30°C. The 12 hour program was followed by 44 hours of engine running on neat fuel to calibrate the test stands. Nozzle performance was checked at the beginning and the end of the dyed fuel testing for 15 of the 30 engine nozzles. Also at the end of the 44 hour test the same 15 nozzles were exercised on the flow stand and reevaluated. Out of the 15 fuel nozzles, 5 showed no degradation at the test's end, 6 were affected during the program but returned to normal performance after 44 hours on neat fuel, two were affected but showed only partial recovery and two nozzles did not recover original performance. In each case only the secondary flow schedule was affected and this at the point where the secondary nozzle flow started. It was, therefore, concluded that the dye was starting to cause deposits to form on the wall of the secondary orifice slot. These results are expected to play a major part in determining any decision regarding emergency operation.

Future Actions

Apart from eliminating the dyeing of certain diesel fuels, an extremely unlikely scenario, the development of an acceptable dye level for continuous engine use appears to be at least a partial solution. The Southwest Research Institute has proposed a program to develop such a dye limit. Each major engine manufacturer would select a critical fuel injector nozzle. As the hottest component in the engine fuel system, nozzles tend to be the most sensitive part of the fuel system. Four different nozzle feed arm and nozzle bodies would be subjected to heated air flow to duplicate severe engine conditions. These nozzles are identified in Table 5. Fuel would pass through the nozzles once and would not be burned. New nozzles would be used for each test run and every nozzle would be run in duplicate. Test variables would include air temperature, initial fuel temperature (fuel preheating), fuel quality and dye contamination levels in the presence and absence of diesel fuel. Nozzle condition would be checked by monitoring flow rate and pressure drop. Fouling life would be defined as the time required to obtain a 10% decrease in flow rate. Based on test results from each engine manufacturer's nozzles, a mutually acceptable maximum dye concentration would

be agreed upon. Consideration is also being given to the inclusion of servo valves from engine fuel controls as another sensitive engine component.

An important part of the program would be an extensive evaluation of a number of high temperature laboratory test procedures. The procedures are to include the JFTOT, the Shell HiRenTS test and the Southwest Institute Short-Tube, High-Heat-Flux Deposition Rig. In addition the JFTOT tube deposits will be rated by at least two different procedures. A comparison of these test results with the nozzle fouling results should lead to the validation of one or more of the tests which could then serve as a future high temperature screening test or possibly even a specification requirement.

Fuel handling organizations will have to continue to tighten their procedures to avoid any dye contamination of jet fuel. If contamination is found, a quantitative device should be used to accept or reject the fuel, a more acceptable approach than exists today.

Altogether the dye contamination problem has once again highlighted the need for constant attention to quality control in the handling of aviation turbine fuels.

Acknowledgements

The release of the CRC data cited above is greatly appreciated, but it should be emphasized that the comments, observations and conclusions in the paper represent only the author's own opinion and not those of any other organization or individual.

References

- (1) Federal Register/ Vol. 54/ pp 35276 & following/ August 21, 1990,
- (2) Federal Register/ Vol. 58, No. 228/ pp 63069 - 63080/ Nov. 30, 1993
- (3) Dept. of the Treasury, IRS, 26 CFR Part 48, RIN 1545-AP48; 1545-AS32, Diesel Fuel Excise Tax; Dye Color and Concentration; Final Regulation
- (4) Environmental Protection Agency, 40 CFR Part 80, Regulation of Fuels and Fuel Additives; Fuel Quality Regulations for Highway Diesel Fuel sold in 1993 and Later Calendar Years, Interim Final Rule, July 5, 1994
- (5) Boeing Service Letter, dated 29 August 1994
- (6) All Operator Letter by McDonnell Douglas, subject: Aircraft Use of Dyed Fuels, dated 23 August 1994
- (7) Letter of W. F. Taylor to Margaret M. Richardson, IRS Commissioner, of June 23, 1993
- (8) Unpublished CRC data of December 6, 1994

- (9) Douglas Aircraft Company, Materials and Process Technology Laboratory Report
No. 18112, dated 4/19/96
- (10) Unpublished CRC data of 10/26/1994
- (11) Unpublished CRC data of 10/11/95
- (12) Unpublished CRC data of 4/26/95
- (13) R. Waite, ed. *ASTM Manual MNL 5*, second edition, American Society of Testing and
Materials, Philadelphia, PA, June 1995, pp. 1-2.
- (14) Unpublished CRC data of 6/25/96
- (15) Boeing Service Letter, dated 22 November 1996 (amending Service Letter of 29 August
1994)
- (16) Unpublished CRC data of 6/25/96 and 12/10/96

Table 1

Membership of CRC Group on Dye in Aviation Turbine Fuel

K. H. Strauss, leader	Consultant
R. D. Anderson	Facet International
F. Barnes	Chevron Products
Y. Barshad	Applied Analytics
T. B. Biddle	Pratt & Whitney Aircraft
G. J. Bishop	Shell International Petroleum
K. Bower	Defence Research Agency (MOD)
J. E. Brown	Colonial Pipeline
S. Bullock	Rolls Royce
J. C. Callison	Amoco Oil
S. E. Casper	United Airlines
P. David	BP Oil International
W. G. Dukek	Consultant
W. L. Easton	Federal Aviation Administration
D. A. Fabry	Ashland Petroleum
H. Gammon	Gammon Technical Products
R. M. Garrett	Exxon Company USA
R. L. Gray	Defense Fuel Supply Center
O. J. Hadaller	Boeing Commercial Airplane Group
D. Hardy	Naval Research Laboratory
C. P. Henry	Octel America
A. Holden	British Airways
D. H. Hoskin	Mobil Technology
C. Tsao-Chin Huang	Pennzoil Products
R. Kamin	Naval Air Warfare Center
J. Kuebrich	Arco Products
R. Leisenring Jr.	Texaco
P. Liberio	U S Air Force
R. P. Lohmann	Pratt & Whitney Aircraft
J. E. McGettrick	Arco Products
S. McLemore	Delta Air Lines
J. W. Muzatko	Chevron Products
R. J. Organ	Caltex Petroleum
K. Polk	Hammonds
S. Seto	GE Aircraft Engines
W. Spitzley	Total Petroleum
C. Taucher	American Airlines
W. F. Taylor	Exxon Research & Engineering

