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Proceedings of the 5th International Conference on Stability and Handling of Liquid Fuels

Rotterdam, the Netherlands
October 3-7, 1994

Volume 1

Edited by Harry N. Giles
Office of Technical Management
Deputy Assistant Secretary for Strategic Petroleum Reserve
Assistant Secretary for Fossil Energy

U.S. Department of Energy

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Washington, DC

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Previous Conferences

Conference on Long Term Storage Stabilities of Liquid Fuels, Tel Aviv, Israel, July 11-14, 1983. Proceedings published by the Israel Institute of Petroleum and Energy, Nahum Por, editor; Tel Aviv, Israel, December 1983.

2nd International Conference on Long-Term Storage Stabilities of Liquid Fuels, San Antonio, Texas, USA, July 29-August 1, 1986. Proceedings published by the Southwest Research Institute, Leo L. Stavinoha, editor; San Antonio, Texas, USA, October 1986.

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.

4th International Conference on Stability and Handling of Liquid Fuels, Orlando, Florida, USA, November 19-22, 1991. Proceedings published by the U. S. Department of Energy, Harry N. Giles, editor; Washington, DC, USA, 1992.

Contents

Volume 1

Session 1: Jet Fuels - I. A. Ishai, Chair.

*Author to whom correspondence should be addressed.

Session 2: Microbiology. Dr. R. A. Neihof, Chair.

Session 3-A: Jet Fuels - II. Dr. A. Roberts, Chair.

Session 3-B: Long-Term & Strategic Storage. H. J. Beverdam, Chair.

Session 3-C: Predictive Systems & Methods. Ms. S. J. Dickout, Chair.

Session 4-A: Test Rigs & Simulators. Dr. E. W. White, Chair.

Volume 2

Session 4-B: Deposit & Insolubles Measurements. Dr. S. J. Marshman, Chair.

Session 4-C: Gasolines. A. E. Zengel, Chair.

Session 4-D: Heavy Oils and Refinery Processing. Dr. J. D. Bacha, Chair.

Session 5: Middle Distillate Fuels - I. Dr. B. Batts, Chair.

Session 6: Middle Distillate Fuels - II. Dr. A. M. Hartstein, Chair.

Session 7: New Fuels & Environmental Mandates. J. D. Crawford, Chair.

Poster Session: Dr. D. R. Hardy, Chair.

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Contributors

Adiwar Research and Development Center for Oil and Gas Technology (Lemigas),
P.O. Box 1089/JKT, Jakarta 10010, Indonesia

Agrawal, K.M. Indian Institute of Petroleum, Dehradun - 248 005, India

Anderson, S.D. USAF Wright Laboratory, 1790 Loop Road North,
Wright-Patterson AFB, OH 45433-7103, USA

Arumugam, R. Fuel Science Program, Department of Materials Science and Engineering,
The Pennsylvania State University, University Park, PA 16802, USA

Aswal, D.S. Indian Institute of Petroleum, Dehradun - 248 005, India

Bacha, J.D. Chevron Research & Technology Co., 100 Chevron Way,
Richmond, CA 94802-0627, USA

Baker, C. BP Research and Engineering Centre, Chertsey Road, Sunbury-on-Thames,
Middx. TW16 7LN, UK

Balster, W.J. Systems Research Laboratories, Inc., 2800 Indian Ripple Road,
Dayton, OH 45400-3696, USA

Batt, R.J. The Associated Octel Company Ltd., Watling Street, Bletchley,
Milton Keynes MK1 1EZ, UK

Batts, B.D. School of Chemistry, Macquarie University, Sydney, NSW 2109, Australia

Bauldreay, J.M. Shell Research Ltd., Thornton Research Centre, P.O. Box 1,
Chester CH1 3SH, UK

Beal, E.J. Naval Research Laboratory, Code 6180, Washington, DC 20375-5342, USA

Beaver, B.D. Department of Chemistry and Biochemistry, Duquesne University,
Pittsburgh, PA 15282, USA

Ben-Asher, J. The Israel Institute of Petroleum and Energy, P.O. Box 17081,
Tel Aviv 61170, Israel

Beverdam, H.J. Netherlands National Petroleum Stockpiling Agency, Blaak 22,
3011 TA Rotterdam, the Netherlands

Binns, K.E. University of Dayton Research Institute, 300 College Park Drive,
Dayton, OH 45469-0140, USA

Boneva, M.I. Institute of Organic Chemistry, Bulgarian Academy of Sciences,
1113 Sofia, Bulgaria

Chesneau, H.L. Fuel Quality Services, Inc., P.O. Box 1380, Flowery Branch, GA 30542, USA

Chin, L.P. Systems Research Laboratories, Inc., 2800 Indian Ripple Road,
Dayton, OH 45400-3696, USA

Clark, R.H. Shell Research Ltd., Thornton Research Centre, P.O. Box 1,
Chester CH1 3SH, UK

Crawford, J.D. Nalco/Exxon Energy Chemicals L.P., P.O. Box 87,
Sugar Land, TX 77487-0087, USA

Dacre, B. Royal Military College of Science, Cranfield University, Shrivenham, Swindon,
Wilts. SN6 8LA, UK
Daniels, D.A. Basic Fuel Services, 2 East Blackwell St., Ste. 29, Dover, NJ 07801, USA
David, P. BP Research and Engineering Centre, Chertsey Road, Sunbury-on-Thames,
Middx. TW16 7LN, UK
Demunshi, R. Department of Chemistry and Biochemistry, Duquesne University,
Pittsburgh, PA 15282, USA
Derst, P. Marie-Curie-Str. 64, D-76139, Karlsruhe, Germany
Dessens, C. W. M. Ministry of Economic Affairs, P.O. Box 20101, 2500 EC The Hague,
The Netherlands
Dickout, S.J. National Defence Headquarters, DSE 6-2-2, MGen George R. Pearkes Bldg.,
Ottawa, Ontario K1A 0K2, Canada
Dieterle, G.L. University of Dayton Research Institute, 300 College Park Drive,
Dayton, OH 45469-0140, USA
Edwards, T. USAF Wright Laboratory, 1790 Loop Road North,
Wright-Patterson AFB, OH 45433-7103, USA
Eser, S. Fuel Science Program, Department of Materials Science and Engineering,
The Pennsylvania State University, University Park, PA 16802, USA
Fass, R. Department of Biotechnology, Israel Institute for Biological Research,
Ness Ziona 70450, Israel
Flohr, K.W. ARTECH Corp., 14554 Lee Road, Chantilly, VA 22021-1632, USA
Georgiev, P.T. SciBulCom, Ltd., P.O. Box 249, 1113 Sofia, Bulgaria
Gergova, K.M. Fuel Science Program, Department of Materials Science and Engineering,
The Pennsylvania State University, University Park, PA 16802, USA
Geva, J. Department of Biotechnology, Israel Institute for Biological Research,
Ness Ziona 70450, Israel
Giannini, R.M. Naval Surface Warfare Center, Carderock Division, 3A Leggett Circle,
Annapolis, MD 21402-5067, USA
Giles, H.N. U.S. Department of Energy (FE-422), 1000 Independence Avenue, SW,
Washington, DC 20585, USA.
Goss, L.P. Systems Research Laboratories, Inc., 2800 Indian Ripple Road,
Dayton, OH 45400-3696, USA
Grinstead, R.R. University of Dayton Research Institute, Aerospace Mechanics
Division/KL-463, 300 College Park, Dayton, OH 45469-0140, USA
Gutman, M. Internal Combustion Engines Laboratory, Faculty of Mechanical Engineering,
Technion, Haifa 32000, Israel
Hardy, D.R. Naval Research Laboratory, Code 6180, Washington, DC 20375-5342, USA
Harrison, W.E, III USAF Wright Laboratory, 1790 Loop Road North,
Wright-Patterson AFB, OH 45433-7103, USA
Hartman, J. Department of Mathematics, Israel Institute for Biological Research,
Ness Ziona 70450, Israel

Hartstein, A.M. U.S. Department of Energy (FE-32), 1000 Independence Avenue, SW, Washington, DC 20585, USA

Heins, R.J. Shell Research Ltd., Thornton Research Centre, P.O. Box 1, Chester CH1 3SH, UK

Henry, C.P. Octel America, Inc., c/o DuPont, Petroleum Laboratory (P), Chambers Works, Deepwater, NJ 08023, USA

Heneghan, S.P. University of Dayton Research Institute, Aerospace Mechanics Division, 300 College Park Avenue, Dayton, OH 45469-0140, USA

Hetherington, J.I. Royal Military College of Science, Cranfield University, Shrivenham, Swindon, Wilts. SN6 8LA, UK

Hietkamp, S. CSIR, P.O. Box 395, Pretoria 0001, South Africa

Hill, E.C. ECHA Microbiology Ltd., Unit M210 Cardiff Workshops, Lewis Road, Cardiff, CF1 5EJ, UK

Hill, G.C. ECHA Microbiology Ltd., Unit M210 Cardiff Workshops, Lewis Road, Cardiff, CF1 5EJ, UK

Hughes, J.M. Naval Research Laboratory, Code 6180, Washington, DC 20375-5342, USA

Ishai, A. P.O. Box 7415, 31073 Haifa, Israel

Ivanov, Sl.K. SciBulCom, Ltd., P.O. Box 249, 1113 Sofia, Bulgaria

Jones, E.G. Systems Research Laboratories, Inc., 2800 Indian Ripple Road, Dayton, OH 45400-3696, USA

Joshi, G.C. Indian Institute of Petroleum, Dehradun - 248 005, India

Kalitchin, Zh.D. SciBulCom, Ltd., P.O. Box 249, 1113 Sofia, Bulgaria

Kamin, R. A. Naval Air Warfare Center, Aircraft Division, Trenton, NJ 08628, USA

Kassinger, R. DNV Petroleum Services, 111 Galway Place, Teaneck, NJ 07666, USA

Kauffman, R.E. University of Dayton Research Institute, Fluid Analysis Laboratory, 300 College Park Avenue, Dayton, OH 45469-0140, USA

Kelly, J.F. CANMET, Energy Research Laboratories, Natural Resources Canada, Ottawa, Ontario K1A 0G1, Canada

Kirzhner, Y. Internal Combustion Engines Laboratory, Faculty of Mechanical Engineering, Technion, Haifa 32000, Israel

Klinkhammer, M.D. Naval Surface Warfare Center, Carderock Division, Annapolis, MD 21402-5067, USA

Koenig, J.W.J. Erdölbevorratungsverband, Postfach 30 15 90, 20305 Hamburg, Germany

Krenis, G. The Israel Institute of Petroleum and Energy, P.O. Box 17081, Tel Aviv 61170, Israel

Lacey, P.I. Belvoir Fuels & Lubricants Research Facility, Southwest Research Institute, P.O. Drawer 28510, San Antonio, TX 78228-0510

Lavie, I. Bromine Compounds Ltd., P.O. Box 180, Be'er Sheva, 84101, Israel

Lavy, Z. Logistics Headquarters, Israel Defense Forces, Military P.O. 02306, Israel

Lenz, U. Rheinbraun A.G., Stüttgenweg 2, 5000 Köln (Lindenthal), Germany

Luria, D. The Israel Ministry of Energy, The Fuel Authority, P.O. Box 33541, Haifa 31334, Israel

Marais, B. National Petroleum Refiners of South Africa (Pty) Ltd., P.O. Box 234,
Sasolburg 9570, South Africa
Marshman, S.J. Defense Research Agency, Fighting Vehicles and Systems/Fuels and Lubricants
Department, Fairmile, Cobham, Surrey KT11 1BJ, UK
Martin, C.J. Defense Fuel Supply Center, Cameron Station, Alexandria, VA 22304-6160, USA
McInnis, L.A. Belvoir Fuels & Lubricants Research Facility, Southwest Research Institute,
P.O. Drawer 28510, San Antonio, TX 78228-0510
McVea, G.G. Airframes and Engines Division, Aeronautical and Maritime Research Laboratory,
506 Lorimer Street, Fishermens Bend, Victoria 3207, Australia
Morris, R.E., Naval Research Laboratory, Code 6181, Washington, DC 20375-5342, USA.
Morris, R.W. U.S. Air Force, Wright Laboratory, 1790 Loop Road North,
Wright-Patterson AFB, OH 45433-7103, USA
Morse, B.W. Nordre Ås, Jeløy, 1514 Moss, Norway
Motohashi, K. Chemical Inspection & Testing Institute, 4-1-1 Higashi-Mukojima, Sumida-ku,
Toyko 131, Japan
Muth, C.L. Nalco/Exxon Energy Chemicals L.P., P.O. Box 87
Sugar Land, TX 77487-0087, USA
Nagpal, J.M. Indian Institute of Petroleum, Dehradun - 248 005, India
Nakazono, K. Chemical Inspection & Testing Institute, 4-1-1 Higashi-Mukojima, Sumida-ku,
Toyko 131, Japan
Neihof, R.A. Naval Research Laboratory, Code 6180, Washington, DC 20375-5320, USA
Oki, M. Chemical Inspection & Testing Institute, 4-1-1 Higashi-Mukojima, Sumida-ku,
Toyko 131, Japan
Pande, S.G., Geo-Centers, Inc., 10903 Indian Head Hwy., Ft. Washington, MD 20744, USA
Passman, F.J. Biodeterioration Control Associates, Inc., P.O Box 268176,
Chicago, IL 60626-8176, USA
Petersen, S. Søren Schierbeck & Co. ApS, Sabroesvaj 15 A 2, DK-3000 Helsingør, Denmark
Pilviö, O. Neste Oy, R & D Services, P.O. Box 310, FIN-06101 Porvoo, Finland
Porlier, B.W. Nalco/Exxon Energy Chemicals L.P., P.O. Box 87,
Sugar Land, TX 77487-0087, USA
Power, A.J. Airframes and Engines Division, Aeronautical and Maritime Research Laboratory,
506 Lorimer Street, Fishermens Bend, Victoria 3207, Australia
Propes, J. Department of Biotechnology, Israel Institute for Biological Research,
Ness Ziona 70450, Israel
Rahimi, P.M. CANMET, Energy Research Laboratories, Natural Resources Canada, Ottawa,
Ontario K1A 0G1, Canada
Roberts, A. Energy Plans & Policy Branch (N420), Strategic Sealift Programs Division,
2000 Navy Pentagon, Washington, DC 20350-2000, USA
Sarkar, G.N. Gujarat Refinery, Indian Oil Corp., Ltd., P.O. Jawaharnagar, Vadodara - 391 320,
India
Saxena, G.C. R.B.S. College, Agra, India

Schobert, H.H. Fuel Science Program, Department of Materials Science and Engineering,
The Pennsylvania State University, University Park, PA 16802, USA
Sharief, V. Department of Chemistry and Biochemistry, Duquesne University,
Pittsburgh, PA 15282, USA
Sharma, Y.K. Indian Institute of Petroleum, Dehradun - 248 005, India
Shaver, B.D. Naval Surface Warfare Center, Carderock Division, 3A Leggett Circle,
Annapolis, MD 21402-5067, USA
Shouse, D.T. USAF Wright Laboratory, 1790 Loop Road North,
Wright-Patterson AFB, OH 45433-7103, USA
Shuftan, M. Logistics Headquarters, Israel Defense Forces, Military P.O. 02306, Israel
Siegert, W. Schülke & Mayr GmbH, Robert-Koch-Straße 2, D-22840 Norderstedt, Germany
Singh, I.D. Indian Institute of Petroleum, Dehradun - 248 005, India
Skoog, P.-Å. Celsius Materialteknik AB, Box 13 200, S-580 13 Linköping, Sweden
Sommer, S. "Delek" - The Israel Fuel Corporation, P.O. Box 50250, Tel Aviv 61500, Israel
Stavinoha, L.L. Belvoir Fuels & Lubricants Research Facility, Southwest Research Institute,
P.O. Drawer 28510, San Antonio, TX 78228-0510
Strauss, K. H., 69 Brookside Road, Portland, ME 04103-4609, USA.
Street, J.P. Nalco/Exxon Energy Chemicals L.P., P.O. Box 87,
Sugar Land, TX 77487-0087, USA
Strucko, R. Naval Surface Warfare Center, Code 859, 3A Leggett Circle,
Annapolis, MD 21402-5067, USA
Sufrin, Y. Logistics Headquarters, Israel Defense Forces, Military P.O. 02306, Israel
Tanielyan, S.K. Seton Hall University, South Orange, NJ 07079-2694, USA
Tartakovsky, L. Internal Combustion Engines Laboratory, Faculty of Mechanical Engineering,
Technion, Haifa 32000, Israel
Taskila, S.M. Amoco Oil Company, Research Center, P.O. Box 3011,
Naperville, IL 60565-7011, USA
Taylor, S.E. BP Research and Engineering Centre, Chertsey Road, Sunbury-on-Thames,
Middx. TW16 7LN, UK
Teng, Y. Department of Chemistry and Biochemistry, Duquesne University,
Pittsburgh, PA 15282, USA
Terebenina, A. Institute of Inorganic Chemistry, Bulgarian Academy of Sciences,
1113 Sofia, Bulgaria
Thomsen, E.S. Søren Schierbeck & Co. ApS, Sabroesvaj 15 A 2, DK-3000 Helsingør, Denmark
Tian, D. Department of Chemistry and Biochemistry, Duquesne University,
Pittsburgh, PA 15282, USA
Todorova, O. Institute of Inorganic Chemistry, Bulgarian Academy of Sciences,
1113 Sofia, Bulgaria
Torres-Ordonez, R.J. Amoco Oil Company, Research Center, P.O. Box 3011,
Naperville, IL 60565-7011, USA

Turner, L. M. Defense Fuel Supply Center, Cameron Station,
Alexandria, VA 22304-6160, USA
Venter, J.J. National Petroleum Refiners of South Africa (Pty) Ltd., P.O. Box 234,
Sasolburg 9570, South Africa
Viljoen, C.L. Sasol Oil R&D, P. O. Box 1, Sasolburg 9579, South Africa
Waynick, J.A. Amoco Oil Company, Research Center, P.O. Box 3011,
Naperville, IL 60565-7011, USA
Wechter, M.A., Department of Chemistry, The University of Massachusetts, Dartmouth,
North Dartmouth, MA 02747, USA
Weiss, A. Logistics Headquarters, Israel Defense Forces, Military P.O. 02306, Israel
Westbrook, S.R. Belvoir Fuels & Lubricants Research Facility, Southwest Research Institute,
P.O. Drawer 28510, San Antonio, TX 78228-0510
White, E.W. Naval Surface Warfare Center, Code 632, 3A Leggett Circle,
Annapolis, MD 21404-5067, USA
Whitesmith, P.R. Conoco Ltd., Conoco Centre, Warwick Technology Park, Gallows Hill,
Warwick CV34 6DA, UK
Williams, T. University of Dayton Research Institute, 300 College Park Drive,
Dayton, OH 45469-0140, USA
Woodward, A.J. BP Research and Engineering Centre, Chertsey Road, Sunbury-on-Thames,
Middx. TW16 7LN, UK
Zabarnick, S. University of Dayton Research Institute, Aerospace Mechanics Division/KL-463,
300 College Park, Dayton, OH 45469-0140, USA
Zengel, A.E. Coordinating Research Council, Inc., 219 Perimeter Center Parkway, N.E.,
Atlanta, GA 30346-1301, USA
Zvirin, Y. Internal Combustion Engines Laboratory, Faculty of Mechanical Engineering,
Technion, Haifa 32000, Israel

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Author Index

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Preface

Two measures of the success of an international conference are the number of attendees and the number of countries that they represent. Based on these criteria, the 5th International Conference on Stability and Handling of Liquid Fuels was very successful, with 203 attendees from 28 countries. This is the largest number of countries ever represented at these conferences. These figures are highly gratifying to me, in my role as conference chairman. Because of the continuing recession that began before the 1991 conference, many companies and organizations have curtailed or eliminated attendance at international conferences. These cutbacks have especially affected attendance at specialized conferences such as this.