Table 1 (continued)

Membership of CRC Group on Dye in Aviation Turbine Fuel

R. D. Tharby	Consultant
M. Thom	Allied Signal Aerospace
R. G. Thompson	Phillips 66
B. Visser	Shell Oil Products
R. Waite	Velcon Filters
G. Wendtland	Buckeye Pipeline
G. Wilson	Varlen instruments

Table 2
RED DYE CONCENTRATIONS IN DIESEL FUEL

Active Ingredient Basis

Percent of required red dye in non-taxed diesel fuel	Solid*	Liquid**	Solid*	Liquid**
	Lbs/1000 Bbls		mg/Liter	
100% (minimum IRS dosage)	3.9	5.6	11.1	16.0
50%	1.95	2.8	5.55	8.0
20%	0.78	1.12	2.22	3.2
10%	0.39	0.56	1.11	1.6
2.5%	0.098	0.14	0.28	0.40
2.0%	0.078	0.11	0.22	0.32
1.0%	0.039	0.056	0.11	0.16
0.5%	0.019	0.028	0.055	0.08

* Solid Red Dye SR 26 (active ingredient)

** Liquid Red Dye (estimated active ingredient)

Table 3

Elastomer Tests with Red Dye

	Dye Dosage	Effect
Airframe Materials⁽¹⁰⁾		
Sealant: DMS 2082, PR 1422 B-2	0, 0.08, 0.4, 0.8mg/L	none on adhesion to primer
Elastomers		
DPM 3710-70, MIL-R-6855, Class 1	same	none on hardness or volume change
DPM 3713-1, MIL-R-83248, Type 2, Class 1	same	none on hardness or volume change
DPM 3717, MIL-R-25988, Class 1, Grade 60	same	none on hardness or volume change
Fuel bladder: BTC 101	same	none on tensile strength or elongation
Tank coating: DMS 1580, composition A and C	same	none on adhesion or film hardness
Engine Materials⁽¹¹⁾		
-113 O-rings	0, 16 ppm	
Nitrile		none on swell or embrittlement
Silicone		none on swell or embrittlement
Fluorocarbon		none on swell or embrittlement
Fluorosilicone		none on swell or embrittlement

Table 4
**Thermal Stability Effects with Red Dye
 Break Points by Alcor JFTOT, °C**

Laboratory-Fuel No.	Liquid Dye Dosage		
	0mg/L	16.0 mg/L*	1.6 mg/L**
A-1	360	270 (-90)	285 (-75)
B-1	375	335 (-40)	375 (0)
C-1	350	350	-
D-1	295	300 (+5)	-
D-2	295	295	-
E-1	290	265 (-25)	280 (-10)
E-2	265	245 (-20)	250 (-15)
F-1	290	280 (-10)	285 (-5)
G-1#	282	280 (-2)	-
H-1	295	285 (-10)	285 (-10)
H-2	315	320 (+5)	-
I-1	300	285 (-15)	300 (0)
I-2	290	275 (-15)	280 (-10)
J-1#	293	293 (0)	-
J-2#	293	293 (0)	-
J-3#	293	293 (0)	-
J-4#	274	274 (0)	-
J-5#	274	268 (-6)	-
J-6#	274	282 (+8)	-
J-7#	304	293 (-11)	-
J-8#	277	268 (-9)	-
J-9#	268	260 (-8)	-
K-1	285	280 (-5)	-
K-2	290	285 (-5)	-
K-3	295	290 (-5)	-
K-4	290	290 (0)	-
K-5	250	250 (0)	-
K-6	255	255 (0)	-
K-7	260	260 (0)	-
K-8	265	255 (-10)	-

* Minimum IRS dosage for tax-free diesel fuel

** 10% of minimum IRS dosage

Run at 5°F intervals

Notes: Numbers in parentheses indicate change in breakpoint after dye addition.
 Bold numbers indicate breakpoints below 260°C.

Table 5
Thermal Stability Effects with Reduced Red Dye Levels

Laboratory-Fuel No.	Break Points, °C			0.16 mg/L##
	0 mg/L	1.6 mg/L* 1.6 mg/L**	0.40 mg/l#	
Liquid Dye Concentration				
A-2	290	250 (-40)	250 (-40)	285 (-5)
C-1	350	-	350 (0)	350 (0)
C-2	270	-	260 (-10)	260 (-10)
E-3	275	250 (-25)	265 (-10)	-
E-4	265	245 (-20)	250 (-15)	-
F-2	295	-	290 (-5)	290 (-5)
H-3	285	-	280 (-5)	285 (0)
H-4	275 ^a	-	290 (+15)	285 (+10)

* Minimum IRS dosage for tax-free diesel fuel

** 10% of minimum IRS dosage

2.5% of minimum IRS dosage

1% of minimum IRS dosage

^a Possible reporting error

Notes: Numbers in parentheses indicate change in breakpoint after dye addition.

Bold numbers indicate breakpoints below 260°C.

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IMPACT OF CAUSTIC TREATING ON THE FILTERABILITY OF JET FUEL

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ABSTRACT

Demand for jet fuel in Australia continues to increase, and refiners are seeking low-cost means of expanding their production capability. An existing caustic treater may be undersized and act as a production bottleneck. When the caustic treater is limited by flow rate and the jet fuel has minimal acidity, caustic treatment of only a part of the jet fuel is an attractive option. An Australian refinery performed refinery trials with the aim of proving that this approach could increase its jet fuel production. Filterability of jet fuel was severely affected, and electrical conductivity became more sensitive to light-induced decay. The filterability problems were caused by traces of sodium and calcium naphthenates in the fuel. A filter blocking tendency test was developed, and became an essential tool for developing a modified processing scheme which now produces 50% more jet fuel. During refinery trials, the filterability test minimised filtration problems at distribution terminals and airports, and it continues to serve a useful quality control role. Salt driers, located between the caustic treater and refinery storage tanks, acted as reservoirs for the filter blocking agent, which was released intermittently into jet fuel. Complete segregation of one of the salt driers from the caustic treater provided a simple means of eliminating the filterability problem.

INTRODUCTION

Demands for transport fuels in Australia continue to increase steadily, with jet fuel experiencing the highest percentage growth. Consequently, Ampol's Brisbane refinery has increased its crude oil distillation capacity by 40% during the past decade. By the mid-1990s, the flow rate of kerosine (unfinished Jet A-1) from the crude distillation units exceeded the capacity of the Jet A-1 caustic treating unit. The caustic treater, which removes traces of organic acids from kerosine to produce Jet A-1, therefore imposed a bottlenecking limit on jet fuel production. A new caustic treater would have required capital expenditure of several million dollars, so a team of engineers and chemists took up the challenge of finding a low-cost means of increasing the refinery's jet fuel production.

Although the prime function of the caustic treater is removal of traces of organic acids, the Jet A-1 acidity specification (< 0.015 mg KOH/g by ASTM D3242) was not limiting the maximum possible flow rate through the caustic treater. Instead, this limit was set by residence time considerations in the caustic settling vessel. Jet fuel flow rates exceeding the limit did not provide enough time for effective separation of the water and hydrocarbon liquid phases. At high jet fuel flow rates, traces of naphthenic acid salts from the caustic treating process could contaminate the treated jet fuel and downstream vessels and tanks, instead of remaining in the waste water phase.

Bypassing some of the kerosine stream around the caustic treater was suggested as a simple means of overcoming the bottleneck. Jet A-1 production would then be a mixture of say 70% caustic treated and 30% untreated jet, with the 30% bypass stream representing increased production. While appealingly simple in concept, implementation of this strategy was difficult, because of unforeseen effects on filterability and electrical conductivity.

JET FUEL PRODUCTION AND SPECIFICATIONS

Figure 1(a) shows the process scheme used for production of Jet A-1 at Ampol's Brisbane refinery prior to implementation of the process changes described in this paper. Figure 1(b) shows the current, improved process scheme. In the original scheme, kerosine rundown from two crude oil distillation units was combined and fed to a caustic treater/settler, followed by a water washing/settling vessel. Hazy (wet) jet fuel from the water wash was split into two streams and directed to two salt driers in parallel. Conductivity additive was injected after the salt driers, and finished jet fuel was directed to refinery tankage. Both the previous and the revised processing schemes are relatively simple, and do not include hydrodesulfurisation, Merox treatment for mercaptan removal, or clay filtration for removal of surfactants.

Ampol's Brisbane refinery is constrained to process only low sulfur crude oils. This has two consequences for jet fuel acidity. First, the average acidity of the kerosine fraction *prior to* caustic treating is 0.011 mg KOH/g, comfortably below the specification limit of 0.015 mg KOH/g. Second, none of the usual crude oils processed has acidity which greatly exceeds the

average. Hence, there appeared to be scope for bypassing a substantial proportion of kerosine around the caustic treater (as much as 100%) on a virtually permanent basis.

Prior to proceeding to refinery trials, laboratory blends of caustic treated and untreated (bypass) jet fuel were prepared from two refinery crude slates. The first of these crude slates contained 80% of Gippsland crude oil, which up to the mid-1990s, had been the refinery's principal feedstock. The second crude slate contained 77% Kutubu crude, which became the refinery's principal feedstock in the mid-1990s. In addition to acidity, properties which may depend on caustic treatment - via more subtle chemical effects - were also tested. These included copper and silver corrosion (ASTM D130 and IP 227), water reaction (ASTM D1094), mercaptan sulfur (ASTM D3227) and microseparometer rating (ASTM D3948). The results are shown in Table 1. It was concluded that for these two cases, Jet A-1 could have been produced with no caustic treating (100% bypass of the caustic treater). Table 1 provided the basis for proceeding to refinery production trials. The refinery trials confirmed the conclusions made from Table 1, but revealed two unforeseen quality problems:

- severe filter blocking problems occurred in terminal and airport filter/separators, and
- electrical conductivity was rendered more susceptible to light-induced decay.

FILTERABILITY

Jet fuel specifications do not contain explicit filterability requirements. Instead, high filterability quality is ensured by the presence of filter/separators in the distribution chain [1]. Filter/separators contain coalescer cartridges, which have the dual function of (i) removing dirt, and (ii) coalescing fine particles of water so that they settle or are separated from jet fuel by downstream separator cartridges. Jet A-1 produced by Ampol's Brisbane refinery during caustic wash bypassing trials passed all required specification tests, but caused severe reduction in the life of coalescer cartridges in filter/separators in the distribution system. In the worst instance, costly coalescer cartridges had to be replaced after a jet fuel throughput of only about 0.5 ML. This is only a few per cent of the normal total throughput (20 - 30 ML) before replacement is required because of pressure drop considerations.

Following the first notification of filterability problems, one of the blocked coalescer cartridges (Facet CA 43-3) from a distribution terminal was cut open for examination. Visual inspection indicated that it was free of gross contamination. In fact, the critical glass fibre element appeared to be remarkably clean. However, examination under a microscope (x40) revealed a layer of greasy material of thickness about 100 µm embedded in the upstream surface of the glass fibre element, which has thickness of about 700 µm. Fourier transform infrared (FTIR) analysis of the greasy material gave strong peaks at 1575, 1539, 1112 and 720 cm⁻¹, characteristic of salts of naphthenic acids. When dried to remove water and jet fuel, the contaminant hardened to a grey/brown solid. Semi-quantitative x-ray analysis in a scanning electron microscope (JOEL JXA 840A electron probe microanalyser) showed high concentrations of calcium, together with substantial peaks for chlorine, magnesium, sulfur, potassium and sodium.