From the papers presented at this conference, jet fuels and other middle distillates continue to be the subject of considerable study. The microbial aspect of petroleum degradation is another subject that still attracts much attention. The use of computer-based expert systems for monitoring storage stability and predicting when products should be used or replaced is on the increase. The causes of fuel degradation apparently are better understood, and less attention was devoted to this topic than in previous years. Interest continues in quality of refined products stored in strategic stockpiles. Test rigs and simulators are now widely used in evaluating stability. New methods for measurement of deposits formed during degradation have been developed and older methods revised. The effects of metals and heterocompounds on gasoline storage stability also continue to be studied.

A broad topic coming to the forefront is that of environmentally-friendly or *green fuels*. Within the United States, legislative initiatives and an enlightened environmental awareness have resulted in stricter practices at fuel handling and storage facilities. The Clean Air Act Amendments of 1990 are requiring refiners to reformulate their fuels or turn to alternate compositions. For marketing in certain ozone nonattainment areas, gasoline must 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. 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. Product imports must also meet current environmental and statutory requirements. This is compelling offshore refineries to upgrade their processes to produce cleaner fuels for the U.S. market. Because reformulated fuels have only recently appeared in the marketplace, little is known how many of them will withstand the rigors of handling and storage, or succumb to microbial attack. In Europe as well, changes are taking place in the composition of fuels in response to a growing environmental awareness. Many countries are beginning to adopt more stringent policies regarding fuel composition. The world crude oil stream is getting heavier and higher in sulfur, which is complicating the need to produce cleaner fuels. 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.

We are witnessing one of the most dramatic changes in the composition of fuels in more than 50 years. Consequently, the timing of the 5th conference probably could not have been better. Several papers were presented that discussed various aspects of the new fuels that are appearing. I expect the stability and handling of these "future fuels" will be a major theme of the 6th conference. Whatever their composition, we will continue to face the same problems identified by the National Petroleum Council more than 50 years ago, namely: instability, incompatibility, and contamination.

I thank the following who provided generous support for this conference: U.S. Al-Ghamdi; Chevron; Biodeterioration Control Associates; Ethyl; Fuel Quality Services, Inc.; Fina Nederland; KLM, Royal Dutch Airlines; Nalco/Exxon Energy Chemicals, L.P.; Octel America; Paktank International BV; and Rohm and Haas. The Dutch Ministry of Economic Affairs was the conference host and provided invaluable support to the organizers. I am also grateful to the many people that helped me in organizing this conference. I am especially indebted to Mrs. Shirley Bradicich and Mrs. Jan Tucker of the Coordinating Research Council who so admirably handled many arrangements and administrative details. Finally, I thank everyone that attended the conference. Their interest and support ultimately make these conferences successful.

Harry N. Giles
Conference Chairman

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

OPENING ADDRESS

Mr. Drs. C. W. M. Dessens, Director-General of Energy

Ministry of Economic Affairs, P.O. Box 20101, 2500 EC The Hague, The Netherlands

Ladies and gentlemen, it is my pleasure and honour to welcome all of you in Rotterdam, the Netherlands. I am delighted that your Association has chosen Rotterdam to be the host city for the 5th International Conference on Stability and Handling of Liquid Fuels. It gives you the opportunity to discover the beauty and the importance of a country which is in many ways the gateway to Europe. Geographically a gateway, as the country near the sea, and Rotterdam as the largest sea port of the world. And Schiphol (Amsterdam Airport) as one of the largest airports of Europe. Also economically a gateway because a large part of the traded goods to and from Europe pass through the Netherlands. And last but not least Rotterdam is the 'oil gateway' to Europe. The oil flow through the port of Rotterdam is impressive.

The Netherlands are exporting about three quarters of the amount of oil (products) we are importing. I would like to give you some figures. In 1993 the Netherlands imported 55 million tonnes crude oil and about 32 million tonnes oil products. In that same year we exported 0.8 million tonnes crude and 54 million tonnes oil products. Another 11 million tonnes left the country by bunkering of sea going vessels. To sum up: this means that in 1993 an amount of 86 million tonnes of crude oil and oil products entered this country and an amount of 66 million tonnes left this country. Of course mainly through the port of Rotterdam. As an oil gateway we are not just passing through the oil. The Netherlands are an important refining centre, with 5 refineries producing about 65 million tonnes in 1993. These refineries are highly efficient and are producing under stringent environmental regulations, because we think that high economic standards should be combined with high environmental standards. Together with this enormous crude oil and oil product flow there are large oil storage facilities in Rotterdam and some other parts of the Netherlands (Amsterdam, Flushing). An oil trading centre needs oil storage facilities as a central element of all activities.

There are various companies operating within this business and you have the opportunity to visit a storage location in one of your technical tours. The total storage capacity in the Netherlands is about 31 million cubic metres. Crude oil and oil products are not only stored for Dutch oil companies, but also for foreign companies. And of course the Netherlands National Petroleum Stockpiling Agency uses these facilities to a great extent.

Oil storage has various aspects. I would like to mention five different aspects. The first aspect is the strategic stockpiling. Although the world has dramatically changed within the last 25 years and the working of the oil market has significantly improved, strategic stockpiling will remain an essential element in the energy policy of oil consuming countries. Most of these countries are united in the International Energy Agency (IEA). One of the main tasks of the IEA is to guarantee a coordinated response during an oil supply crisis. In this response the IEA member countries have a shared responsibility. In the end all member countries are willing to share the total amount of oil available to the IEA. Nevertheless, it is obvious that it is in the interest of all nations -both consuming and producing oil- to avoid a supply disruption. The second aspect is a pure economic one: storage is business. The oil industry needs the so called 'working stocks'. This means storage of crude oil to ensure that the refinery can continue the producing process. Storage of product can be important for anticipating seasonal demand changes and other marketing reasons. It is interesting to see that also companies from producing countries -for example Aramco- use the storage facilities in Rotterdam. We regard this integration of producer and consumer markets as valuable. It also stresses the importance of Rotterdam as the 'oil centre' of Europe. The third important aspect of oil storage I would like to touch upon is the environmental impact. As in so many economic activities the impact of the activity on the environment should be minimised. Oil storage in itself is a 'clean' process, with very small effect on the environment. But even there progress is possible. To give you two examples: better storage facilities to protect the environment and the stored products, and advanced techniques to reduce evaporation to prevent spillage. Also the safety aspect should be mentioned. Together with environment, safety is an aspect that cannot and should not be ignored. The storage facilities in the Netherlands belong to the best of the world. The fifth and last aspect that I would like to mention is probably the most important. It is about quality. Looking at the program of this conference I can see that a lot of attention will be paid to the quality of the stored product. The main issue is how to avoid degradation of the stored product. There are of course different techniques to stop or at least slow down this process. And as I am told a lot of progress will still be possible in the future.

Ladies and gentlemen, I am impressed by the amount of different topics and issues you will discuss in the coming days. There are so many different topics and various aspects about the stability and handling of liquid fuels I never knew about. There will be sessions about jet fuel. Attention will be paid to the microbiological aspects of storage. Also there will be a presentation on the long-term and strategic storage and product quality control by predictive systems and methods. Of course there will be attention paid to a lot of other topics. The fact that I did not mention these does not mean that they are not important. It is just that the program is so various.

The Ministry of Economic Affairs is honoured to host this conference and to welcome so many people from so many different countries all together. I am confident that it will be an inspiring conference. I hope that you will enjoy the technical tours and for those of you who have some time left that you enjoy the tourist program. It is a honour to declare the 5th International Conference on Stability and Handling of Liquid Fuels to be opened.

5th International Conference
on Stability and Handling of Liquid Fuels
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COMMERCIAL JET FUEL QUALITY CONTROL

Kurt H. Strauss[A]

Abstract

The paper discusses the purpose of jet fuel quality control between the refinery and the aircraft. It describes fixed equipment, including various types of filters, and the usefulness and limitations of this equipment. Test equipment is reviewed as are various surveillance procedures. These include the Air Transport Association specification ATA 103, the FAA Advisory Circular 150/5230-4, the International Air Transport Association Guidance Material for Fuel Quality Control and Fuelling Service and the Guidelines for Quality Control at Jointly Operated Fuel Systems. Some past and current quality control problems are briefly mentioned.

INTRODUCTION

The history of jet fuel quality control dates back to the introduction of commercial turbine powered aircraft, when it was discovered that both the procedures and equipment commonly used for aviation gasoline were inadequate for the new fuel type. Initially new procedures concentrated on viscosity and density differences to develop longer settling rates in tankage and new types of filters which would remove water as well as particulates. A landmark was set in the early 1960's when an international airlines-fuel supplier conference decided on a maximum free water limit of 30 ppm into aircraft. Over time more subtle, one might almost say insidious, contaminants and problems were identified and have had to be guarded against. One concern carried over from aviation gasoline and very much alive today is the possible contamination with other petroleum products.

The paper describes current equipment used to control the quality of jet fuel between the refinery and the aircraft. It presents summaries of major procedures inside and outside the USA and points out differences, imposed to some extent by differences in airport fuel custody. Although important, only limited reference is made to construction standards which are a separate major subject.

[A] 69 Brookside Road, Portland, Maine 04103

QUALITY CONTROL EQUIPMENT

DESCRIPTIONS

Fixed equipment

Fixed equipment includes filter-separators, clay filters, other types of filters, monitors or fuses, floating suctions, internal floating roofs and internal coatings.

Filter-separators can be considered the key equipment in jet fuel quality control. They are designed to remove free or suspended water and particulates to lower levels than other equipment. In fact, other filtration equipment is normally used to reduce the work load on filter-separators or to remove materials which might keep filter-separators from doing their job. Filter-separators incorporate two stages of filtration with the first stage called the coalescer stage and the second stage the separator stage. The filtration media in the first stage are layered such that extremely small water droplets are coalesced by a densely packed medium (coated fiberglass) and emerge on the outside of the elements as droplets which are mostly large enough to settle by gravity ahead of the second stage. In order to coalesce the droplets the filtration media are packed tight enough to also collect very fine particulates, therefore the term "filter-coalescer" for this stage. Layers ahead of the coalescing layers selectively remove particulates to keep the coalescing medium from early plugging by solids. The water droplets which are too small to settle are carried by the fuel against the second stage, the separator stage. These hydrophobic elements, usually made of teflon-coated mesh, repel the fine droplets and keep them out of the filter-separator's discharge, thereby allowing these units to furnish clean, dry fuel.

The elements in each stage have a flow rating per unit length, depending on qualification results. The desired flow rating for the entire filter-separator then dictates the total length of elements installed. Element installation may be either vertical or horizontal. The sump between the two stages collects the separated water which is removed either manually or automatically. Element replacement is based on pressure drop, operating time, the cleanliness of the filtered fuel or evidence of surfactant disarming by evaluating daily sump samples. Elements are replaced whenever the maximum allowable limit is reached for one of these parameters. Industry and government specifications, listed in Table 1, govern the performance of these units. Only filter-separators qualified against an agreed-upon specification should be used in jet fuel systems.

Field clay filters have only one purpose, to remove low concentrations of polar materials ("surfactants"). These surfactants which are soluble in both fuel and water can coat the glass fibers and destroy the water-attracting nature of the surfaces in the coalescers and separators, thereby keeping them from coalescing and removing water droplets and effectively disarming the filter-separators. In addition to water, disarmed filter-coalescers will also pass fine solids which would normally be removed. Clay filter elements are filled with calcined Attapulgus clay which attracts and adsorbs polar materials. Refinery or bulk clay filters serve the same purpose, but because of their large volume and low velocities, have much more removal capacity than the smaller field clay units. Clay field units contain stacks of individual elements, the number of elements depending upon the rated flow of the housing. However, unlike filter-separators, clay filters are not governed by industry performance specifications and their ratings are based on hydraulic pressure drop considerations. Clay filters are always placed ahead of filter-separators to protect the filter-separators and to avoid the possibility of clay fines in the filtered fuel.

Another filter type, also known as a prefilter, primarily removes solid particulates ahead of filter-separators or clay units. Their relatively inexpensive paper elements makes them an advantageous way of extending the life of the more expensive filter-separator elements. In addition, haypacks or excelsior filters, ahead of clay filters, can remove large quantities of water which might cause the clay to revert to mud under such wet conditions.

Monitors or fuses are another category of water removal devices. Unlike filter-separators which are designed to continue to operate with fairly high concentrations of water, monitors are designed to shut off fuel flow in the presence of water. Usually this is achieved by a layer of treated paper fibers which swell in the presence of water and block fuel flow. Monitors are used in several configurations. They are available in separate housings to take the place of filter-separators. They can be mounted inside filter-separators in place of the second stage separator elements or they can be a third stage following the normal two stages in a filter-separator. When used as separate units, monitors are changed when reaching a maximum pressure drop or when they have shut off fuel flow. Table 1 lists applicable specifications for these devices.

Other items, which are more in the category of construction materials, contribute to quality control. One widely used piece of equipment, the floating suction, is installed in airport storage tanks. This device is a pipe which pivots at the bottom end, the outlet, so that the top end, supported by floats, can move up and down with the fuel level and take suction near the top fuel surface. Floating suctions reduce the required settling time and assure that fuel is not removed from the bottom of the tank where contamination tends to concentrate. Internal floating roofs with a fixed cover over the tank keep dust out of the fuel and also reduce vapor emissions. Lastly, internally coating the entire airport fuel system with paints such as epoxy enamels has eliminates the generation of rust in these systems. However, eliminating corrosion by the use of copper or copper-containing alloys is not permitted because copper in extremely low concentrations acts as a catalyst which reduces the fuel's resistance to high temperatures in jet engines. Zinc ("galvanizing") is not permitted as an internal surface coating because it prevents rusting by acting as a sacrificial material which ends up in the fuel as insoluble solids. Stainless steel or aluminum are sometimes used as tanks for aircraft fuelers, but care must be taken to avoid salt water contact with the aluminum.

Test Equipment Peculiar to Quality Control

A variety of test equipment is used routinely in jet fuel quality control. Some of it is standardized by ASTM or other authorities, some is not, but all of it is described in ASTM Manual 5,[B],[1]. Some equipment detects water in various forms, some identifies or quantifies solids, some does both. Table 2 lists these tests which are in routine field use and gives references to sources for more information.

For water detection the least refined tests are the white bucket test and water finding paste. In the former a white porcelain-coated or stainless steel bucket is employed to sample a transport compartment or tank water drain to find free water which is concentrated by swirling the bucket contents slowly. Suspended water can be detected by trying to read the small lettering on a coin through some 20 cm of fuel. Dyed fuel such as aviation gasoline or darker colored products such as diesel fuel can be identified by their appearance. Water finding paste turns a bright reddish color when it contacts a water layer in the bottom of a tank or compartment. The paste is normally applied to gaging tape or a gaging stick. The

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[B] Superscript numbers refer to references at end of paper.

length of changed color is a direct measure of the depth of water. However, water finding paste does not react to water suspended in droplet form.

A more sensitive water test is the visual appearance or "clear and bright" test. A sample of product is collected in a clear, one liter bottle and is held against the light. A haze caused by free, undissolved water down to concentrations of 50 ppm can be detected by an experienced operator. Swirling the bottle slowly will concentrate larger water droplets and solid contaminants in the center of the bottle's bottom. A chart with different width black lines is now available as an adjunct to ASTM D 4176 to qualitatively rate the concentration of suspended water.

Several tests identify a suspended water concentration of 30 ppm or greater. As mentioned in the Introduction, such a maximum level is generally acceptable during aircraft loading. Three different tests depend on the color change of a filter or of a powder added to the product. In the Shell Detector test 5 ml of product are drawn into a syringe through a plastic monitor holding a chemically treated filter; 30 ppm or more of water will turn the yellow filter a bright blue-green. This test is now also available with a 10 ml syringe, placing the color change at the 15 ppm free water level. In the Velcon Hydrokit (formerly Exxon Hydrokit) fuel is drawn into a sealed test tube containing a powder. A color change in the powder from a light to a stronger pink again indicates the failing water level of 30 ppm. The Metrocator test rates water content by comparing the concentration of black spots on a special paper in the bottle cap after the sample has been shaken inside the bottle. This test is stated to identify 10 ppm of water or greater.

The most sensitive water test, the AquaGlo, quantitatively measures the fluorescence level of a specially treated filter pad after a 500 ml sample has been pushed through the pad under line pressure. This test will identify free water concentration down to a few ppm.

Depending upon particle size and concentration, different tests for solids are appropriate. For large particles, 1 mm or larger, the white bucket or clear and bright tests are satisfactory. For particulates in the micron sizes, a more elaborate test is needed. In the membrane filtration test 4 L or more of product are filtered through an extremely fine membrane (normally 0.8 μm pore size) under line pressure. The mass of solid particulates can be determined by weighing the filtrate in a laboratory or the filter color can be rated by comparison to a standard chart. Membrane color tends to be most useful for detecting abrupt changes in color and tracking the trend of filter effluent quality over a long period of time. There is no direct relationship between membrane color and weight.

The condition of coalescer elements is rated with a more elaborate technique by removing one filter-coalescer element from the housing and testing its coalescing quality by flowing fuel and water through it in a special single element test rig. Failure of this element to coalesce water is cause for removal of all first stage elements in the parent unit. The second stage teflon-coated elements can be tested by simply flowing water over them and assuring that the water does not wet the elements. Clay filter condition can be checked by MSEP testing or installing a sidestream sensor containing clay in parallel with the clay vessel. Periodically the sensor element is removed and tested for its remaining surfactant absorbency. This information can be used to change clay elements when necessary. Water swells monitor elements and causes an increase in differential pressure and then fuel flow shut-off. Therefore, these elements cannot be performance tested before change out.

LOCATIONS

Fixed Equipment

Filter-separators are normally installed at the end of a terminal fuel system, ahead of the delivery system to the airport. The same installation applies to refinery storage when fuel is delivered from a refinery directly to an airport. Filter-separators are also placed at the airport entrance into the fuel system, out of the fuel storage into airport fuelers or into an underground hydrant system and at the end of the delivery system, immediately ahead of the aircraft. Additional units may be present at the airport or the terminal, but between the refinery and the aircraft jet fuel passes through at least four filter-separators in series.

The installation of other filtration equipment depends heavily on operating experience in a particular system. In the USA clay filter are commonly installed in terminals receiving jet fuel from multi-product pipelines and, to a lesser extent, in terminals supplied by marine transport. Clay filters are seldom installed in airport fuel systems because of the preceding cleanup system in the supplying terminals. Again depending on experience, paper filters may be used in terminals, less frequently at airports. As stated earlier, paper filters are simply a cost reduction item when filter-separator life is too short because of high solids content of the fuel. Outside the USA clay filters are less common, probably because of the lack of major multi-product pipelines, the increased use of coated tankers with compartments segregated to jet fuel and the widespread use of conductivity additive which is removed by clay.

On airports, floating suctions are mandatory for fuel tanks as are internal epoxy coatings for systems built of mild steel. Some companies prefer stainless steel tanks for airport fueler compartments, others do not. Off airports, transport trucks supplying airports do not carry product filters and normally have uncoated interiors. The smaller pipelines from terminals to airports are normally internally coated. The large multi-product lines are not coated and depend on the presence of corrosion inhibitors in other products for rust protection.

Test Equipment

Test equipment location depends upon the specific requirements of quality control procedures discussed in the next section.

QUALITY CONTROL PROCEDURES

GENERAL

For a long time quality control was the responsibility of the fuel supplier who had custody of the fuel up to the aircraft. In some cases certain cleanliness requirements were specified in individual airline contracts, often the result of some specific operating problem. However, quality procedures or cleanliness limits have not been included into commercial industry-wide fuel specifications, in part because differences in fuel custody make a universal approach almost impossible. In addition, as will be seen, detailed procedures can differ significantly because of differing handling experience. However, in more recent times a consolidation of commercial airport procedures has taken place and will be discussed here. All procedures assume that all fuel leaving a refinery fully complies with industry fuel specifications. All control procedures start after that approval in the refinery.

WITHIN THE USA

The responsibility for fuel quality control at airports is one major difference between the USA and the rest of the world because in the USA fuel custody changes at the airport boundary, whereas outside the USA custody remains with the fuel supplier up to the aircraft fuel inlet. In the USA, therefore, airlines handle the fuel on airports, outside the USA the fuel suppliers do. Third party fuel handling agencies, where used, reflect this difference as they are responsible to the airlines in the USA but to fuel suppliers outside the USA.

ATA 103

Under the aegis of the Air Transport Association, US airlines have developed ATA Specification 103, Standards for Jet Fuel Quality Control at Airports[2]. This specification is applied wherever ATA member airlines jointly own or operate the airport fuel system or are supplied by independent airport dealers at smaller airports. Otherwise the specification is not binding on such dealers or other fuel handlers at small airports.

ATA 103 requirements are summarized in Figure 1 which lists the tests and other inspections by location and frequency. (The actual document is some 50 pages long and describes other required inspections and construction details.) Note the emphasis on filter-separator performance which, at a minimum, is checked monthly by membrane and free water tests. However, free water tests are made at least once a day at the fueling vehicle and are also done during every aircraft fueling. Filter-separator and storage tank sumps are drained manually every day to prevent a possible buildup of microbial growth. The manual drain is necessary because automatic drains may not be actuated over a long period of time in a relatively dry system. An important part of the process is the maintenance of written records of tests and inspections, including the storage of membrane filters for visual inspection.

Other Quality Control Procedures

The Federal Aviation Administration has issued an Advisory Circular AC 150/5230-4[3] which lists most of the requirements of ATA 103. However, it is advisory, is specifically aimed at airline operations and does not address smaller airports which do not have airline operations. It also does not contain maximum allowable limits for various quality control parameters such as solids or water content.

The API has issued Bulletin No. 1500 entitled "Storage and Handling of Aviation Fuels at Airports"[4]. This bulletin stresses design considerations and lists recommended inspections but does not contain maximum or minimum limits for fuel quality.

API bulletin No. 1542 [5] contains recommendations for airport equipment marking for fuel identification. Such standard markings are particularly important for airports carrying more than one fuel grade.

The US Air Force has issued a Military Standard, MIL-STD-1548B[6], covering the minimum performance and quality requirements for the delivery and service of fuels and oils under US Government procurement contracts at commercial airports. This document parallels the ATA 103 procedures. In addition the standard covers the addition of and testing for antiicing and conductivity improver additives required in military fuels. (The procedures used by the military in its own systems are not covered by this standard.)

Another area of quality control is the prevention of mixing other petroleum products and jet fuel in transportation systems. Where feasible, marine compartments and transport vehicles are maintained in jet fuel so that mixing does not take place. However, in some situations various products may precede jet fuel. There are no industry standards for such fuel handling. Instead, each individual hauler has to have specific procedures which must be followed for non-segregated operation. These procedures can include draining, flushing, compartment cleaning as well as prohibitions against following certain products such as black fuel oils or lubricating oils.

In one major situation product segregation is impossible. Large multi-product pipelines carry the majority of refined products in the USA from the refinery to distribution terminals. Here quality control depends on large tender sizes, turbulent line flow, product sequencing and careful cutting to minimize product contamination on one hand and product loss due to intermixing on the other. There is no segregation by supplier and each product type meets a common specification. Normally, when product is to be removed into a terminal, withdrawal starts after the leading interface passes and is completed before the trailing interface appears. However, at the end of the pipeline all product must be removed and there product cuts are made to protect the higher quality product. For example, some higher octane gasoline is cut into the lower octane product to protect the octane rating. Similarly, some diesel is cut into the low octane gasoline to protect diesel flash point. In each case the most sensitive property must be protected. The importance of large tenders to minimize product degradation is clear. However, some product loss and interface mixing is unavoidable and disposing of the off-specification product becomes part of the pipeline operating cost.

OUTSIDE THE USA

Joint Operated Systems Guide Lines

As pointed out earlier, fuel handling on airports outside the USA is the responsibility of the fuel suppliers or their agents. Eleven major oil companies have therefore agreed on a system of quality control whenever an airport fuel system contains fuel by more than one supplier. Most of the time such a system is operated by one company under the supervision of a local fuel committee. The Guide Lines are summarized in Figures 2 and 3. One major difference with ATA 103 is the required fuel recertification when fuel is delivered by a non-segregated system. Other differences are relatively minor.

The same group also issues fuel specification guidelines to apply to the same airports. These guidelines are distinct from the quality control guidelines and are a combination of the most stringent requirements of ASTM D 1655, DERD 2494 and the IATA Fuel Guidelines. By combining the requirements of the three major specifications, these guidelines assure the acceptability of jet fuel in most parts of the world.

Other Procedures

In airports not jointly operated, the local fuel supplier must have his own quality control manual which normally becomes part of the fueling contract. Such procedures usually contain the procedures in ATA 103 or the Joint Systems Guidelines as a minimum.

To assist in airline supervision of international airports, IATA has issued fuel quality control and fuelling service guidance material[7]. Unlike ATA 103 this document does not contain acceptable quality control limits, but instead furnishes an airline representative a set of forms to be used when inspecting an airport fuel system.

SUMMARY

The preceding review makes clear the importance of fuel quality control in the commercial aviation system. Effective quality control depends heavily on redundant equipment and testing because otherwise the failure of a single system could have catastrophic consequences. Particularly today, operating economics play a critical part in all operations, but cost cutting in quality control can be a dangerous exercise.

The review also illustrates that there is no single road to heaven in jet fuel quality control and a useful and practical system should be based heavily on operating experience.

Acknowledgements

The assistance of Mr. Rick Waite of Velcon Filters Inc. in furnishing some materials for this paper and its presentation is gratefully acknowledged.

Table 1

Equipment Specifications

Filter-separators		
	Commercial	API 1581 [8]
		Group 1 = base fuel only
		Group 2 = base fuel + additives
		Class A = at terminals
		Class B = at airport storage
		Class C = at fueling vehicle
	Military	
	Element performance	MIL-F-8901 [9]
	Element design and dimensions	MIL-F-52308 [10]
	Housing design (600 gpm unit)	MIL-F-27630 [11]
Monitors or fuses	**Commercial**	IP Specification [12]
	Military	MIL-M-81380C [13]
Other filter types		no industry or military specifications

Table 2

Quality Control Test Equipment

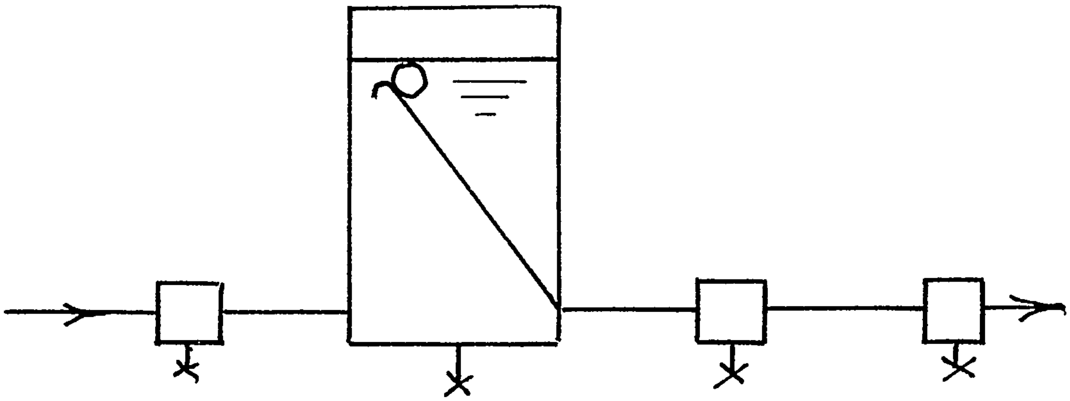
Name	ASTM Standard No.	Manual 5, Page No.
White bucket test	-	7
Water detection paste	-	54
Clear and Bright test	D 4176	7
Shell Detector test	-	47
Velcon Hydrokit	-	48*
Metrocator kit for Undissolved Water	-	50
Aqua-Glo Water Detection Kit	D 3240	52
Membrane filtration test	D 2276	39
Single element coalescer test	-	66
Side-stream clay sensor	D 5000	-

*Listed under Exxon Hydrokit

Figure 1

Airport Jet Fuel Quality Control - per ATA 103

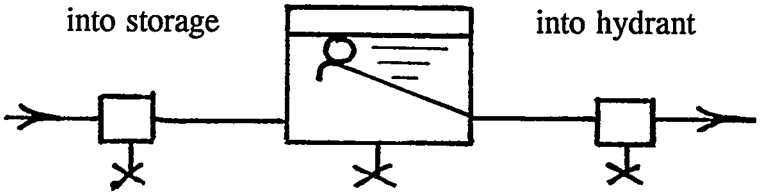
F/S #1 Tank F/S #2 Pipeline F/S #3 to A/C



Requirements				
Density	Each receipt	-	-	-
Clear & bright	Each receipt	-	-	-
White bucket	Each receipt	-	-	-
sumps	Daily	Daily	Daily	Daily
Press. drop	Each receipt, daily	-	Daily	Daily
Membrane test	P/L receipt	-	Monthly	Monthly
color	3 max/3 gal	-	2 max/3 gal	2 max/3 gal
Free water	P/L receipt	-	Monthly	Monthly
	30 ppm max	-	15 ppm max	15 ppm max
Replace elements	Yearly	-	Yearly	Yearly
Inspect inside	Yearly	Yearly	Yearly	Yearly
Clean	--------------------------as required--------------------------			

Figure 2

Jointly Operated Airport Depots (Storage) - Quality Control

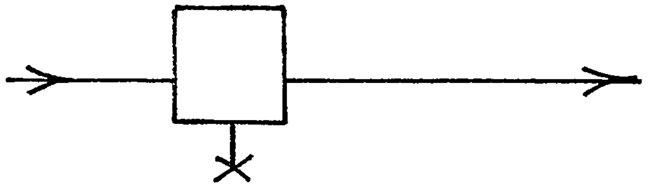


Requirements	Filter-separator into storage	Tank	Filter-separator into hydrant
Each receipt			
Dedicated supply	-	Control check	-
Non-segregated supply	-	Recertification	-
Periodic test	-	6 months	-
Settling time			
Vertical tank	-	2 hours	-
Horizontal tank	-	1 hour	-
Drain water	Daily	Daily	Daily
Pressure drop	Daily	-	Daily
Water check-sump (Chemical test)	Daily	prior to release	Daily
Conductivity	-	Monthly	-
Membrane test			
Sample size	5 L	-	5 L
Colorometric	Monthly	-	Monthly
Gravimetric	3 months	-	3 months
Inspect internally	Yearly	Yearly	Yearly
Element changes	max press. drop	-	max press. drop
	or 24 months	-	or 24 months
Extend with single element test	to 3 years	-	to 3 years
F/S specification, API 1581	Gp II, Class B	-	Gp II, Class B
Clean	-	Every 3 years	-

Figure 3

Jointly Operated into Plane Service - Quality Control

-------Refueller or Hydrant Vehicle-----



	Filter-separator	Hose end
Drain water	Daily	-
Visual test	After start of every pumping After every pumping	-
Chemical water test	After start of every pumping After every pumping	-
Sample retention	24 hours	-
Pressure drop	Daily	-
Membrane test		
Sample size	-	5 L
Colorometric	-	Monthly - 2 max
Gravimetric	-	3 months - 0.2 mg/L max
Inspect internally	Yearly	-
Element changes	Max press. drop or 24 months	-
Extend with single element test	to 3 years	
F/S specification, API 1581	Group II, Class C	-

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THE TRANSITION OF NEW TECHNOLOGY TO SOLVE TODAY'S PROBLEMS

Richard A. Kamin 1 Calvin J Martin 2 and Lynda M. Turner 2

1 Naval Air Warfare Center, Aircraft Division, Trenton, NJ 08628
2 Defense Fuel Supply Center, Cameron Station, Alexandria, VA 22304

Extensive research has been conducted in the development of methods to predict the degradation of F-44 in storage. The Low Pressure Reactor (LPR) has greatly enhanced the stability prediction capabilities necessary to make informed decisions concerning aviation fuel in storage. This technique has in the past been primarily used for research purposes. The Naval Air Warfare Center, Aircraft Division, Trenton, NJ, has used this technique successfully to assist the Defense Fuel Supply Center, Cameron Station, Alexandria, VA, in stability assessments of F-44. The High Performance Liquid Chromatography/Electrochemical Detector(HPLC/EC) antioxidant determination technique has also aided in making stability predictions by establishing the amount of inhibitor currently in the product. This paper will address two case studies in which the above new technology was used to insure the rapid detection and diagnosis of today's field and logistic problems.

INTRODUCTION

Due to its unique requirement to store aviation fuel at strategic locations throughout the world, the United States military must be assured the product stored will not significantly degrade prior to usage.

Since 1976, the MIL-T-5624 specification has required the addition of phenolic type antioxidants into fuel to inhibit hydrocarbons from reacting with dissolved oxygen during storage. The antioxidant is added at the refinery prior to exposure to air at a concentration between 17.2 ppm (minimum) and 24 ppm (maximum). Until recently, the refiner added the antioxidant at an acceptable concentration and it was never subsequently measured in the distribution system. A study conducted by the National Institute for Petroleum Energy and Research (NIPER) for the Naval Air Warfare Center, Aircraft Division, Trenton (NAWCADTRN) reported that the degradation process for aviation fuel containing antioxidants and/or any naturally occurring inhibitors begins with the presence of an initial induction period where the formation of significant peroxides is prevented. The induction period is followed by a period of rapid depletion of antioxidant and an increase in peroxide content. The final period is characterized by decreasing peroxide content, darkening in color, and increasing sediment formation. This study also observed that although antioxidant additives will increase the induction period, the free radical chain oxidation mechanism occurring in a reactive fuel will only be delayed.[1] Since the observance of this phenomenon, it has been thought that if the antioxidant concentration is monitored for product in storage, this may provide added information to the stability of the product.

A F-44 Refinery Sampling Survey[2] conducted by the NAWCADTRN indicated that the composition of F-44 has moved from a straight-run distillate to a blend of various process streams which can include significant hydroprocessed material. Since hydroprocessing removes the naturally occurring inhibitors and creates branched chain compounds which have been proven to be extremely susceptible to oxidation, it has become increasingly important to assess a fuel while in storage. In addition, due to the increase hydroprocessing, it is now more than ever necessary for the U.S. military to inject an acceptable concentration of an approved antioxidant to inhibit the free radical initiation of hydrocarbons.

BACKGROUND

From 1982 to 1993 the U.S. Navy conducted an extensive program that addressed many aspects of storage stability. The Program's goal was to develop a reliable, accelerated method for predicting the long-term storage stability of military aviation turbine fuel reserves that could also be used to determine antioxidant effectiveness. The two major test procedures developed in this program were the Low Pressure Reactor (LPR) for predicting the storage stability of fuel and the High Performance Liquid Chromatography/Electrochemical Detector (HPLC/ECD) method for determining antioxidant concentration.

The LPR was developed after considerable research and verification work as a predictive test method to be used for the determination of the stability of aviation fuel.[3] Prior to the LPR, the only test available to measure fuel for their long term oxidative stability was a Go-No-Go test developed by the Coordinating Research Council (CRC).[4] This test was a cumbersome bottle storage test that took three weeks to complete. The LPR improved upon the CRC test and is capable of predicting a fuel's behavior in storage in only 24 to 96 hours of testing.

The HPLC/ECD method for the determination of phenolic antioxidant was developed by Hayes and Hillman[5] and later modified by Vogh.[6] The method was further modified by NAWCADTRN[7] to detect the antioxidants in F-44 regardless of refinery processing technique used. This method consists of an HPLC system coupled with an electrochemical detector. At the current level of antioxidant addition, 17 to 24 mg/L other analytical methods with commonly used detectors did not provide sufficient resolution for identifying antioxidant type or concentration. The addition of the ECD allowed for the identification of the major components contained in all five antioxidants currently approved for use in F-44.

This paper will discuss two case studies in which the LPR and HLPC/ECD test methods were used in the assessment of the stability of F-44 fuel after procurement. The two test methods described and utilized in this study are not included in the MIL-T-5624 specification for procurement and until recently both were used primarily in research studies. However, when used in conjunction with one another a reasonably accurate prediction may be made of a fuel's degradation tendency.

EXPERIMENTAL

The LPR, developed by the Naval Research Laboratory, is a simplified version of the reactor bomb used in the procedure of ASTM D525 (Oxidation Stability of Gasoline, Induction Period Method). After significant evaluation and testing, optimum test conditions of 35 psig air overpressure and 100°C were selected. Testing is conducted for 24 hours with the option to extend to 96 hours if necessary. The 100°C stress temperature has been validated to be predictive of long term storage at ambient conditions.[8] The use of air overpressure prevents oxygen depletion at this elevated temperature and test duration. The Navy has established that the 24 hour/100°C stress test simulates at least six months of ambient storage[3]. Each fuel sample is tested for peroxide concentration (ASTM

D3703), particulates (ASTM D2276) and antioxidant concentration (HPLC/ECD). Additional tests for color (ASTM D156), total acid number (ASTM D3242) and existent gum (ASTM D371) are performed when necessary.

RESULTS AND DISCUSSION

Case #1 F-44 in Long Term Strategic Storage

The U.S. military stores large quantities of product for emergency readiness in strategic reserves throughout the world. As the product ages, rotation of stock may be necessary to ensure the quality of the product. This study addresses 1.5 million barrels of F-44 that has been in storage since 1988.

The fuel, stored in three separate tanks, is required to be tested for limited properties every six months. Although a thorough review uncovered many missing data points in the periodic testing, the results for particulates, existent gums, peroxides and color all met specification. These tests only provide a picture of the current stability of the F-44 and do not allow any prediction of its future stability. It is well documented, however, that a F-44 exhibits stable characteristics until the antioxidant additive is depleted and then can peroxidize at an alarming rate causing rapid degradation.

Due to the quantity and age of the fuel, it was decided to utilize the LPR and HPLC/ECD techniques to evaluate the potential for the fuel to become unstable in the future. In September 1993, "as received" testing was performed on samples from all three F-44 storage tanks. This data included peroxide concentration, existent gum, total acid number, color, and antioxidant concentration. As shown in Table 1, the results for each tank sample were within MIL-T-5624 specification. The antioxidant concentration was below the minimum concentration required at procurement for two of the tanks but was still sufficient to provide adequate protection to the fuel. Since several shipments of fuel were commingled into these tanks, the exact antioxidant was difficult to determine. Therefore, the antioxidant concentrations reported in Table 1 are a measurement of the major antioxidant components detected in each tank. This isn't an exact determination of the antioxidant in the fuel but it is sufficient to evaluate the amount of antioxidant protection available.

The results of the LPR accelerated storage stability testing, Table 2, show after 96 hours of testing the peroxide and existent gum concentrations were within specification for all three tanks. Although the antioxidant concentration was reduced during the LPR testing, it still was 8 ppm or greater for the two tanks measured.