Very similar FTIR and electron probe microanalysis results were obtained for:

- light brown solids filtered from jet fuel with high filter blocking tendency, produced during subsequent refinery trials,
- solids recovered from emulsion material present in the water phase of the refinery's water wash vessel, and
- solids recovered from emulsions on the surface of the rock salt and its gravel support bed in the salt driers.

A further identifying characteristic of this material is its distinctive odour, which is particularly persistent after it comes into contact with human skin.

It was concluded that the filter blocking material was a mixture of jet fuel, water and:

- sodium naphthenates and phenolates, formed when sodium hydroxide reacted with naphthenic acids and phenols (constituents of crude oil) in the caustic treater;

- calcium and possibly magnesium naphthenates, formed in the caustic treater. Brisbane's hard town water, used for diluting the commercial-grade caustic soda used in the refinery process, was the source of the calcium and magnesium; and
- lesser concentrations of inorganic salts such as sodium chloride.

These naphthenic acid salts are extremely strong agents for blocking glass fibre filters, including coalescer cartridges. They appear to have a strong affinity for glass fibres, and are trapped as a greasy layer embedded among the fibres, near the upstream surface. During bypassing trials, concentrations as high as 12 mg/L of naphthenic acid salts were intermittently entrained in jet fuel, necessitating special filtration of the fuel prior to its release from the refinery. So potent are these salts that we estimate that their concentration has to be kept below 0.2 mg/L to guarantee acceptable life for coalescer cartridges.

Refinery trials and mechanisms of fuel contamination

After investigating the first reports of filterability problems, there was ample evidence to indicate that the filterability problems experienced in the distribution system were a direct consequence of the first refinery caustic treater bypassing trial. However, the detailed mechanism by which the contamination occurred was far from clear. The central idea of the bypassing strategy was to *reduce* the carryover of emulsions containing salts of naphthenic acids and phenols, by allowing a longer residence time for phase separation in the caustic settling and water wash vessels. The intention of the refinery was to bypass about 30% of the total jet fuel production around the caustic treater, enough to have a strong beneficial effect on separation of the water and hydrocarbon phases in the caustic-wash and water-wash vessels.

Over a nineteen month period ending in mid-1996, eight refinery trials were conducted to develop an understanding of the mechanism by which the filterability of jet fuel had been so badly affected during the initial trial. The fact that it took a total of eight trials is a true reflection of the frustration involved in studying trace-component chemical reactions on a refinery scale. For example, in laboratory experiments, chemists ensure that reaction vessels are clean prior to experiments, but this is impractical for refinery production trials. Also, in laboratory-scale experiments, it is not too difficult to ensure homogeneity of products and

intermediates. The caustic bypassing trials involved flow rates of jet fuel of up to 1300 t/day, with the possibility that the contaminant was being introduced into the jet fuel intermittently. Hence, even with intensive and extensive sampling, there was always some doubt about the accuracy of surveys of contaminant concentrations.

After the initial refinery trial, several mechanisms were proposed to explain the disappointing outcome. These formed the basis for future trials, from which new or refined mechanisms arose. Among the possible mechanisms considered were:

- Existing sediments in the refinery's jet fuel storage tanks (or perhaps in downstream terminal tanks) were "solubilised" by the partly caustic-treated jet fuel produced during the trials. It was known that emulsions containing naphthenic acid salts accumulate on the floors of refinery jet fuel tanks even in the absence of refinery trials, necessitating tank cleaning every two years. When downstream filterability problems were experienced after the bypassing trial, there was speculation that the subtle change in jet fuel acidity could be responsible for entraining traces of these sediments in the jet fuel during the tank mixing process.¹
- Naphthenic acids in the untreated jet fuel were reacting with sodium chloride in the salt driers. This potential mechanism arose from a 1977 Chicago conference paper on fuel treating processes. It states that some crudes, *eg.* Trinidad, contain troublesome naphthenic acids in their straight-run middle distillates, and that problems arise from the formation of sodium naphthenate when contacted with sodium hydroxide during refinery treating, or when contacted with salt water during shipment.
- Existing sediments in the salt driers were being released into jet fuel by the bypassed jet fuel, either because of subtle changes in the overall acidity and/or surfactant properties of the jet fuel, or by introduction of a higher concentration of water² in the jet fuel entering the drier.

¹ Tank mixing to ensure homogeneity for quality certification is accomplished by 600 mm propellers rotating at 420 rpm, mounted on the tank wall near the tank floor. A slow movement of the entire tank of jet fuel is induced, but in the vicinity of the mixer, the movement of jet fuel is fast enough to move floor sediments.

² Kerosine (untreated jet fuel) from the crude distillation units contains about 1600 mg/kg of water from steam stripping to control flash point. The water concentration is reduced to about 400 mg/kg by passage through the caustic and water wash vessels. Bypassing therefore raises the concentration of water in jet fuel entering the driers.

- The most potent filter blocking species were the calcium and magnesium salts of the naphthenic acids, with sodium naphthenate being less of a problem. This led to speculation that relief from the filtration problems could be available by switching from town water to demineralised water for dilution of caustic soda.
- Contamination of jet fuel was occurring intermittently, and particularly when the water in the water wash vessel was dumped and renewed³.

Development of a filter blocking tendency test

Development of a jet fuel filter blocking tendency test was essential for determining which of the proposed mechanisms were in fact occurring, and to maintain customer satisfaction with the quality of the jet fuel. Standard test method ASTM D2068 *Filter Blocking Tendency of Distillate Fuel Oils* was adapted in the following manner:

- The filter element is cut from a commercial Facet CA 43–3 coalescer cartridge, using just the finest porosity glass fibre membrane, with nominal porosity of 0.5 µm. A single cartridge provides enough filters for thousands of tests, enough to last a laboratory for many years. Selection of this filter membrane was attractive because it provided a direct comparison with the field coalescer cartridges which had been so strongly affected by small concentrations of naphthenates in jet fuel.
- A jet fuel flow rate of 60 mL/min for 10 minutes is used, compared with 20 mL/min for 15 minutes for ASTM D2068. This provides greater sensitivity for detection of fuel contaminants.

A numerical value is obtained for the filter blocking tendency (FBT) of the jet fuel sample by using the appropriate equation:

$$\text{FBT} = [1 + (P / 105)^2]^{1/2}$$

³ Water was changed three times each day. When fresh water is admitted to the vessel, the flow rate of jet fuel entering the salt drier increases substantially.

where P (kPa) is the final pressure recorded after passage of 600 mL of jet fuel, or

$$\text{FBT} = [1 + (600 / V)^2]^{1/2}$$

where V is the volume recorded in cases when the pressure reaches 105 kPa prior to passage of 600 mL of fuel.

Table 2 shows the classifications for jet fuel filterability quality. This classification system was developed by direct correlation (Figure 2) of the total throughputs that were achieved through the field filter/separator between Ampol's Brisbane refinery and its products distribution terminal. It can be seen that jet fuel with an FBT rating of 1.002 - 1.003, which is the typical normal high quality, will allow the coalescer to pass more than 30 ML of jet fuel before replacement is required. On the other hand, if fuel of marginal quality (FBT = 1.005) passes through the coalescer, cartridges will have to be replaced after only about 10 ML of fuel has passed. Hence, this small increase from 1.002 to 1.005 in filter blocking tendency will increase the total cost of coalescer cartridges consumed by a factor of three.

Also shown in Figure 2 are the results of laboratory runs through the FBT test apparatus, in which we simulated a field filter/separator running until the differential pressure rose to 105 kPa, the pressure at which new cartridges must be introduced. These tests required the laboratory rig to be run for long times, especially for higher quality jet fuel. The simulated throughput for a commercial cartridge was calculated by scaling-up the laboratory throughput by a factor corresponding to the ratio of surface areas of the commercial coalescer cartridges and the laboratory filter. It can be seen that this predicts a shorter life (lower throughput) for coalescer cartridges than is actually obtained in field units. This serves to highlight the importance of directly correlating laboratory data against field experience when developing laboratory tests for fuel quality.

Benefits and conclusions derived from the filter blocking tendency test

The jet fuel filter blocking tendency test was progressively refined and used intensively during the eight refinery trials. This eventually led to a successful introduction of the caustic treating bypassing strategy and a 50 % increase in the refinery's jet fuel production capability. It

required only a very modest capital investment when compared with the cost of a new caustic treating plant.

The following conclusions were reached with respect to the proposed mechanisms discussed above:

- Filter blocking naphthenates residing in the salt driers were a particularly significant cause of the poor filterability of jet fuel produced during trials 2 through 7. In early trials, it was assumed that the poor jet filterability was caused by release of naphthenates distributed throughout the salt beds. When filterability problems persisted even after a trial with fresh salt and complete bypass of the caustic treater, it became apparent that there was a reservoir of naphthenates in the gravel distributing layer which supports the salt bed. During early trials, the gravel support layer had been assumed to be free of contaminants after being washed by an overhead fire hose for several hours. Inspections during preparations for a later trial revealed that this washing procedure was ineffective, apart from cleaning the surfaces directly exposed to the fire hose water.
- Contamination of jet fuel by release of naphthenates resident in the salt driers was induced mainly by the higher water content of the jet fuel entering the salt drier, rather than by subtle changes in the acidity of the jet fuel caused by partially bypassing the caustic treater.
- Sudden changes in the flow rate of jet fuel through the salt driers may release stationary deposits of naphthenates from the salt driers, resulting in short periods of grossly naphthenate-contaminated jet fuel being passed to refinery storage tanks. Fast changes of the water in the water wash vessel can cause such upsets. For water wash systems which do not have continuous withdrawal of dirty water and clean water makeup, it is preferable to decrease the water change-out frequency, and allow the wash water to become more contaminated with naphthenates.
- Naphthenic acids in jet fuel do not react with sodium chloride to yield filter blocking naphthenates.

- Sodium naphthenates are extremely potent filter blocking agents. While introduction of demineralised water for caustic dilution and water washing may have had some impact by eliminating calcium and magnesium naphthenates from jet fuel, jet fuel filterability was still severely degraded whenever it contained even trace concentrations of sodium naphthenates.

Complete segregation of one of the salt driers from the caustic-treated jet fuel stream [Figure 1(b)] provided a simple means of keeping it free of filter blocking naphthenates. At the same time, this segregation sends lower flow rates through the salt drier serving the caustic treated stream of jet fuel, thereby minimising contamination of this stream by naphthenates.

Current refinery procedure, implemented as a result of this study, is to measure the filter blocking tendency of all batches of jet fuel prior to release. Following testing, the appropriate response from Table 2 for non-bottom tank samples is enacted. There is also a classification system for dead-bottom tank samples, which is used for three-monthly surveys of jet tank cleanliness.

To be acceptable for release from the refinery, jet fuel should have a filter blocking tendency below 1.005. This corresponds to a very small but easily measured increase in the pressure differential across the test filter as a consequence of passing the 600 mL test sample through the filter. It is interesting to note that a common benchmark for acceptable filter blocking tendency of automotive diesel fuel is <1.4 by ASTM D2068. This highlights the extremely high filtration quality required of jet fuel.

ELECTRICAL CONDUCTIVITY

An operational quality control problem was observed during the first bypassing trial. With 30% of jet fuel bypassing the caustic treater, jet fuel electrical conductivity became much more sensitive to light-induced decay. To control conductivity within the specification range of 50 to 450 pS/m, the normal refinery practice was to take daily samples of the finished jet fuel stream going to refinery tankage, and also a tank average sample from the tank being filled. These samples were taken by refinery operators in clear glass bottles (poor practice), which typically stood in direct sunlight on a sample rack for an hour or so before collection by

laboratory analysts. Because of the sunlight-induced conductivity decay, the laboratory reported low conductivity results, and the refinery operators responded by increasing the concentration of Stadis 450 conductivity additive being injected into the jet fuel stream to tankage. Sampling for certification of the filled tank was done by the laboratory analysts, with the jet fuel receiving minimal exposure to sunlight. As a result of the extra additive dosing, conductivity of these samples exceeded the allowed upper limit of 450 pS/m.