Based on the results of the LPR accelerated testing, it was determined that the F-44 could continue to remain in extended storage. This decision allowed the significant costs involved in the rotation of the F-44 stock from the three tanks to be avoided. Additionally, it was recommended that the fuel be tested using the LPR accelerated storage stability test protocol every 18 to 24 months to continue to ensure adequate future stability.

CASE #2 Abnormally Dark F-44

In February 1992, a complaint was received that a F-44 issued for aircraft use aboard U.S. Navy ships had developed an abnormally dark color. This fuel also formed a dark stain on the filter pads of the shipboard Contaminated Fuel Detector (CFD) that the Navy uses to measure the particulate concentration of its F-44. The dark stain on the pads caused the CFD to give false high particulate readings which significantly effected flight operations. Subsequent complaints were received about abnormally dark F-44 at other locations.

In response to this operational problem, samples of the F-44 in question were evaluated. Specification testing was performed and found that the fuel met all specification properties except for JFTOT thermal stability (ASTM D3241) which failed at both 260°C and 245°C. Color, only a report value, was measured at less than -16, which is significantly below typical values. From this testing and follow-up conversations with the field, contamination was determined not to be the cause of the problem. Instead it was hypothesized that the F-44 had degraded and additional storage was not advisable. To confirm this theory, non-specification LPR and HPLC/ECD testing was conducted. As shown in Table 3, both peroxide and particulate concentration increased over the 96 hour LPR accelerated storage stability test. The fuel, as received, had a low concentration of antioxidant (8 ppm) that was totally depleted after only 24 hours of testing.

The source of the problem F-44 was tracked to a single refinery. Results from the Navy's F-44 Refinery Sampling Program revealed that this refinery produced F-44 from a combination of product streams, some of which consisted of severely processed and/or thermally cracked stock material. In addition, the Navy's Refinery Sampling Program had shown that the F-44 produced by this refinery had significantly higher nitrogen concentrations (30-40 ppm) than any other F-44 (0-10 ppm nitrogen) currently being produced. The F-44 from the initial field complaint was determined to have a nitrogen concentration of 90 ppm.

In order to evaluate the rapid degradation theory, the procurement specification test results were obtained for the batch identified to have caused the initial problem. At procurement the F-44 batch under investigation had a saybolt color of +25 and easily passed the JFTOT thermal stability test at 275°C (1 Visual, 0 delta P). Similar comparisons were made with other F-44 batches from this refinery that had also degraded in the field. In each case, the when the F-44 left the refinery, it was of significantly better quality than when it was measured three to six months later in the field.

After discussions with the refiner could not positively identify the cause of the problem or guarantee the problem would not reoccur, it was decided that LPR accelerated stability testing would be performed on each batch of F-44 produced by the refinery until a satisfactory resolution was obtained. While the LPR test would not solve the problem, it would at least alert the Navy of potential problems and allow them to utilize their stocks accordingly. Additional LPR testing was also performed at six month intervals on F-44 produced by the same refinery but already distributed to other locations. Table 4 shows representative LPR data from this refinery testing. As shown in figures 1 and 2, the 96 hour LPR testing of this sample differs significantly from those determined from the F-44 under investigation. The increase of peroxide concentration and particulates is much lower. Although the refinery will not acknowledge any difference in their production, the results of the LPR testing clearly shows that a more stable product was produced. As expected, the "good stability" F-44 as determined by the LPR did not cause any operational problems in the field.

Although, the LPR and HPLC/ECD did not determine the cause of the instability (those results and testing are beyond the scope of this paper), each played a significant role in ensuring that the problems encountered in the field would not be repeated.

CONCLUSION

As research & development budgets continue to shrink and cost savings become the top priority by which programs are evaluated, it is essential that technology developed in these programs be successfully transitioned into the field. Although the LPR and HPLC/ECD may never become formal

ASTM Society approved test methods or parts of a procurement specification, they do represent two significant tools that improve the U.S. military's ability to evaluate its aviation fuel after procurement. These tools have not only saved the U.S. Navy millions of dollars in the two cases documented in this paper, but more importantly, provide additional assurance that the quality of the product will be acceptable whenever it might be needed.

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

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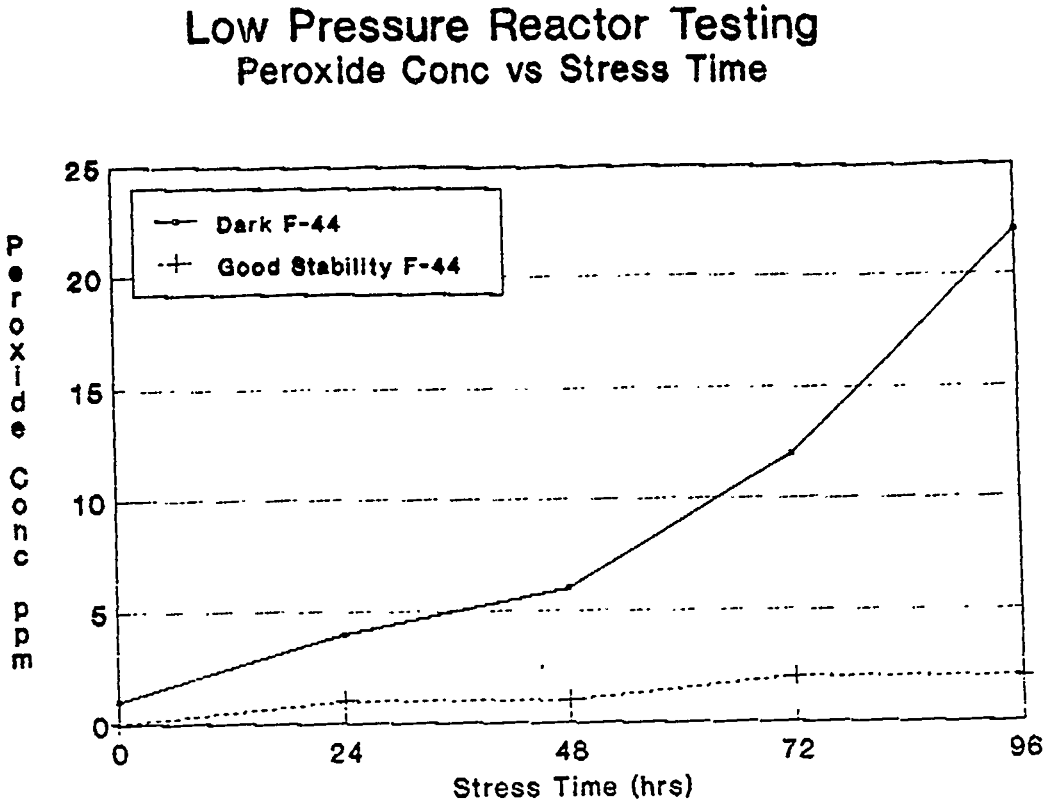
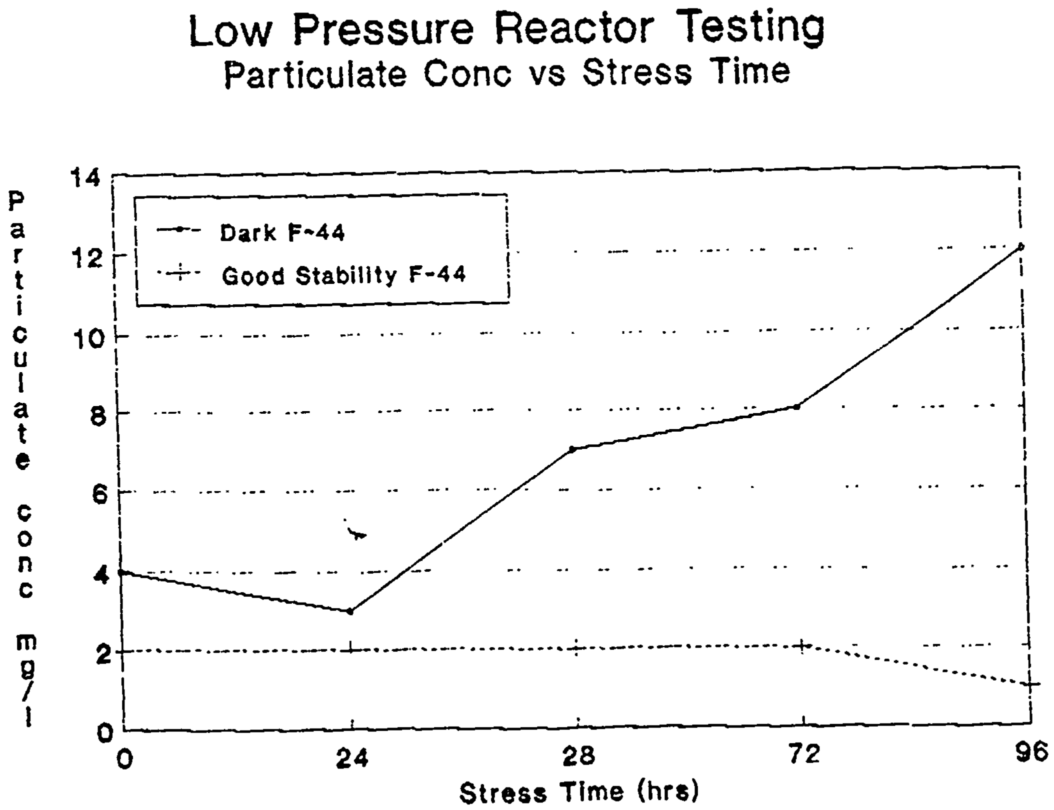


Low Pressure Reactor Testing
Peroxide Conc vs Stress Time

Figure 1



Low Pressure Reactor Testing
Particulate Conc vs Stress Time

Figure 2

Table 1

TANK SAMPLES "AS RECEIVED"

Tank #	Peroxides (ppm)	Existent Gums (mg/100ml)	Total Acid # (mg KOH/g)	Saybolt Color	Antioxidant Concentration (ppm)*
716	0	0.4	0.004	17	20.1
726	0	0.0	0.006	14	13.9
736	0	0.2	0.004	15	14.2

* Combination of a mixture of Antioxidants

Table 2

LPR ACCELERATED STORAGE STABILITY TEST DAT

TANK # 716					
LPR Test Time (hr)	0	24	48	72	96
Peroxide No. (ppm)	0	1	1	1	1
Existent Gum (mg/100ml)	0.40	0.20	0.60	0.60	0.40
Antioxidant Conc. (ppm)*	20.1	18.6	16.1	13.5	11.2

TANK # 726					
LPR Test Time (hr)	0	24	48	72	96
Peroxide No. (ppm)	0	0	1	2	2
Existent Gum (mg/100ml)	0.00	0.20	0.40	0.00	0.40
Antioxidant Conc. (ppm)*	13.9	12.8	11.6	9.8	7.9

TANK # 736					
LPR Test Time (hr)	0	24	48	72	96
Peroxide No. (ppm)	0	0	1	1	2
Existent Gum (mg/100ml)	0.20	0.40	0.40	0.00	0.40
Antioxidant Conc. (ppm)*	14.2	nm	nm	nm	nm

*Combination of a mixture of Antioxidants
nm - not measured

Table 3

LPR ACCELERATED STORAGE STABILITY TEST DAT

Abnormally Dark F-44					
LPR Test Time (hr)	0	24	48	72	96
Peroxide No. (ppm)	1	4	6	12	22
Particulates (mg/l)	4.0	3.0	7.0	8.0	12.0
Antioxidant Conc. (ppm)*	8.2	0.0	0.0	0.0	0.0

*Conc of 2,6-di-tert-butylphenol

Table 4

LPR ACCELERATED STORAGE STABILITY TEST DAT

Good Stability F-44					
LPR Test Time (hr)	0	24	48	72	96
Peroxide No. (ppm)	0	1	1	2	2
Particulates (mg/l)	2.0	2.0	2.0	2.0	1.0
Antioxidant Conc. (ppm)*	14.3	5.2	5.0	4.6	4.7

*Conc of 2,6-di-tert-butylphenol

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ANALYTIC TESTS AND THEIR RELATION TO JET FUEL THERMAL STABILITY

Shawn P. Heneghan*[1] and Robert E. Kauffman[2]

[1] University of Dayton Research Institute, Aerospace Mechanics Division, 300 College Park Ave.
Dayton, OH 45469-0140, USA
[2] University of Dayton Research Institute, Fluid Analysis Laboratory, 300 College Park Ave.
Dayton, OH 45469-0161, USA

The evaluation of jet fuel thermal stability (TS) by simple analytic procedures has long been a goal of fuels chemists. The reason is obvious: if the analytic chemist can determine which types of material cause his test to respond, the refiners will know which materials to remove to improve stability. Complicating this quest is the lack of an acceptable quantitative TS test with which to compare any analytic procedures. To circumvent this problem, we recently compiled the results of TS tests for 12 fuels using six separate test procedures. The results covering a range of flow and temperature conditions show that TS is not as dependent on test conditions as previously thought. Also, comparing the results from these tests with several analytic procedures shows that either a measure of the number of phenols or the total polar sulfur present in jet fuels is strongly indicative of the TS. The phenols have been measured using a cyclic voltammetry technique and the polar material by gas chromatography (atomic emission detection) following a solid phase extraction on silica gel. The polar material has been identified as mainly phenols (by mass spectrometry identification). Measures of the total acid number or peroxide concentration have little correlation with TS.

INTRODUCTION

The issue of jet fuel thermal stability (TS) has been the subject of numerous studies and reviews[1,2] during the last 30 plus years. Since 1973, the standard for evaluating jet fuel TS has been the jet fuel thermal oxidative tester (JFTOT) and American Society of Testing and Materials (ASTM) D-3241. While this test may be adequate for determining a go/no-go fuel rating, its usefulness is limited in fuels stability research because:

- the JFTOT is based on a high (260C) operating temperature, and
- the measurement of fuel quality is based on a qualitative visual measurement.

As a result of the JFTOT's limitations several "advances" in evaluating fuel TS have been suggested and implemented in laboratory situations during the last decade. These tests include the hot liquid process simulator (HLPS), JFTOT breakpoint, gravimetric JFTOT[3], quartz crystal microbalance[4,5] (QCM), and a variety of single-tube heat exchangers[6-10] The range of temperatures has been expanded to cover temperatures from 140C to 335C and a range of flow conditions is covered by these new tests. Despite the variety of conditions, they all have one basic item in common with the JFTOT – each laboratory test attempts to determine fuel stability under accelerated test conditions. The accelerated conditions used by the TS tests are limited versus what occurs on an aircraft.

In addition to the development of new TS tests, analytic tests have been designed in an attempt to facilitate understanding of the deposition process and to assist in the evaluation of input parameters (i. e. A-factors and activation energies) for modeling and effectively predicting fuel TS[11]. This has long been a quest of fuel chemists for two major reasons. The first reason is the possible ease of operation of a quantitative analytic procedure. This may result in more rapid sample measurement, more reproducible results, and/or less waste product and simpler apparatuses. The second, and more interesting, reason is that once an analytic test is developed and chemists determine the precise nature of the compounds that yield a given response in a particular test, refiners/suppliers will know how to improve fuels. Complicating the quest for a good analytic test has been the lack of an acceptable quantitative fuel stability standard.

In this paper, we discuss the quantitative TS results from five separate tests covering a range of temperatures from 140C to 335C under both flowing and static conditions. We use the results of these tests for 12 different fuels to develop an "average" TS scale. This scale can then be used to compare several different analytic test procedures. Helping researchers to understand which test prcedures should be weighted heavily and which should not. Comparisons among the different tests allow significant insight into some of the major causes of jet fuel instability and detail a simple method of improving fuel stability.

The analytic tests discussed here have been designed to study oxygen-containing fractions of fuel components. We have chosen these tests (versus other available tests such as alkene or mercaptan sulfur because (a) oxygen-containing compounds are known to concentrate in the deposits, (b) the autoxidation reactions are known to stimulate deposit formation, and (c) many antioxidant molecules are known to be phenolic and antioxidant molecules have been predicted to be deposit precursors[2].

FUELS AND EXPERIMENTS

The U.S. Air Force acquired and distributed a series of jet fuels for test and additive evaluation. These fuels were assigned a four-digit number by the Fuels Branch, Fuels and Lubrication Division of Wright Laboratories (POSF). These fuels are listed in Table 1.

Two modified procedures for the JFTOT have been used to provide two quantitative measures of fuel TS under flowing conditions[12].The first, HLPS, uses stainless-steel tubes and a 335C operating temperature. The total carbon on the tube, measured by carbon burn off, is used as a quantitative measure of TS. The second measure assesses the maximum operating temperature at which the fuel fails ASTM D-3241. This is reported as the JFTOT breakpoint temperature.

Two static tests were also used to evaluate fuel TS. The isothermal corrosion oxidation test (ICOT) heats fuel (185C) under reflux with bubbling air for 5 hours. The quartz crystal microbalance (QCM) is a closed system heated to 140C. In the ICOT[13], the fuel stability is evaluated by gravimetric measure of the filterable deposits formed. In the QCM, the mass of deposits collected on the surface of the quartz crystal is determined by the shift in crystal frequency. The total mass measured at 8 and 15 hours is used in this study[5,14].

The last TS test for each of these fuels is the micro carbon residue test (MCRT). In the MCRT, the fuel is distilled in air at 250C. The resulting deposits remaining in the distillation flask are reported as a measure of fuel TS[13].

The fuels were analyzed for total acid number (TAN) (ASTM D-3242). The total phenol and total peroxide numbers were determined using cyclic voltammetry[15]. The absorbance of a 10-μl fuel sample extracted into basic water (pH=13) was measured using a UV/VIS spectrometer[16]. The absorbance near 300 nm is proportional to the concentration of phenols in the fuel[17]. The total polar carbon, sulfur, and oxygen were determined using solid phase extraction[18,19] on a silica gel and subsequent extraction of the polar material from the gel into methanol. The quantity of material was determined by gas chromatography with atomic emission detection (GC-AED)[20]. Identification of these materials was made by gas chromatography with mass spectrometry (GC-MS) detection.

RESULTS

The results of the six TS tests for each of the 12 fuels are shown in Table 2. The results of the seven analytic test measurements for each of the 12 fuels are shown in Table 3. The total carbon and oxygen areas reported do not include DIEGME (a fuel system icing inhibitor) that is present in some of the fuels. A complete list of the identified compounds and their relative occurrence in the 12 base fuels is given in Table 4.

DISCUSSION

Before proceeding with a discussion of analytic tests, we must first evaluate the TS tests to determine if there is a meaningful and quantifiable TS scale. To evaluate such a scale (if one exists) requires us to compare each available TS test, which we believe in some way measures TS, to this "real" TS scale. The differences between "reality" and the individual tests should be quantifiable and small.

The comparison among different TS tests is complicated by the fact that no two tests are necessarily measuring the same thing. Often a least square fit between one of the tests, JFTOT breakpoint, is used as a measure of the "goodness" of a particular test. These kinds of least square analysis may be valid, but there is no guarantee that the relation between temperature (C) and deposits (mg/l) or some other types of inappropriate comparisons should yield a straight line. Normalization of the test results before comparison does not remove the assumption of linearity between tests. Such a non-linearity was observed by Kauffman[15] even while the relative ranking of the jet fuels was maintained.

A more important criterion for test evaluation is that the tests show the same or a similar ranking of the fuels. The ability to rank fuels similarly relies on the assumption that the individual TS tests exhibit monotonic behavior, even if not linear. That is, one test might discriminate well among fuels that are very thermally stable, while another is better at discriminating between fuels that are not particularly good. A least squares comparison of these two tests would be poor, yet all fuels could be ranked identically. The assumption of monoticity is significantly weaker than linearity and should yield a more robust analysis. Therefore, to evaluate the TS of a jet fuel, we have changed the absolute measurements in Table 2 to reflect the ranking of the fuels (see Table 5). The fuels are listed in order from best to worst average ranking (see Equations 1,2, and 3).

Several items are apparent from Table 5:

- JPTS (2976) is the most stable fuel in each TS tests.
- The second best fuel is POSF-2747.
- All of the tests measure POSF-2985 as one of the two worst fuels.
- While there is general agreement concerning the ranking of the jet fuels, none of the tests are in perfect agreement with the average ranking.
- Interestingly, none of the tests is in agreement with any other test.

The first three statements show that despite the diversity of test conditions, good fuels and bad fuels can be identified by any of the TS tests. That is, while there may not be an absolutely correct TS test, there is at least good general agreement by all tests concerning what constitutes a good or a bad fuel.

The last two statements, however, are the most important to the evaluation of analytic tests. No pair of tests agree completely with each other, and no individual test agrees with the average. Not even the rankings for QCM at 8 and 15 hours are identical. If we are to attempt to develop an analytic test to evaluate TS, we have to understand that an exact match to all tests is not possible. In fact, the goal of any analytic test should not be to match any particular TS test, but rather to be within the noise level of the TS tests. To define the noise of the TS tests, we need to know how far from "reality," or at least from some definable goal, the ranking is. Since the "real" ranking is not a known, we proceed on the assumption that the average of these tests is a good estimate of reality. The difference between the measured ranking and the average ranking (for a given TS test) is defined in Equations 1 and 2. The difference measurement (D_j) for each of the six TS tests is shown in the last row of Table 5.

$$D_j = \sum_{i \text{ fuels}} \frac{|R_{ij} - R_{iave}|}{12} \qquad 1)$$

where R_{ij} is the integer rank of the i^{th} fuel in the j^{th} test when compared to the other 11 fuels (Table 5), R_{iave} is the integer rank associated with r_{iave} (the average ranking in Table 5), and

$$r_{iave} = \sum_{j \text{ tests}} \frac{R_{ij}}{6} \qquad 2)$$

To recap, each combination of fuel i and test j has a rank R_{ij} (an integer between 1 and 12). The average of the R_{ij} averaged over tests j is the average ranking of the fuel I and is called r_{iave}. The average ranking of a fuel r_{iave} can also be considered a TS test and can be ranked just as the other TS tests. The rank of the average ranking is called R_{iave}. The average difference for a test (D_j) is the average of R_{ij} - R_{iave} averaged over the i fuels.

The value D_j is a measure of how far out of place (versus the rank of the average, R_{ij}) on average the j^{th} test ranks all fuels. Clearly the MCRT is the furthest from average and the QCM (8 hrs) test is the closest. The average D (Equation 3) for the six TS tests is 1.11. This is a measure of how close the set of TS tests comes to measuring the "real" thermal stability scale (remember "reality" is assumed to be represented by the average). An analytic test need not be any better than this (D_j =1.16) to be as good as a TS test at predicting thermal stability.

$$D = \sum_{j \text{ tests}} \frac{D_i}{6} \qquad 3)$$

We are now in a position to quantify one of our original observations – that there is general agreement among the TS tests. First, let us consider the meaning of D_j. Starting with the correct order for a fuel (1,2,...12), the smallest change is the switching of two neighboring fuels (2,1,3,4,...12). This is a single permutation. Any ordering can be described as a number of permutations from the correct ordering. Each permutation of neighboring values will increase or decrease D_j by 0.17.

If the order of the fuels for a given test were ranked in a completely inverted order (12,11,10 ... 1), D_j would be 6. The same value (6) comes from a "six-step rotation" (7,8,...12,1,2,...6). We believe this to be a maximum but have not proved it (there are 12! possible arrangements, so the maximum can be found in principle). If one fuel is completely misplaced (12,1,2,3,4...), D_j is 1.83. If the fuels are pairwise misplaced (2,1,4,3,6,5...), D_j is 1. A random test (totally uncorrelated to TS) would be expected to have D_j equal to 3.83 (measure by 25 randomly generated test results for a confidence interval of ± 0.17). The average D for the six tests is 1.16 (seven permutations out of order). Even the MCRT, a distillation test, has a D_j of only 1.67 (ten permutations out of order). If we were to drop the MCRT from consideration as a valid TS test, D would decrease to 1.0.

Now that we have both a working TS scale, the "rank of the average scale (R_{iave})," and an idea of the precision with which the TS tests can reproduce that scale, we can consider the analytic tests and evaluate their ability to predict TS. Again, rather than assume some linear behavior for the analytic tests to reproduce a given TS test, we will rely on the weaker assumption of monotonic behavior. Table 6 shows the ranking of the fuels by analytic test. The fuels are listed in order of average ranking as in Table 5 and ranked by increasing measure of the analytic test. The difference (D_j) between the ranking of the fuels by analytic test versus the average stability scale (R_{iave}) is also shown.

Some observations from Table 6 are as folows:

- TAN and Peroxide number are only slightly better than random guesses for TS.
- One test (UV/VIS) is as close as the TS tests are to the average TS scale.
- Two other tests (Phenols and Sulfur) are as close as the worst TS test (MCRT).
- Similarly to the TS test, the analytic tests (neglecting TAN and Peroxides) can pick both the very good and the very bad fuels.

CORRELATIONS

A simple first guess is that each of the analytic tests is somehow related to thermal stability. A least squares linear fit between the rank (R_{ij}) for the analytic tests and the average rank of the fuel in thermal stability tests (r_{iave}) shows that the average thermal stability test can be predicted from the given set of analytic tests. The correlation coefficient (r^2) is 0.94, and the sum of the squares of the residuals is 6.5. The rank of the prediction of the linear regression shows a difference (D_j) of 0.67. This is well within the range of differences that individual TS tests achieve. The regression parameters are given in Equation 4.

$$r_{iave} = 0.28*\text{Peroxide} + 1.28*\text{Carbon} + 0.31*\text{TAN} + 0.27*\text{UV/Vis} - 1.94*\text{Oxygen} + 1.11*\text{Phenols} - 0.07*\text{Sulfur} \qquad 4)$$

A quick look at the values of the coefficients shows that the absolute value of the coefficients of sulfur, UV/VIS, and peroxides are all 0.3 or less. The correlation is still 0.90 when peroxides and UV/VIS have been removed from the basis set of analytic data, and D_j is an identical 0.67. For comparison, we note that individual TS tests generally have r^2 of 0.7 to 0.9 for correlation with the r_{iave}. The individual analytic test r^2 values are shown on the diagonal of Table 7.

Using the total polar materials (carbon, sulfur, and oxygen) and the phenol number only yields a correlation r^2 of 0.84 and D_j of 1.0. The regression parameters for this fit are given in Equation 5.

$$r_{iave} = 0.19 \text{ Sulfur} + 0.94 \text{ Carbon} - 1.35 \text{ Oxygen} + 1.09 \text{ Phenols} + 0.87 \qquad 5)$$

At the opposite side is the question of how simple can we go and still achieve a reasonable TS prediction. As shown in Table 6 and again on the diagonal of Table 7, only one analytic test is a reasonable predictor of thermal stability (UV/VIS). However, if two tests are combined, several combinations are good predictors of TS. Table 7 shows the two-parameter correlations to r_{iave}. The values in the lower triangle of the table are the r^2 for the correlation of r_{iave} with the least squares fit linear combination of two analytic tests (from the row and column headings). The diagonal contains the one parameter r^2. The upper triangle area shows the D_j for the two-parameter test. This table shows again the importance of the sulfur and phenol compounds which have the largest two-parameter correlation (0.80), and a D_j of only 1.33, one permutation higher than the average thermal stability test. For oxygen and UV/VIS, r^2 is 0.80 and D_j is 1.16, emphasizing the need to eliminate phenols (measured by the UV/VIS) and polar oxygen.

APPLICATIONS

Two major applications of the above ranking scheme are immediately available. First, once a sufficient number of fuels have been tested (with both TS and analytic tests) analytic tests alone may be used to evaluate jet fuel TS. A passing test would indicate average TS performance at or above a pre-selected fuel. At a minimum, as suggested by Kauffman[15], only those fuels that pass the analytic tests would be tested in thermal stability tests.

The second application is in making fuels better. As indicated previously, once the source of response to the given analytic is determined it should follow that the removal of that species would improve the fuel. Our strongest correlation is with the UV/VIS test that we believe measures the concentration of base extractable phenols. The second best correlation is with the phenols measured by cyclic voltammetry. The correlation of jet fuel TS with cyclic voltammetry tests has been discussed previously[15].The third strong correlation is with the polar sulfur compounds. The necessity of oxidizable sulfur compounds[21] and the importance of polar sulfur compounds[1] to the formation of deposits has also been discussed previously. These compounds were removed from the fuel by silica gel solid phase extraction. An analysis of the compounds that were removed from all the fuels is shown in Table 4. Interestingly, no sulfur-containing compounds have been identified. However, the gel was effective at removing many of the polar N- and O- compounds identified by Hazlett as key players in the formation of insolubles. These compounds have been identified as mainly substituted phenol and amine compounds.

A less obvious use of the TS scale is in the evaluation of jet fuel additives. TS of the fuels and the relative increase in their TS as a result of additives can now be more easily quantified as to how much improvement was achieved, and appropriate wighting schemes for the individual tests can now be determined.

CONCLUSION

By using a ranking procedure, the results of TS tests can be compared to one another without resorting to a normalization that amounts to an assumption of linearity that may not exist. Once the ranking system is established, it becomes apparent that several of the TS tests yield results that are similar to each other. That is, the concept of TS of a jet fuel may be reasonably well-defined, independent of the conditions. A TS scale indicative of the average of six TS test measurements was developed. The noise associated with TS has been established. Analytic tests, alone and in combination, have been shown to reproduce the TS scale as well as the individual TS tests (i.e., to within the same noise level as the TS tests).

A series of analytic tests for oxygenates/polar materials showed several important correlations with the TS scale. In particular, there was a very strong correlation with phenols and polar sulfur. Analysis of the polar material showed that a majority of it is phenolic in nature with secondary quantities of amine-type material. Despite the importance of polar sulfur material shown by its correlation with the TS scale, no sulfur compounds have yet been identified. Tests for TAN and peroxides showed only slightly better than random chance at correlating fuel TS.

Tests for polar oxygen and carbon showed better than random chance correlations, but they were not as good as any TS test at measuring the TS scale.

Several pairs of analytic tests were found to adequately describe the TS scale. Each pair which exhibits good comparison to the TS scale contains at least one analytic test which measures phenols or polar-sulfur compounds.

The importance of polar-sulfur compounds appears obvious from D_j for the polar sulfur test and from the two parameter correlations but becomes less obvious during multiple regressions. Peroxide and TAN are not strongly related to thermal stability. A set of five analytic tests gave a 0.94 correlation to the TS scale.

The removal of phenols appears to be crucial to the development of higher thermal stability fuels. The importance of as yet unidentified polar-sulfur compounds is probably important, but the correlation is not as well-established.

ABBREVIATIONS

ASTM	American Society for Testing and Materials	JFTOT	Jet Fuel Thermal Oxidative Tester
AED	Atomic Emission Detection	JPTS	Jet Propellant, Thermally Stable
D_j	Difference measurement for jth test	MCRT	Micro Carbon Residue Test
D	D_j averaged over j tests	MS	Mass Spectroscopy
GC	Gas Chromatography	QCM	Quartz Crystal Microbalance
HLPS	Hot Liquid Process Simulator	r^2	Correlation Coefficient
i	index of fuels	R, r	Integer, Average Rank
j	index of tests	TS	[illegible] Stability
ICOT	Isothermal Corrosion Oxidation Test	TAN	[illegible]ber
		UV/VIS	U[illegible]olet/Visible

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Table 1. Test Fuels

POSF#	Type	Comments
2976	JPTS	Jet Propellant -Thermally Stable
2747	Jet A-1	Meets super K-1 kerosene spec
2827	Jet A	
2922	Jet A	Hydrotreated
2926	Jet A	
2928	Jet A	contains 15% hydrocracked stock
2934	Jet A-1	High acid number
2936	JP-5	
2959	Jet A	Merox-treated
2963	JP-5	Copper-spiked 50 ppb
2980	Jet A	Merox-treated
2985	JP-5	High nitrogen

Table 2. Thermal Stability Test Results

Fuel	ICOT mg/L	MCRT mg/g	QCM-8hrs $\mu g/cm^2$	QCM-15hrs $\mu g/cm^2$	JFTOT Breakpoint C	HLPS $\mu g/cm^2$
2976	0	0.5	0.3	0.8	427	6
2747	5	1.2	0.6	0.85	332	7
2827	87	3	2	3.6	282	48
2922	104	1.7	1.8	2.4	277	18
2926	64	2.2	3.2	4	288	43
2928	89	1.8	3	3.2	279	36
2934	358	1.9	5	5.7	266	121
2936	72	1.6	4	6.9	277	65
2959	43	1.4	1.4	2.5	293	113
2963	485	1.9	5.4	6.1	232	153
2980	83	2.1	5	6.2	288	52
2985	755	3.9	9.5	10.5	266	127

Table 3. Analytic Test Results

Fuel	TAN μg KOH/g	Phenols mmole/l	UV-VIS	Peroxide μmole/L	Carbon Area	Sulfur Area	Oxygen Area
2976	3	0	0.07	3	3.4	1.4	6.1
2747	0	0.4	0.10	0	2710	8.5	10.1
2827	1	2.6	0.9	29	7650	91.5	25.4
2922	4	0.2	0.25	12	2012	21.1	8.5
2926	2	0.8	0.32	27	2450	26.8	9.0
2928	13	1	0.50	25	4990	43.2	21.4
2934	43	7.1	2.65	0	11800	13.8	85.3
2936	14	3.6	0.77	0	2140	28.9	14.6
2959	2	1.5	0.33	31	4130	20.1	21.5
2963	4	2.1	0.67	22	2766	71	14
2980	1	2.1	0.80	34	14200	34	80
2985	3	16	3.69	33	33600	122	128

Table 4. Identifiable Polar Compounds and Their Number of Occurrences in the Base Fuels

Compound	Occurrences	Compound	Occurrences
Phenol	3	Methyl aniline	3
Methyl phenol	8	Ethyl aniline	3
Dimethyl phenol	10	Dimethyl aniline	2
Ethyl phenol	8	Diethyl aniline	1
Trimethyl phenol	5	Propyl aniline	1
Propyl phenol	3	C3 aniline	1
C3 phenol	9	C4 aniline	1
C4 phenol	10	C5 aniline	1
C5 phenol	6		
C6 phenol	3	C4 pyridine	1
C4 benzenemethanol	1	Ethylmethyl pyridine	2
1-methoxy-4-1-methylpropylbenzene	1	Propyl pyridine	1
Bis 2-ethylhexylpthalate	1	Trimethyl pyridine	2
C3 benzodioxole	1	T-butyl pyridine	1
C3 cyclohexanone	1	Dimethyl pyridine	1
Ethoxybenzaldehyde	1	C4 pyridine	2
Methoxy benzenes	1		
Trimethyl bicyclohytanone	1	Trimethyl quinoline	1
Phenol ethyl benzene ethanomine	1	Tetrahydro 3-methyl isoquinoline	1
Indoles	1	Dimethyl tetrahydro quinoline	1
C3 benzoic acid methyl ester	1	Napthalamine	1

Table 5. Integer Ranking (R_{ij}) of Fuels by Thermal Stability Tests

Fuel	ICOT	MCRT	QCM 8hrs	QCM 15hrs	J FTOT	HLPS	Average ranking (r_{iave})	Rank of average (R_{iave})
2976	1	1	1	1	1	1	1	1
2747	2	2	2	2	2	2	2	2
2959	3	3	3	4	3	9	4.17	3
2922	9	5	4	3	8	3	5.33	4
2928	8	6	6	5	7	4	6	5
2926	4	10	7	7	4	5	6.17	6
2827	7	11	5	6	6	6	6.83	7
2936	5	4	8	11	8	8	7.33	8
2980	6	9	9	10	4	7	7.50	9
2934	10	7	9	8	10	10	9.00	10
2963	11	7	11	9	12	12	10.33	11
2985	12	12	12	12	10	11	11.50	12
(D_j)	1.33	1.75	0.42	1.00	1.42	1.17		

Table 6. Integer Ranking (R_{ij}) of Fuels by Analytic Test

Fuel	TAN	Phenols	UV/VIS	Peroxide	Carbon	Sulfur	Oxygen
2976	6	1	1	4	1	1	1
2747	1	3	2	1	5	2	4
2959	4	6	5	10	7	4	8
2922	8	2	3	5	2	5	2
2928	10	5	6	7	8	9	7
2926	4	4	4	8	4	6	3
2827	2	9	10	9	9	11	9
2936	11	10	8	1	3	7	6
2980	3	7	9	12	11	8	10
2934	12	11	11	1	10	3	11
2963	8	7	7	6	6	10	5
2985	7	12	12	11	12	12	12
Difference(D_j)	3.67	1.58	1.17	3.50	2.33	1.67	2.17

Table 7. Correlations: 2 Parameter Analytic Test to r_{iave} in Lower Triangle, 1 parameter to r_{iave} on Diagonal, and Difference Measurements (D_j) of 2 Parameters Tests in Upper Triangle.

	Oxygen	Sulfur	Carbon	Phenols	Peroxide	TAN	UV/VIS
Oxygen	0.44	1.83	2.17	1.50	2.17	2.00	1.16
Sulfur	0.67	0.57	1.67	1.50	1.67	1.67	1.16
Carbon	0.44	0.64	0.40	1.50	2.33	1.67	1.33
Phenols	0.70	0.78	0.66	0.70	1.50	1.50	1.33
Peroxide	0.44	0.58	0.40	0.69	0.14	2.17	1.17
TAN	0.56	0.70	0.61	0.67	0.48	0.18	1.67
UV/VIS	0.80	0.79	0.74	0.74	0.73	0.77	0.73

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BEHAVIOUR OF CONDUCTIVITY IMPROVERS IN JET FUEL

Brian Dacre* and Janice I Hetherington

Royal Military College of Science,
Cranfield University, Shrivenham,
Swindon, Wiltshire, SN6 8LA
United Kingdom.

ABSTRACT

Dangerous accumulation of electrostatic charge can occur due to high speed pumping and microfiltration of fuel. This can be avoided by increasing the electrical conductivity of the fuel using conductivity improver additives. However, marked variations occur in the conductivity response of different fuels when doped to the same level with conductivity improver. This has been attributed to interactions of the conductivity improver with other fuel additives or fuel contaminants. The present work concentrates on the effects of fuel contaminants, in particular polar compounds, on the performance of the conductivity improver. Conductivity is the fuel property of prime interest. The conductivity response of model systems of the conductivity improver STADIS 450 in dodecane has been measured and the effect on this conductivity of additions of model polar contaminants sodium naphthenate, sodium dodecyl benzene sulphonate, and sodium phenate have been measured. The sodium salts have been found to have a complex effect on the performance of STADIS 450, reducing the conductivity at low concentrations to a minimum value and then increasing the conductivity at high concentrations of sodium salts. This work has focused on characterising this minimum in the conductivity values and on understanding the reason for its occurrence. The effects on the minimum conductivity value of the following parameters are investigated: (a) time, (b) STADIS 450 concentration, (c) sodium salt concentration, (d) mixed sodium salts, (e) experimental method, (f) a phenol, (g) individual components of STADIS 450. The complex conductivity response of the STADIS 450 to sodium salt impurities is discussed in terms of possible inter-molecular interactions.