Figure 3 shows the results of laboratory experiments in which jet fuel was dosed with conductivity additive in a 20 L steel drum, a 2.5 L brown glass bottle, and in normal one litre refinery sample bottles. For the normal bottles, experiments were conducted for the bottles (i) as received, (ii) as received but externally covered with aluminium foil, (iii) pre-rinsed with isopropyl alcohol according to ASTM D2624 to eliminate any water, and (iv) washed with methanol then dried at 160°C for an hour. All samples stood on a laboratory bench under typical fluorescent lighting for 20 h, after which the three unprotected clear bottles were exposed to 30 min of diffuse sunlight. After a further 30 minutes to allow the samples to re-equilibrate to laboratory temperature, conductivities were measured. At the 24 h point, the aluminium foil was removed from the two foil-covered bottles, and these samples (and some other samples) were exposed to diffuse sunlight for two periods of 15 minutes. The following conclusions are evident from Figure 3:

- Both fully caustic-washed jet fuel and jet fuel produced with 30% bypass of the caustic treater were prone to sunlight-induced conductivity decay.
- Jet fuel produced with 30% bypass of the caustic treater was particularly sensitive to sunlight-induced conductivity decay. More than half of the conductivity was destroyed by sunlight exposure for 30 minutes.
- Provided jet fuel is not exposed to light, jet fuel produced with 30% bypass of the caustic treater has stable electrical conductivity following dosing with conductivity additives.

Changing from glass to metal sample containers provided a simple solution, with only minor inconvenience.

CONCLUSION

By developing an understanding of the mechanisms involved in the formation of naphthenic acid salts, and their entrainment in jet fuel, a modified process scheme for jet fuel production was introduced at Ampol's Brisbane refinery in late 1996. The most important modification was the complete segregation of one of the two salt driers from the caustic treater. This ensures that the salt drier receiving untreated jet fuel remains completely free of naphthenic acid salts, and thereby eliminates the possibility that filter blocking contaminants can be released into jet fuel by causes such as high flow rates or high water content of jet fuel. Jet fuel production capacity was increased by 50% by introduction of the modified processing scheme, with a low capital investment.

This study has highlighted the extreme potency of naphthenic acid salts for causing blockage of coalescer cartridges in the jet fuel distribution system. It also shows that departures from recommended practices - in this case those listed in ASTM D2624 and ASM D4306 for conductivity sampling - are counterproductive.

While carryover of naphthenic acid salts with jet fuel as it moves from caustic treaters through process units such as salt driers can be minimised, it is probably inevitable that traces of filter blocking naphthenates will accumulate in jet fuel storage tanks. Even with the improvements made as a result of this study, it is likely that coalescer cartridge life in downstream filter/separators is still limited by extremely small concentrations of naphthenic acid salts. If so, the cost of manufacturing and distributing jet fuel could be decreased by eliminating the caustic treating process whenever permitted by jet fuel acidity requirements. Of course, other jet fuel properties, *eg.* thermal stability, would have to carefully assessed, but our experience suggests that it would be better to leave low concentrations of organic acids and phenols in jet fuel, rather than converting them to filter blocking salts, which are difficult to completely remove by water washing. In their unreacted acidic form, they present no filtration problems, and are simply burnt in jet engines along with bulk jet fuel.

REFERENCE

1. API Publication 1581 (1989). "Specifications and Qualification Procedures for Aviation Jet Fuel Filter/ Separators", third edition.

Table 1 Properties of laboratory blends of caustic treated and untreated (bypass) jet fuel

	Specification limit	Caustic treater bypass (Gippsland)			Treater bypass (Kutubu)
		0%	20%	100%	100%
Acidity, mg KOH/g	0.015 max	0.0010	0.0014	0.013	0.011
Copper corrosion, 2 h at 100°C	1 max	1a	1a	1a	1a
Silver corrosion, 4 h at 50°C	2 max	0	0	0	0
Separometer rating (MSEP-A)	70 min	84	99	99	94
Water reaction	1b(2)	-	1(1)	1(1)	1(1)
Mercaptans, mg/kg	30	9	9	9	3

Table 2 Classification of jet fuel by the Ampol jet fuel filter blocking tendency (FBT) test

Non-bottom tank samples

FBT	Rating	Response
1.002 - 1.003	Typical quality	Release to off-takers
<1.004	Acceptable quality	Release to off-takers
1.004 - 1.005	Marginal quality	Can be released, subject to off-taker sensitivity and recent history
1.005 - 1.01	Major filtration problem	Consider settling, filtration, segregation for Ampol Terminal

Dead-bottom tank samples

FBT	Rating	Response
<1.10	Acceptable	No action required
1.10 - 1.50	Major tank contamination	Monitor FBT of dead-bottom samples for each jet batch
>1.5	Extreme tank contamination	Consider tank cleaning

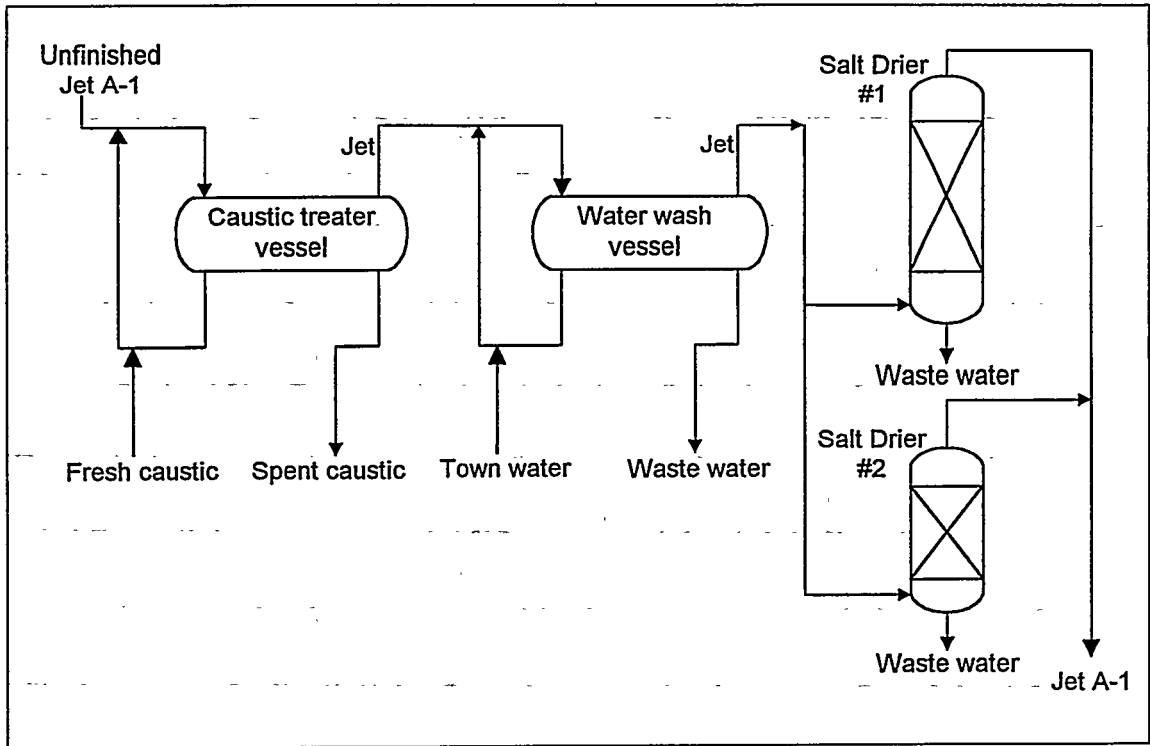


Figure 1 (a). Caustic treating and salt drying prior to introducing the bypass strategy.

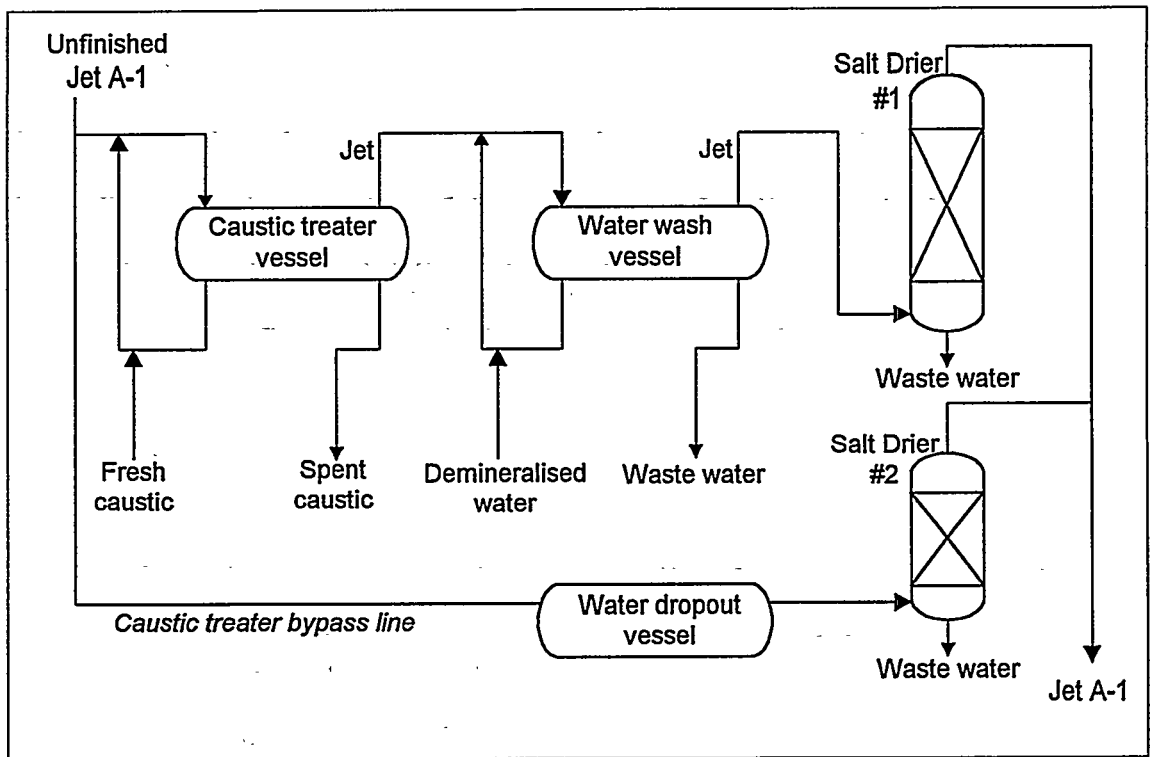


Figure 1 (b). The current caustic treating and salt drying process, with one drier completely segregated from the caustic system.