1 INTRODUCTION

Jet fuel has very low natural electrical conductivity, usually less than **5pSm^{-1} (CU).** It is well known that dangerous accumulation of electrostatic charge can occur due to high speed pumping and microfiltration of jet fuel (1,2). This can be overcome by increasing the electrical conductivity of the fuel which is achieved by the use of conductivity improver additives.

Two additives have been used, namely, Shell ASA-3 , employed outside the USA since 1962 and DuPont STADIS 450 which was introduced in the mid 1970's. Both additives were considered for US Military use only after service tests in 1978. Shell discontinued supply of ASA-3 at the end of 1991 and for this reason, since January 1992, this work has concentrated entirely on the behaviour of STADIS 450.

Considerable variations are observed in the conductivity response of fuels from different crude sources when doped with the same concentration of additive. It was for this reason that the UK MOD tasked the Royal Military College of Science to investigate interference with additive performance.

2 AIMS OF THE WORK

The aims remain similar to those in our earlier published work (3):

(a) to investigate the influence of fuel components on the performance of conductivity improver additive and

(b) to attempt to understand the nature of important intermolecular interactions.

Earlier (3) we reported on the effects of a wide range of additives and compounds, representative of naturally-occurring fuel components, on the electrical conductivity of solutions of conductivity improvers. Large reductions in conductivity can be caused by dodecylbenzene sulphonic acid (DDBSA) and other highly polar substances. For example, preliminary results on the sodium salt of DDBSA showed this to have a large antagonistic effect on 3 ppm STADIS 450 in dodecane.

The acidity in fuel is due to the presence of naturally-occurring phenols and naphthenic acids plus sulphonic acids which are refinery produced by certain processes. In addition the presence of sodium salts is also a possibility. Data indicate that clay treatment of fuels, whilst giving substantial reduction in naphthenates and probably sulphonates, rarely removes substantial amounts of phenolic components.

Table 1 is a summary of our knowledge on the concentration of these highly polar constituents observed in jet fuel. We note the following:

Naphthenates show a large concentration range but with a fairly modest maximum concentration. However, there is a possibility of some salt being present, at estimated concentrations of 1ppm or greater.

Phenolics show a very large concentration range and very large concentrations. Here there is no information on phenate concentration and 10ppm has been estimated.

Sulphonates occur only at low concentrations, possibly up to 0.3ppm. Some higher total sulphonate values, up to 5ppm, have been reported (4).

In our research programme it is our intention to examine these substance types in detail. However, in this paper we shall concentrate on the influence of the most highly polar types, namely salts, on the conductivity of STADIS 450 in dodecane solutions. For this purpose we have used a sodium naphthenate, for which extensive measurements are presented, sodium dodecyl benzene sulphonate and a sodium phenate. The parameters studied were : (a) time, (b) STADIS 450 concentration, (c) sodium salt concentration, (d) salt mixture concentration and (e) STADIS component effects.

3 EXPERIMENTAL

3.1 Materials

Details and purification of most substances used here are as previously described (3).

STADIS 450 was supplied by **Instar/DuPont.**

The sodium phenate (NaP) was prepared by neutralisation of dodecylphenol (Aldrich) by sodium hydroxide in methanolic solution followed by recovery of the solid phenate by rotary evaporation of the methanol. Sodium naphthenate (NaN) has been prepared in a similar way. A sample of the latter was acquired from Kodak which is used in this work. Sodium dodecyl benzene sulphonate (NaDDBS) is a Sigma product. m-cresol was obtained from BDH Chemicals.

STADIS 450 fractions: Gel Permeation Chromatography of STADIS 450 showed that three major components were present of high, medium and low molecular weight. Selective precipitation was used to separate the three molecular weight fractions.

3.2 Conductivity Equipment and Conditions

Previously (3) we discussed in some detail the difficulties caused by adsorption effects on conductivity measurements and described how these were taken into account in the interpretation of data. Adsorption was a particular problem with ASA-3. For STADIS 450 however, adsorption losses were small. In this work STADIS 450 has been used exclusively and conductivity losses due to adsorption are generally insignificant. Measurements were made with the range of apparatus already described (3) and temperature controlled at 25 C unless stated otherwise.

The experimental conditions were selected in order to examine the general behaviour of these systems, rather than to mimic any special field conditions.

4 RESULTS AND DISCUSSION

4.1 Effects of Salts on the Conductivity of Dodecane

The effects of each of the three salts alone, on the conductivity of dodecane, are shown in figure1. NaDDBS gives a significant increase in conductivity which is substantially larger than the small increase caused by NaN. NaP has virtually no effect.

4.2 Time Effects on the Conductivity of STADIS 450 Solutions Containing Salt

Addition of salts to a stable conductivity solution of STADIS 450 causes the conductivity to change with time as illustrated by the data for NaN shown in figure 2. Similar behaviour is observed for NaDDBS and NaP though there are quantitative differences. We note that below a certain concentration of salt, conductivity *decreases* with time, eventually reaching a constant value. Above this certain concentration, conductivity *increases* with time to a constant value. These time dependencies cannot be accounted for in terms of time-for-mixing, nor can they be explained by any adsorption effects on cell surfaces. They are real solution effects which are probably a consequence of the time dependence of conformational changes induced in the polymer components and which will be discussed further in sections 5.3 and 5.5. Conductivities reach constant values after about 5 to10 minutes from the additions and remain constant for many hours. For experimental purposes, additions were made at 5 minute intervals. This procedure provides a satisfactory basis for comparisons to be made.

4.3 Dependence of Conductivity on Salt Concentration at Constant STADIS Concentration.

The behavior of NaN and NaDDBS are shown respectively in figures 3 and 4. There are striking qualitative similarities. The general behaviour is characterised by a depression of conductivity at low salt concentration leading to a minimum, then an increase, until the net effect is enhancement relative to the initial STADIS value. We note the considerable range of behaviour which is possible. In particular, and possibly most important, is the large antagonistic effect at low salt concentrations.

4.4 Dependence of Conductivity on STADIS 450 Concentration

In these experiments we observe the conductivity response of STADIS 450 additions to dodecane containing prepared concentrations of sodium salts. These experiments are more relevant to field use of the additive. Data from such experiments are shown in figures 5 and 6. It can be seen that, in the absence of salts, the conductivity increases approximately linearly with STADIS concentration.

At low concentration of salts, <10ppm, the conductivity of the STADIS solution is lower than in the absence of salts for STADIS concentrations <20 ppm. Above 20ppm STADIS the differences are probably not significant when the uncertainties in measurements are taken into account.

At high concentration of salts, ~200ppm, a large increase in the conductivity of STADIS solutions occurs for STADIS concentrations <20ppm. At STADIS concentrations >20ppm the conductivity decreases with increasing STADIS concentration and is considerably lower than the value expected without the sodium salts.

4.5 Effect of STADIS Concentration on the Position of the Minimum Conductivity.

Figures 3 and 4 illustrate the effects of both salt and STADIS concentration.

Sodium naphthenate. Fig 3 shows a pronounced shift in the conductivity minimum to higher sodium salt levels as the STADIS concentration increases. The gradient of the initial part of the curve, where the conductivity is decreasing, is approximately constant for each concentration curve. As shown in Table 2, the ratio of the concentration of STADIS to NaN at the minimum of each curve is approximately constant. Also the depth of the minimum is approximately constant if allowance is made for the uncertainty in the conductivity values, when normalised for the concentration of STADIS.

Sodium dodecylbenzenesulphonate. Figure 4 shows that the ratio for STADIS to NaDDBSA has a similar effect to NaN on the conductivity of STADIS solutions.

4.6 Effects of Salt Mixture Combinations on the Conductivity of STADIS Solutions

The effects of sodium salt mixtures, covering the ranges: naphthenate 0.1-10 ppm, phenate 100-500 ppm and suphonate 1-2 ppm, on solutions of STADIS in dodecane show that the magnitudes of observed conductivities are close to those predicted assuming additivity of individual salt conductivities. Data for one series of measurements are included in figure 5. The 212ppm of mixed salts includes: 200ppm NaP, 10ppm NaN and 2ppm NaDDBS.

4.7 Effects of a Parent Phenol on the Conductivity of STADIS 450 Solutions

Preliminary measurements on dodecylphenol and meta-cresol up to a concentration of ~1000ppm are shown in figure 7. Conductivity decreases non-linearly with phenol concentation and the two phenols show differences in behaviour. Comparison with the low concentration effects of NaP illustrates the considerable difference, mole for mole, between phenol and salt. No minimum is observed for the phenol.

4.8 Comparison and Verification of Behaviour for Research and Field Equipment

The conductivity measurements outlined in section 4.3 were repeated using the EMCEE Portable Conductivity Meter and the procedure given in ASTM D2624. The same dependence of conductivity on salt concentration, and the minimum in conductivity were found . The results were similar to those shown in figures 3 and 4 from the research equipment.

4.9 Conductivity Response of Individual Components of STADIS 450 to Sodium Salts

DuPont patents published in 1975 and 1977 (5,6) suggest that in STADIS 450 the two major components for conductivity performance are the polysulphone and the polyamine, with a sulphonic acid as the third major component, thought to act as a stabiliser. STADIS components, separated as described earlier in section 3.1, are a high molecular weight fraction assumed to be mainly polysulphone, a medium molecular weight fraction assumed to be mainly polyamine and a low molecular weight fraction which seems to be the sulphonic acid.

The conductivity response of each of these fractions and their sensitivity to sodium salts were measured. Each fraction was used at 3ppm in dodecane.

The *high molecular weight fraction* gave the greatest increase in conductivity. A minimum occurs with each salt. The stability of this fraction seems to be impaired by separation from the other components. In all cases the conductivity increases with time, rapidly at first, and only after approximately 2 hours is the conductivity sufficiently constant to begin the addition of salts. It seems likely that this polysulphone fraction is responsible for the minima observed with solutions of fully-constituted STADIS 450.

The *medium molecular weight fraction* shows a minimum with the salts but this is much less pronounced than is the case for the polysulphone fraction. This may be due to traces of polysulphone still being present. A decrease in conductivity occurs with NaDDBS.

The *low molecular weight fraction* shows a small increase in conductivity on addition of each salt, but a minimum does not occur.

These observations are illustrated by the data for NaN in figure 8.

4.10 Practical Significance for Fuels.

Although these results are for model dodecane systems, the trends could be significant for fuels. For fuels containing low concentrations of salt impurities, <10ppm, the performance of STADIS might be reduced. Adding more STADIS would cause the conductivity to increase less than would be expected if no salts were present. High concentrations of salts, >100ppm, could greatly enhance the conductivity performance of STADIS. In some cases the conductivity at 3ppm to 5ppm STADIS could be so high that values would be off-scale on the EMCEE Portable Conductivity Meter, when measured according to ASTM D2624. In the unlikely situation of high concentrations of STADIS, >30ppm, combined with high concentration of salts, >10ppm, the addition of further STADIS will give little or no increase in conductvity.

5 SPECULATION ON THE MECHANISM OF ION PRODUCTION IN SALT-STADIS 450 SOLUTIONS

5.1 General Comments

The general factors which determine ion concentration are:

(a) the intrinsic ability of a molecule to produce ions combined with
(b) the ability of the system to stabilise ions.

The latter we suggest is related to the tendency for molecules to aggregate and to incorporate ions into the aggregates formed. The factors which control aggregation of substances in non-aqueous hydrocarbon solutions have recently been reviewed (7). In the case of surfactant-type molecules the driving force for aggregation in non-aqueous solutions differs from that in aqueous solutions. In the latter case, the so-called hydrophobic interaction between water and hydrocarbon groups is the major factor which gives rise to a favourable entropy increase, whereas for non-aqueous solutions it has been argued that the dipole-dipole interaction between polar head groups provides the major interaction (8-11). An important consequence of this is that in non-aqueous solutions aggregates form at very low concentrations with a range of sizes. This size range changes continuously and slowly with concentration and there is no critical micelle concentration as seen in aqueous solutions.

Consider a sodium salt of general formula NaX. The aggregation process can be then conceived as follows:

$$2NaX \rightarrow (NaX)_2 \qquad \text{(i)}$$

$$NaX + (NaX)_2 \rightarrow (NaX)_3 \qquad \text{(ii)}$$

$$NaX + (NaX)_{n-1} \rightleftharpoons (NaX)_n \qquad \text{(iii)}$$

These equilibria involve only uncharged dipoles. Ions are then produced via processes such as:

$$(NaX)_n \rightleftharpoons [(NaX)_p Na]^{+} + [(NaX)_q X]^{-} \qquad \text{(iv)}$$

where $n = p + q + 1$

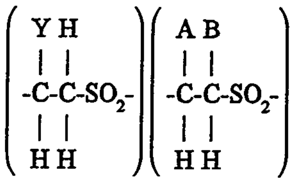
Charged groups such as these will, of course, be present at extremely low concentrations and will give rise to electrical conductivity. Theoretical treatment of such equilibria is being examined but will not be reported in this paper.

5.2 STADIS 450

In a previous paper (3) we briefly discussed the conductivity-improving mechanism of STADIS 450 and argued that an increase in acid strength of one carboxyl can occur due to the combined activating influence of neighbouring sulphone and carboxyl groups. This effect, combined with the proton-acceptor properties of the polyamine component, could lead to ion production. However, polyamine is not essential for conductivity improvement and polysulphone alone is sufficient (6). The polysulphone present in STADIS 450 and that described by Johnston (6) are apparently identical and contain the carboxyl group.

5.3 Conformational Properties of the Polysulphone Component of STADIS 450.

The polysulphone component is a co-polymer of an alkene with suphur dioxide of general formula:



$$\left(\begin{array}{c} Y\;H \\ |\;\;| \\ -C-C-SO_2- \\ |\;\;| \\ H\;H \end{array}\right)\left(\begin{array}{c} A\;B \\ |\;\;| \\ -C-C-SO_2- \\ |\;\;| \\ H\;H \end{array}\right)$$

According to Mansfield (12) such polymers exist as random coils or helices depending on the presence or absence of groups A and B in trans positions. Sulphone groups which are present in helix structures interact co-operatively to give large dipole moments. For STADIS 450 the range of polysulphone structures can vary from 0% of (b), in which case the repeat unit has only a single side group and helix formation is favoured, to 10% of (b), in which case one-in-five repeat units has one side group on each of the two adjacent carbon atoms. The latter will be trans and will disrupt the helix structure. Any percentage between these values will clearly give a product mixture which includes some degree of helix development.

We can envisage that a given polysulphone molecule will contain a series of helical segments, each having a dipole moment determined by the number of repeating units present, joined by single units containing trans-configured carboxyl groups. The latter will add flexibility into the total chain and may allow helical segments from the same molecule to interact. We also note that the polysulphone can be considered as a polyelectrolyte and this is discussed in sections 5.4 and 5.5.

5.4 Polysulphone Conductivity

Since polysulphone alone is capable of imparting conductivity this implies that the polysulphone molecule itself is able to stabilise ions. The candidate group for this role, within the molecule, is the sulphone group which has been shown to have proton acceptor properties as indicated by its interaction with phenol (14). Phenolic hydroxyl groups are, in general, considerably weaker proton donors than carboxyl, as measured in both aqueous and non-aqueous solution (15). This suggests that sulphone-carboxyl interactions will be even stronger. We therefore suggest the following two-step process:

$$R\,COOH + R\,SO_2 \rightleftharpoons R\,COOH\,O_2SR \qquad \text{(v)}$$

where R represents the remainder of the polymer chain

$$R\,COOH\,O_2SR \rightleftharpoons [R\,COO]^- + [HO_2SR]^+ \qquad \text{(vi)}$$

Additional stabilisation will arise from interaction of ions with dipolar helical segments either from a part of the same or a different molecule. It is important to bear-in-mind that ion concentrations are always very low and that the majority of carboxyl groups remain undissociated.

5.5 Effect of Salts on STADIS 450

We interpret the effects as being due to interaction with polysulphone. The interaction of salts with this polyelectrolyte (polysulphone) is considered to involve ion exchange in which Na exchanges with H from a carboxyl group. The resulting sodium carboxylate has no proton donor properties so that reactions (v) and (vi) are no longer possible and the conductivity decreases. From equilibrium arguments we should expect the extent of exchange to depend directly on the salt concentration in solution. We note that the kinetics of this process need not be instantaneous and this may account for time-dependent effects.

Another effect of such exchange is that it is accompanied by a considerable change in polarity, expected to influence the coil and cause it to extend. Any ions stabilised by such extended chains will now have reduced mobilities and this will also contribute to a reduction in conductivity.

A given concentration of STADIS corresponds to a certain concentration of carboxyl groups and replaceable hydrogen. As salt concentration increases the number of hydrogens replaced will increase to a limit determined by carboxylate concentration. We therefore expect the conductivity to *decrease* to a limit. However, as salt concentration increases, ion stabilisation via aggregation processes, similar to reaction (iv), may increase in importance. Self aggregegates of salt may be of secondary importance and we suggest that the primary stabilisation of ions is due to interaction with the polysulphone and /or polyamine. In the former case favourable sites could be strong helix dipoles.

We suggest that the combined influences of polymer chain expansion, proton reduction and sodium ion increase, provide a qualitative explanation of the conductivity minimum.

5.6 Effect of Parent Phenol

We suggest that the detrimental effect of dodecylphenol is caused by reduction in the availability of sulphone groups due to complexation with phenol in reactions similar to that represented by equation (v). In this instance however, the phenol complex does not undergo the ion-producing step, principally because it is a much weaker proton donor.

6 CONCLUSIONS

6.1 Sodium salts of acidic species, present in jet fuel, interfere with the conductivity improving properties of STADIS 450.

6.2 The precise effects on conductivity depend on both STADIS 450 concentration and salt concentration. In general, increasing salt concentration causes the conductivity of the STADIS solution to fall to a minimum and thereafter to increase continuously.

6.3 For normal doping levels of STADIS 450, conductivity losses of up to 50% are observed at 'low' salt concentrations.

6.4 Related to 6.3 is the fact that at low salt concentrations the conductivity response, to STADIS 450 addition, is much reduced.

6.5 For normal doping levels of STADIS 450, significant conductivity enhancement occurs at 'high' salt concentrations.

6.6 Phenols can have a large detrimental effect on STADIS performance. Conductivity losses of up to 70% have been observed at phenol concentrations 'typical' of those in jet fuel.

6.7 The conductivity of these solutions has been explained in terms of the ionisation propensity of groups, the ability of other molecular groupings to stabilise ions and the conformational properties of polyelectrolytes.

7 ACKNOWLEDGEMENTS

The authors wish to thank additive manufacturers and oil companies, especially BP, for their helpful cooperation and supply of additives and fuels. They would also like to express their gratitude to the sponsors of this work, The Procurement Executive, M O D, Dept. F S(AIR) 53, St Giles Court, London WC2H 8LD under Contract FS 1a/375,1993.