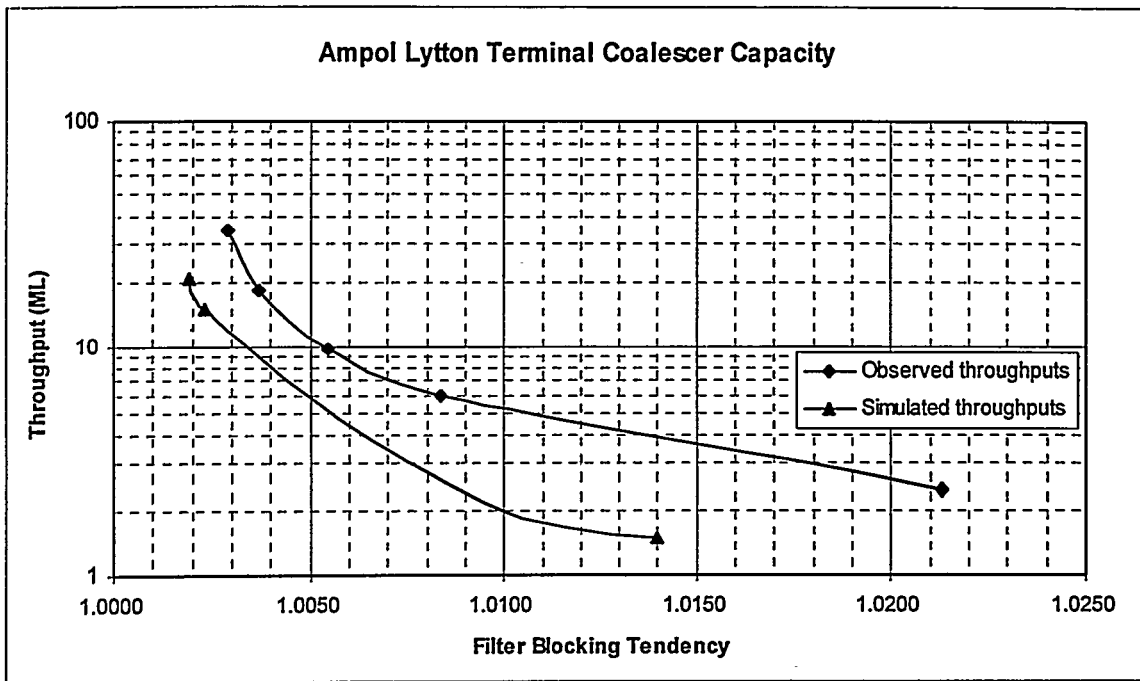
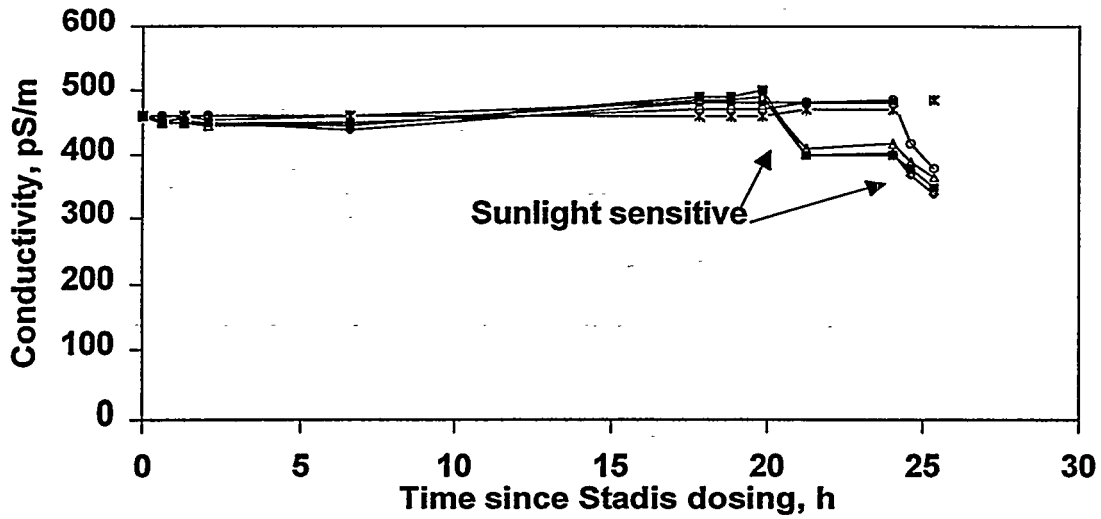


Figure 2 Limiting throughput of jet fuel through 0.5 micron coalescer cartridges as a function of jet fuel filter blocking tendency.

No Caustic wash bypass



30% Caustic wash bypass

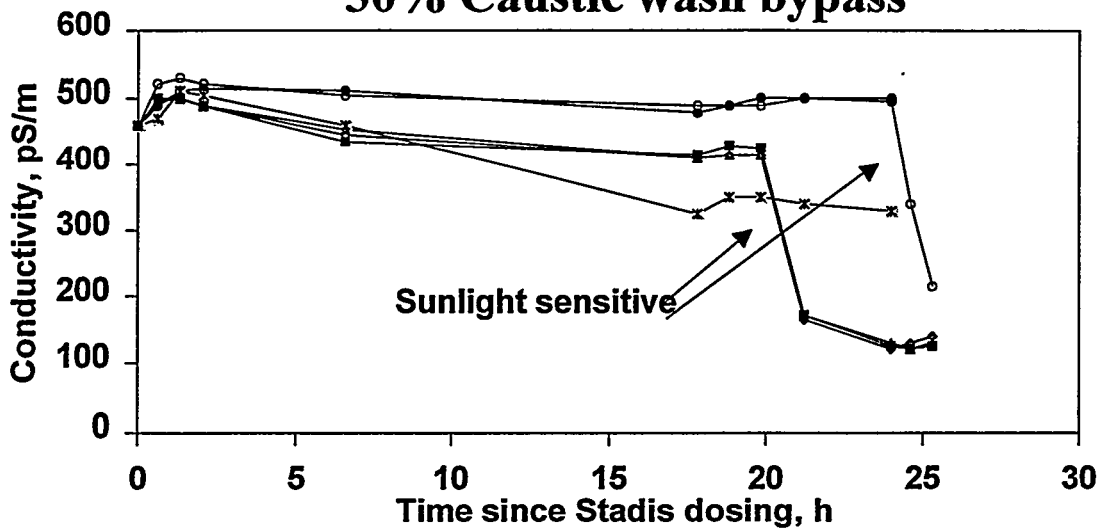


Figure 3. Conductivity changes for caustic treated jet fuel (top) and partially treated jet fuel (bottom).