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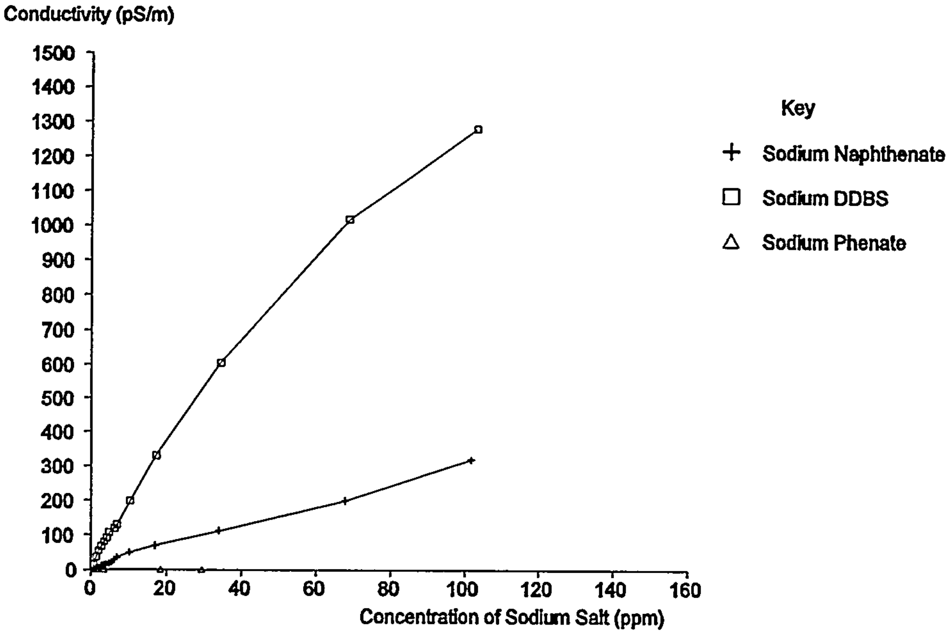

Figure 1 Effect of Sodium Salts on the Conductivity of Dodecane

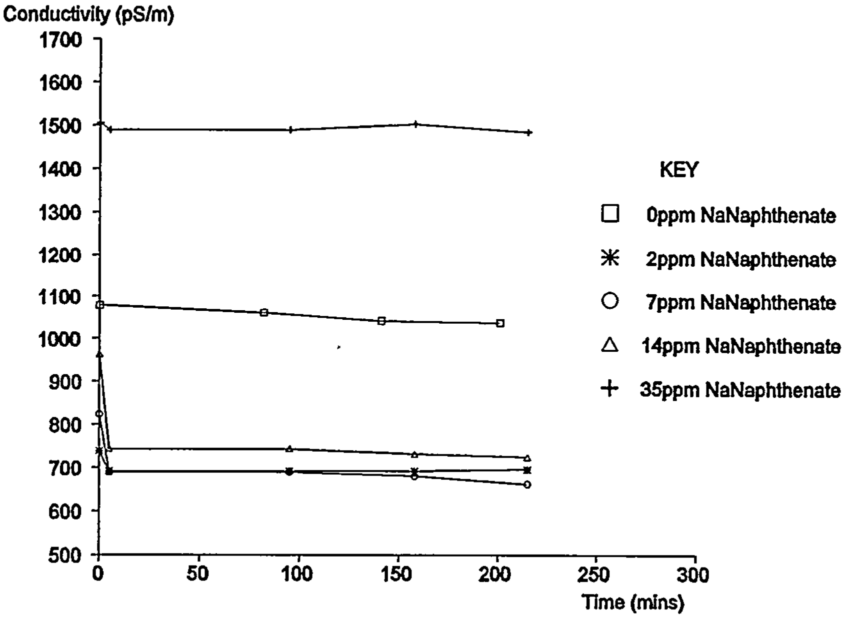

Figure 2 Change in Conductivity with Time for 3ppm STADIS/Dodecane Solution Containing Sodium Naphthenate

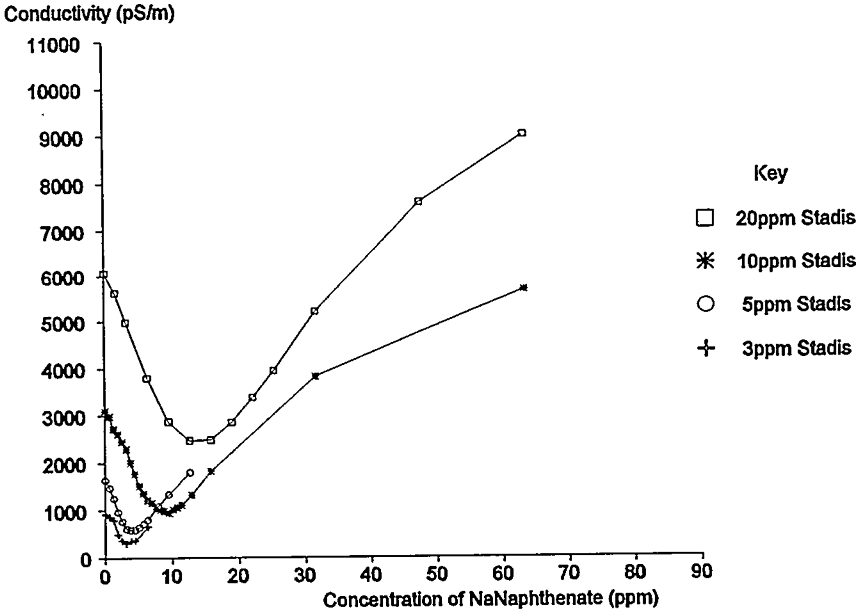

Figure 3 Change in Position of Conductivity Minimum with STADIS Concentration for STADIS/Dodecane/NaNaphthenate Systems

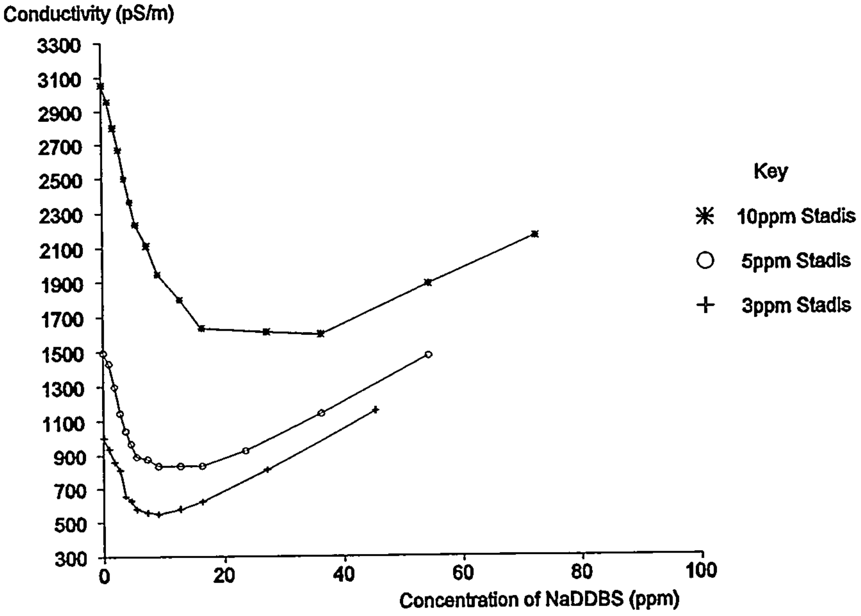

Figure 4 Change in Position of Conductivity Minimum with STADIS Concentration for STADIS/Dodecane/NaDDBS Systems

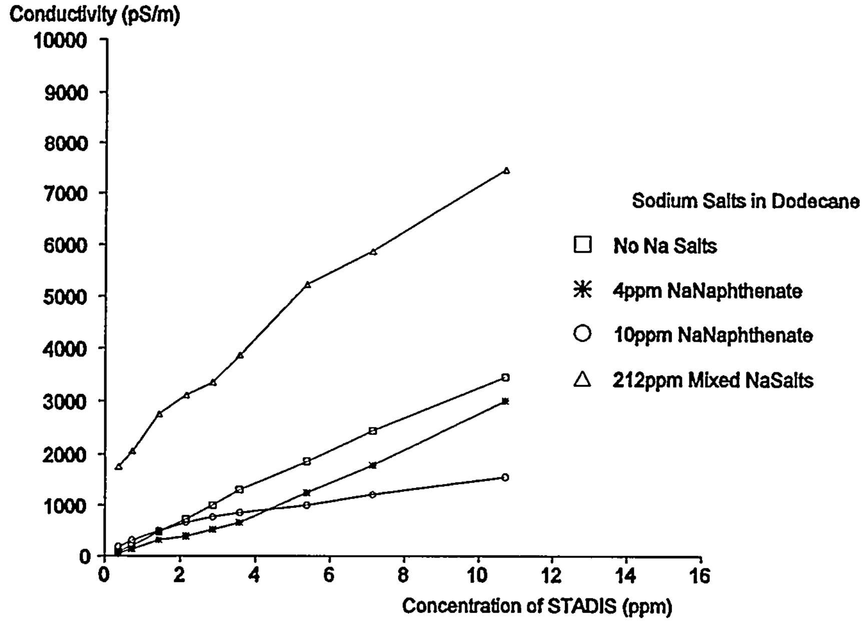

Figure 5 Additions of STADIS to Dodecane Containing Sodium Salts Effect on Conductivity

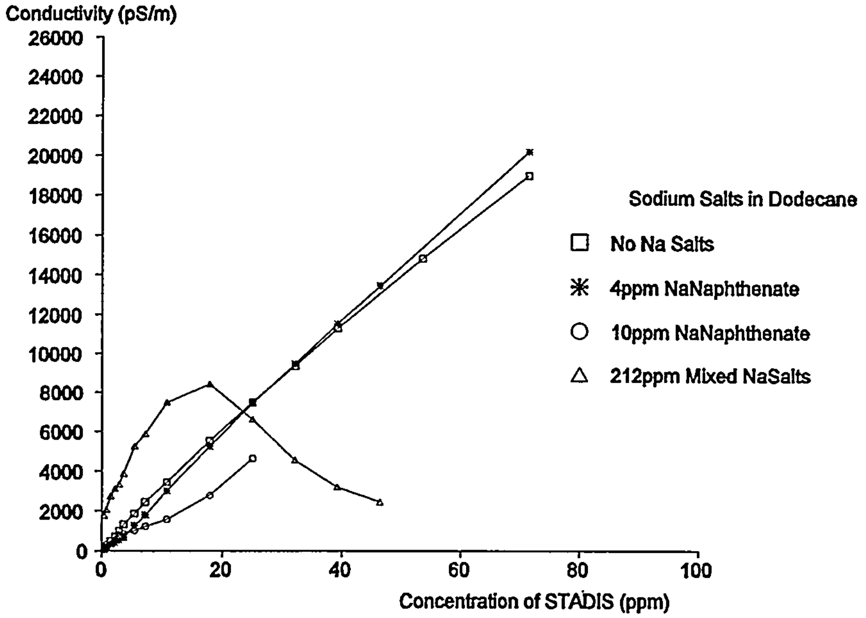

Figure 6 Additions of STADIS to Dodecane Containing Sodium Salts Effect on Conductivity

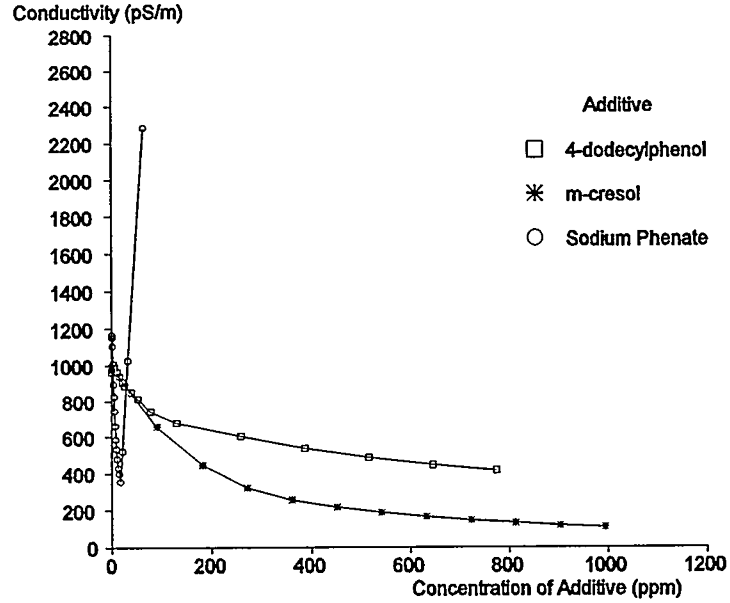

Figure 7 **Effect of Phenols on the Conductivity of 3ppm STADIS in Dodecane**

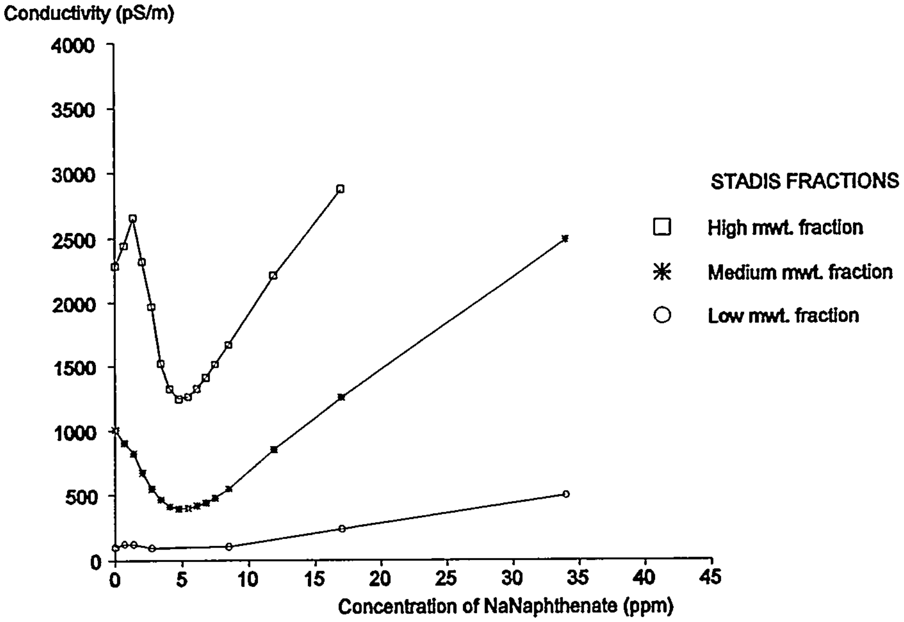

Figure 8 **Effect of NaNaphthenate Concentration on the Conductivity of STADIS Fractions in Dodecane**

Substance type	Merox Fuel
Naphthenic Acid + Naphthenate	<0.1 to 10ppm
Sodium Naphthenate	to ~10ppm
Phenol + Phenate	160 to 750ppm
Sodium Phenate	to ~10ppm (?)
Sulphonic Acid + Sulphonate	~0.3ppm[1] [2]

Table 1 **Suggested Concentrations of Polar Constituents in Jet Fuel**

Parameters at minimum in conductivity curves	Concentration of STADIS in Solution			
	3ppm	5ppm	10ppm	20ppm
Concentration of Sodium Naphthenate (ppm)	3.2	4.2	9.4	14.2
Ratio of STADIS (ppm) to Sodium Naphthenate (ppm)	0.9	1.2	1.1	1.4
Conductivity at minimum (pSm^{-1})	305±12	580±23	960±39	2400±96
Conductivity at minimum normalised for concentration of STADIS (pSm^{-1})/ppm	101±4	116±5	96±4	120±5
Depth of minimum (pSm^{-1})	616±49	1057±89	2138±161	3658±338
Depth of minimum normalised for concentration of STADIS (pSm^{-1})/ppm	205±16	211±18	214±16	183±17

Table 2 **Values of Parameters at Minima in Conductivity Curves for STADIS/NaNaphthenate/Dodecane Solutions.**

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[1] By methylene blue method. Determination limit is 0.03ppm. Only surfactant sulphonates are detected and therefore some sulphonates could be missed.

[2] Higher values for strong acids, 5 to 14ppm, have been measured for two sweetened fuels (ref.4).

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STADIS® 450 IN MEROX-SWEETENED JET FUELS

Cyrus P. Henry

Octel America Inc., c/o DuPont, Petroleum Lab (P), Chambers Works, Deepwater NJ 08023.

ABSTRACT

Stadis® 450 has been used in aviation fuels since 1983, and in many cases is the additive of choice due to conductivity retention of treated fuels during distribution, and other characteristics. In the past several years, manufacture of Shell ASA-3 (the other aviation-approved static dissipator additive) has been discontinued; current stores are being drawn down and for some refiners conversion from ASA-3 to Stadis® 450 is underway. In fuels sweetened by hydrogen-treating, Stadis® 450 performs very well and there are few reported difficulties. Chemically sweetened fuels sometimes contain trace materials not removed by the sweetening process. When treated with Stadis® 450 some of these fuels have exhibited two behaviors which are being addressed: in one case, the formation of a precipitate which disarmed coalescers; in several other cases, reduced conductivity response and loss of conductivity during storage coupled with unusually large effects on the microseparometer water separation properties. In late 1992, a Coordinating Research Council (CRC) Panel on Coalescer Deactivation was formed to address these problems. The results of DuPont and CRC efforts are discussed, along with actions taken and underway to eliminate these problems.

HISTORY

Stadis® 450 has been increasingly used in aviation turbine fuels since 1983, when approvals by turbine and airframe manufacturers were obtained and followed by ASTM, the United Kingdom Ministry of Defence, International Air Transport Association, Canadian General Standards Board, and the United States Air Force acceptance. This culminated a nine-year effort, during which more background data were generated in support of acceptance than for any other additive before or since that time. These data included studies of compatibility with co-additives, effects on aircraft fuel system materials, extensive electrostatic performance studies, and so on.

Use of Stadis® 450 in aviation fuels which are hydrotreated has not presented known difficulties; in fact, in most fuels Stadis® 450 provides superior retention of conductivity during distribution and minimally affects water separation properties. In 1984, however, it became clear that jet fuels from certain refineries presented difficulties in meeting both conductivity and water separation requirements. These refineries used Merox™ processes to sweeten fuel. Fuels produced

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by this process sometimes give poor initial conductivity response, and/or show loss in conductivity during storage, and often have greater reduction in the ASTM D3948 water separation rating than hydrotreated fuels. The overall effect is to make it difficult to deliver fuel to airports meeting both conductivity and water separation requirements. Studies of these fuels resulted in several conclusions.

- **The Merox process itself did not add trace materials.**

This conclusion resulted from studies at three refineries where fuel samples were obtained before and after Merox processing; in all cases Stadis® 450 gave better performance in the fuel samples obtained following the complete process. For purposes of this discussion, the "Merox Process" is defined as the typical combination of caustic pre-wash, exposure to the sweetening catalyst, water wash, salt drying, and clay filtration. In addition, Merox-sweetened fuel from another refinery using Stadis® 450 with no difficulties was evaluated; in that case, the feed to the Merox process also gave lesser performance. The Merox process (and probably, other less-studied chemical sweetening processes) simply fails to remove trace contaminants as effectively as hydrotreating.

- **Refinery Chemicals can be the cause of conductivity/MSEP interactions.**

This conclusion resulted from analysis of trace fuel components from one refinery's fuel, and from comparison with the effects of a filming amine used in the refinery.

- **Studies showed similarity in the behavior of Stadis® 450 and ASA-3.**

Figure 1 shows data previously published[1] from addition of several refinery additives to a clean Jet A fuel. These data showed, surprisingly, that some materials which affected Stadis® 450 also gave similar results with ASA-3. The antifoulants and filming amine corrosion inhibitor used in this study were obtained from a refinery where they were in use. Other conductivity additives, not approved for aviation fuels, also are affected by trace materials in fuels.

In spite of these findings, however, a period of equilibrium was established, during which refiners and others evaluated both Stadis® 450 and ASA-3 in their fuel, chose the one which gave the better performance, and went their way - even though, in a few cases, they may not have been happy with their choices.

RECENT FINDINGS

In 1991, the equilibrium changed. Shell announced that manufacture of ASA-3 was being discontinued, and refiners and others who had been using that product began a transition to use of Stadis® 450. Most refiners, regardless of the sweetening process in use, are able to provide fuel in which the performance of Stadis® 450 is satisfactory. One has had continuing problems; some have "spot" problems which come and go, apparently due to crude slate.

In the meantime, another concern was raised: coalescers from the Munich airport were found to contain a significant quantity of a fuel-insoluble sulfonate, ultimately identified as sulfonates of dodecylbenzenesulfonic acid, which is a component in Stadis® 450. These materials appear to originate from an interaction of a fuel component with dodecylbenzenesulfonic acid - which normally remains dissolved in the fuel - to form a viscous liquid precipitate which tends to collect on coalescer elements.

The sulfonate precipitate is thought to be a salt. The primary fuel supply for Munich is from one refiner, who produces a Merox-processed high-quality fuel in all other aspects; it is derived from Libyan crude oil and generally has aromatics content in the 12-14% range. Isolation of the cation from the sulfonate has not been possible. Examination of coalescers from several other locations has revealed traces of dodecylbenzenesulfonates, which are expected due to simple absorption by the filtration media, but many times less than the level found on the coalescer from the Munich airport fuel system. Figure 2 shows results from analysis of toluene extracts from the Munich and other filters. "Sulfonate" levels refers to the total strong acid content of the filter, determined by a spectrophotometric technique. "Solids" are the content of dissolved, non-volatile material determined by evaporation of the toluene extract. "DDBSA" is the actual level of dodecylbenzenesulfonates, determined by HPLC. These data show that the DDBSA content of the Munich filter is higher than that from other filters in long service. Similar levels of "sulfonates" and DDBSA were found on the inner filter pleats and the outer fiberglass wraps.

As a consequence of these concerns, a CRC Panel on Coalescer Deactivation was formed to gather knowledgeable individuals and address both types of problems. This group is currently co-chaired by Edward Matulevicius, Exxon R&E, and Victor Hughes, Shell- Thornton. The group has met several times in the USA and in Europe. This group has work underway to identify interfering species in fuels leading to both types of concerns, and other efforts; in addition, the group provides a vital advisory function to help guide DuPont and recommend industry action.

The conductivity/water separation difficulties and the insoluble sulfonate problem require separate approaches, and hereafter will be discussed separately. These differ both in origin and the nature of the solution(s) to be applied. The sulfonic acid in Stadis® 450 is present as a storage stabilizer for the neat additive; when the additive has been diluted to use concentration it is no longer essential, although it has an obvious effect on water separation properties. The conductivity/water separation problems, however, are due to trace contaminants which interact with all the major components in Stadis® 450.

INSOLUBLE SULFONATES: PROBLEM DEFINITION AND SOLUTION

The sulfonates on a Munich airport filter were extracted with hot toluene. Sodium was the only metal cation present in high concentration relative to toluene extracts from other filters, although the sodium content of the fuel was known to be very low, in the 10 to 15 parts-per-billion range. Unless pre-dissolved in a solvent such as ethanol, sodium sulfonate has very poor solubility in jet fuel. It appears possible that sodium may be involved along with perhaps other materials such as amines, which in the relatively low aromaticity fuel have poor solubility as dodecylbenzenesulfonates.

ÖMV, the primary fuel supplier to the Munich airport, has carried out a number of refinery tests and has developed a rig test to further define the circumstances under which insoluble sulfonates occur. The rig test involves passing 700 liters of dry fuel through a section of a coalescer, then challenging the coalescer section with a fuel/water emulsion to determine if it is disarmed. If not disarmed, the fuel is considered to have passed; if disarmed, the result is considered a failure. Results are summarized as follows. Visual assessment is a primary criteria, as in a single element coalescer test.

- **Stadis® 450 in Berghausen fuel fails.**
- **Stadis® 450 components without dodecylbenzenesulfonic acid pass.**
- **Dodecylbenzenesulfonic acid alone fails.**
- **Stadis® 450 in a hydrotreated jet fuel passes.**
- **Stadis® 450 formulated with dinonylnaphthylsulfonic acid in place of dodecylbenzenesulfonic acid passes.**
- **Fuel Blends containing regular Stadis® 450 in hydrotreated fuel and modified Stadis® 450 in the Berghausen fuel pass.**

These results have led us to consider modification of the Stadis® 450 formulation to use dinonylnaphthylsulfonic acid (DINNSA) in place of dodecylbenzenesulfonic acid (see Figure 3). Substantial efforts have been carried out to evaluate the modified formulation; this has included comparison of electrostatic charging properties, comparisons of conductivity-improving performance and effects on water separation in various Merox-processed and other fuels, verification that thermal stability is not affected, and evaluation of compatibility with other additives used in aviation fuels. These studies have not revealed any flaws in the modified formulation.

Metal salts of DINNSA are well-known to have uniquely good solubility properties in hydrocarbons. A C23 alkylbenzenesulfonic acid was also evaluated and gave improvement, and it is likely a source of such acid could be found which would give satisfactory results. However, DINNSA has several advantages - while more expensive, it is a higher-quality, uniform product which can be expected to remain consistent as a component in Stadis® 450; formulations containing it gave somewhat better conductivity, and DINNSA is registered on all the major chemical inventories.

Utilization of this approach to solve the insoluble sulfonate problem is considered necessary because of failure to identify the cation responsible for the problem, and because formation of very minute levels of insoluble sulfonates is not easily detectable by the usual aviation fuel quality control tests or other laboratory tests suitable for quality control purposes.

Additional testing has been completed in ÖMV facilities to determine whether commingling of fuels containing regular and modified Stadis® 450 give satisfactory performance. Results were satisfactory.

In the meantime, data to support the modified formulation has been presented to representatives of fuel suppliers, airlines, and equipment manufactures at the December 1993 meeting of ASTM Committee D-2 Subcommittee J on Aviation Fuels[2]. There were no objections to field trials with modified Stadis® 450. Test quantities are being supplied to coalescer manufacturers and others on request, and a field trial will hopefully be arranged at the Munich Airport. If satisfactorily completed, it is expected that the modified product will become the only product manufactured, following full acceptance by equipment manufacturers and specification bodies.

An alternate solution to modification of the acid component in Stadis® 450 would be to use the other components independently, so that the storage stabilizer is not needed. This approach was not considered practical. Still another approach would be to eliminate the causative factor from the fuel. Unfortunately, that could be accomplished with assurance only by a requirement to hydrogen treat, or by development of an appropriate test to determine whether fuel would react to form insoluble sulfonates. Thus far, this has not been possible. Overall, the use of DINNSA-modified Stadis® 450, where one alkyl aryl sulfonic acid is substituted for another alkyl aryl sulfonic acid, is the best solution. In terms of chemical activity, these two materials are very similar. The primary difference is in the size of the hydrocarbon moiety, which affects solubility of sulfonate salts in hydrocarbons.

CONDUCTIVITY/MSEP INTERACTIONS

Having some assurance of an ultimate solution of the insoluble sulfonate problem, our full attention is now turning to resolution of the conductivity/water separation interaction concerns. We are assuming that extraordinary measures to resolve these concerns are inappropriate. Thus, for example, a recommendation to install hydrogen-treating facilities to replace Merox or other chemical sweetening units is not a satisfactory solution, since the cost of these units for that purpose alone is totally unreasonable.

In general, conductivity/MSEP interactions do not appear to be a continuing problem for many refiners. We are aware of one refiner who encounters serious, ongoing interactions to the point of extreme difficulty in meeting conductivity/MSEP requirements using Stadis® 450. ASA-3 also causes problems at this location, but when conductivity declines with ASA-3 the MSEP values recover, so that re-doping is more practical. Several others have moderate but tolerable ongoing concerns. The most frequent occurance is at refineries where Stadis® 450 is normally used with no problems - then for reasons not yet defined but perhaps due to crude oil slate, poor conductivity/MSEP values are occasionally obtained. In such cases, the quality of the Stadis® 450 in use is often questioned, and in all cases to date it has proved to be typical.

Modified Stadis® 450 may provide some relief for these refiners; however, preliminary results show that a change in the stabilizer acid component does not result, on average, in improved behavior in problem Merox-sweetened fuels. However, there are some fuel-to-fuel differences which might be of benefit for some refiners. Other changes in Stadis® 450 composition are probably not acceptable without re-initiating the entire approval process. An effort is underway to assure that the individual components in Stadis® 450 are optimized within the bounds of the "aviation approvals" so that effects on water separation are minimal.

Conductivity-improving performance and the effect on water separation should not be used as independent parameters for the purpose of evaluating this phenomenon. The primary concern is not the amount of additive needed to achieve a conductivity of 50 pS/m or more when measured; it is the balance of conductivity improvement and effect on water separation which interests refiners and others. It is helpful to use a combined parameter which has been dubbed the "Conductivity Microsep Factor", or "CMF"(see Figure 4).
A DuPont test method has been written[3] to define CMF and cites an experimental procedure to obtain CMF values, which are defined as follows:

$$\mathrm{CMF} = \frac{\Delta\ \mathrm{CONDUCTIVITY}}{\Delta\ \mathrm{MSEP\ VALUE}}$$

CMF values are simply pS/m of conductivity obtained in a fuel per unit of ASTM D3948 loss. Preferably, these values are obtained on fuels which are first treated with 1 mg/L of Stadis® 450, then stored for a period of two weeks. The conductivity after two weeks will at least substantially indicate any trace materials, if present, which cause a loss in conductivity during storage. The D3948 MSEP test is carried out on the fuel; a CMF value can then be calculated which reflects both conductivity improvement (including storage effects), and water separation effects. The weak link in this test is the MSEP value; the test should be replicated at least twice.

Typically, the CMF values for clean, hydrotreated Jet A-1 fuels are 15 to 30, which means that when treated to give a conductivity of 150 pS/m, an MSEP loss of 5 to 10 units is obtained; clearly acceptable performance. As CMF values approach 10, less favorable results are expected. For values of less than 5, significant difficulties are likely since to achieve a conductivity of 150 pS/m or more, a MSEP loss of more than 30 is obtained.

When the current effort was initiated, it appeared that low CMF values were likely due to carryover of refinery chemicals such as filming amines. In a few instances that has indeed been the case, and refiners should be aware of this possibility when low CMF values occur. A more likely cause, it appears now, is carryover of trace materials from the crude oil. Several ways to eliminate or reduce these impurities which have been explored to date.

Clay filtration under vigorous laboratory conditions, such as in ASTM Test Method D3948 Appendix X1, has in nearly every case removed trace materials and resulted in fuel which gives high CMF values. In the refinery, however, it appears that clay filtration begins to pass through some interacting species more quickly than strongly polar surfactants. Nonetheless, the refiner should review the operation of the Merox unit, examining the adequacy of the caustic wash, water wash, and the condition of the clay tower.

Several other approaches have been examined to date; each has shown some promise in limited evaluations.

- **Alumina filtration as a follow-on to clay filtration.**

Results from laboratory long-term filtration through clay has shown that its capacity to remove interacting species is quickly exhausted with some fuels. Supplemental filtration through alumina, a more active absorbent, has proven effective; the alumina activity is long-lived and it might be regenerated. If regeneration proves practical, alumina filtration economically competitive when clay disposal costs are also considered. See Figures 5 and 6, which illustrate results of laboratory filtration.

- **Improved water wash is effective.**

Three refiners' fuels were satisfactorily improved by simply water washing the fuel.

- **Dilute acid wash can be effective.**

Caustic washing is part of the Merox process and effectively removes acid species. Some amines are not removed by caustic or water washing; use of an acidic water wash (containing sodium dihydrogen phosphate or citric acid, for example) removed interacting species from two refiner's fuel. This solution may be appropriate if caustic carryover to water wash is minimal. Figure 7 illustrates the degree to which amines are removed from fuels by washing fuel with aqueous solutions of various pH. In general, water or dilute acid washed fuel should be passed through a laboratory salt dryer before evaluating Stadis® 450 performance. What is now needed, however, is an examination of these solutions over a period of time at specific refineries, so that effects of varying crude slates are understood.

Overall, it appears that modest improvements to the Merox process may overcome all but the most recalcitrant fuels. We are working closely with a few refiners to seek solutions to their particular cases. In the meantime, we welcome discussions with other refiners regarding specific circumstances at their locations. Two DuPont test methods[4,5] have been developed and written to determine trace levels of acidity and basicity in jet fuels; these are known to affect Stadis® 450.

We are suggesting that refiners who find significant conductivity/MSEP interactions should carry out response evaluations over a period of time so that the scope of the issue at their location is understood. We are quite willing to work cooperatively with anyone so interested. A package of literature has been developed for that purpose which is available on request.

As an aside, findings about the effect of sulfur dioxide on Stadis® 450 have been recently disclosed[6]. These results show that concentrations of SO2 which might result from inadequately scrubbed flue gases used to inert shipments of jet fuel can interact with Stadis® 450 components to give a 50-70% loss in conductivity. Further studies showed that clay-filtering of shipped fuel removes sulfur dioxide and subsequent treatment with Stadis® 450 is unaffected. These findings are in agreement with other studies which show strong suppression of conductivity from acidic species[7].

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FIGURE 1

SOME ADDITIVES GIVE EFFECTS OBSERVED IN MEROX FUELS

COADDITIVE (CONC,PPM)	COND. ADD. (0.7 MG/L)	INITIAL pS/m	7 DAY pS/m	MSEP D3948
NONE	ASA-3	238	242	92, 95
NONE	S450	200	208	93, 95
ANTIFOUL.1 (5)	ASA-3	94	26	60
	S450	59	71	55
ANTIFOUL.2 (5)	ASA-3	250	215	88
	S450	195	178	84
CORR.INH. (5)	ASA-3	185	65	56
(FILMING AM.)	S450	155	128	66
NaOH (2)	ASA-3	250	190	91
(1% IN WATER)	S450	210	175	99
WATER (200)	ASA-3	270	255	94
	S450	225	221	94

FIGURE 2

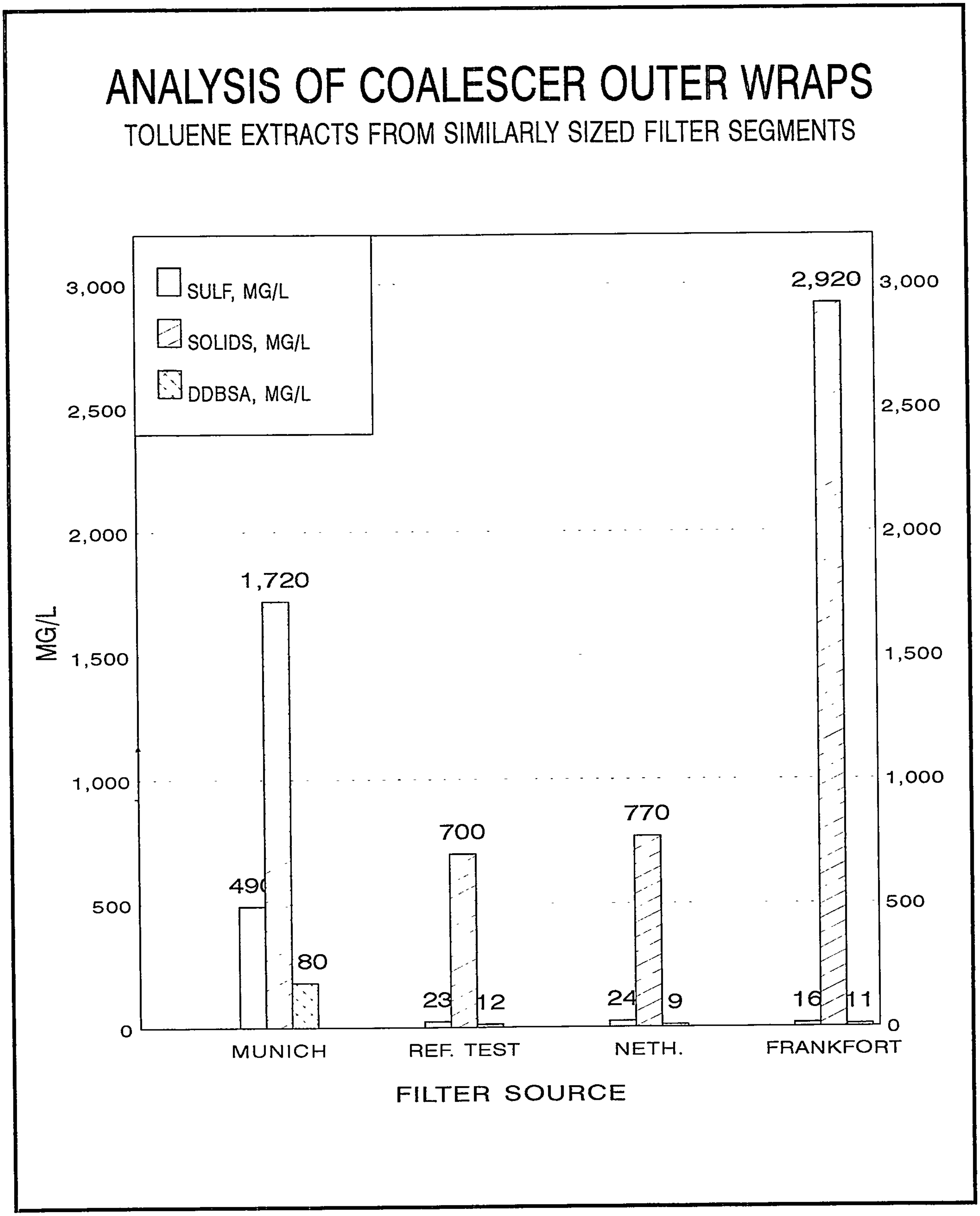

ANALYSIS OF COALESCER OUTER WRAPS
TOLUENE EXTRACTS FROM SIMILARLY SIZED FILTER SEGMENTS
SULF, MG/L
SOLIDS, MG/L
DDBSA, MG/L
MG/L
3,000
2,500
2,000
1,500
1,000
500
0
1,720
490
80
700
23
12
770
24
9
2,920
16
11
MUNICH
REF. TEST
NETH.
FRANKFORT
FILTER SOURCE

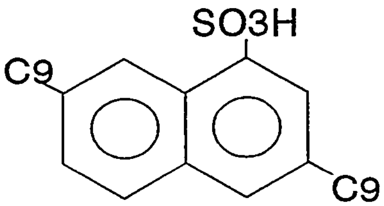
FIGURE 3

PRECIPITATE PROBLEM

HOW TO SOLVE?

1. IDENTIFY AND ELIMINATE CO-REACTANT FROM FUEL
    - -- NOT POSSIBLE TO DATE
    - -- MAY NOT BE PRACTICAL
2. ELIMINATE THE OTHER CO-REACTANT IN STADIS® 450
    - -- ELIMINATE DDBSA
    - -- USE ALTERNATE ACID

DINONYLNAPHTHYLSULFONIC ACID
(DINNSA)



DODECYLBENZENESULFONIC ACID
(DDBSA)

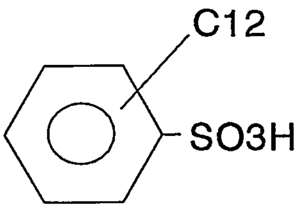


FIGURE 4

PROBLEM DEFINITION

EVALUATION OF FUEL TO DEFINE BEHAVIOR

- DETERMINE BASE FUEL CONDUCTIVITY AND D3948 MSEP RATING
- DETERMINE CONDUCTIVITY WITH 1 MG/L STADIS®450 (500 ML OR 1 L TEFLON® BOTTLES)
- STORE TWO WEEKS AT ROOM TEMPERATURE (PROTECT FROM LIGHT EXPOSURE)
- RE-MEASURE CONDUCTIVITY AND DETERMINE MSEP VALUES
- CALCULATE CONDUCTIVITY/MSEP FACTOR

CMF = 2 WK CONDUCTIVITY/MSEP LOSS

$$= \frac{\Delta \text{ CU}}{\Delta \text{ MSEP}}$$

EXAMPLE: BASE FUEL MSEP = 95

2 WK CONDUCTIVITY = 275 PS/M

MSEP = 82

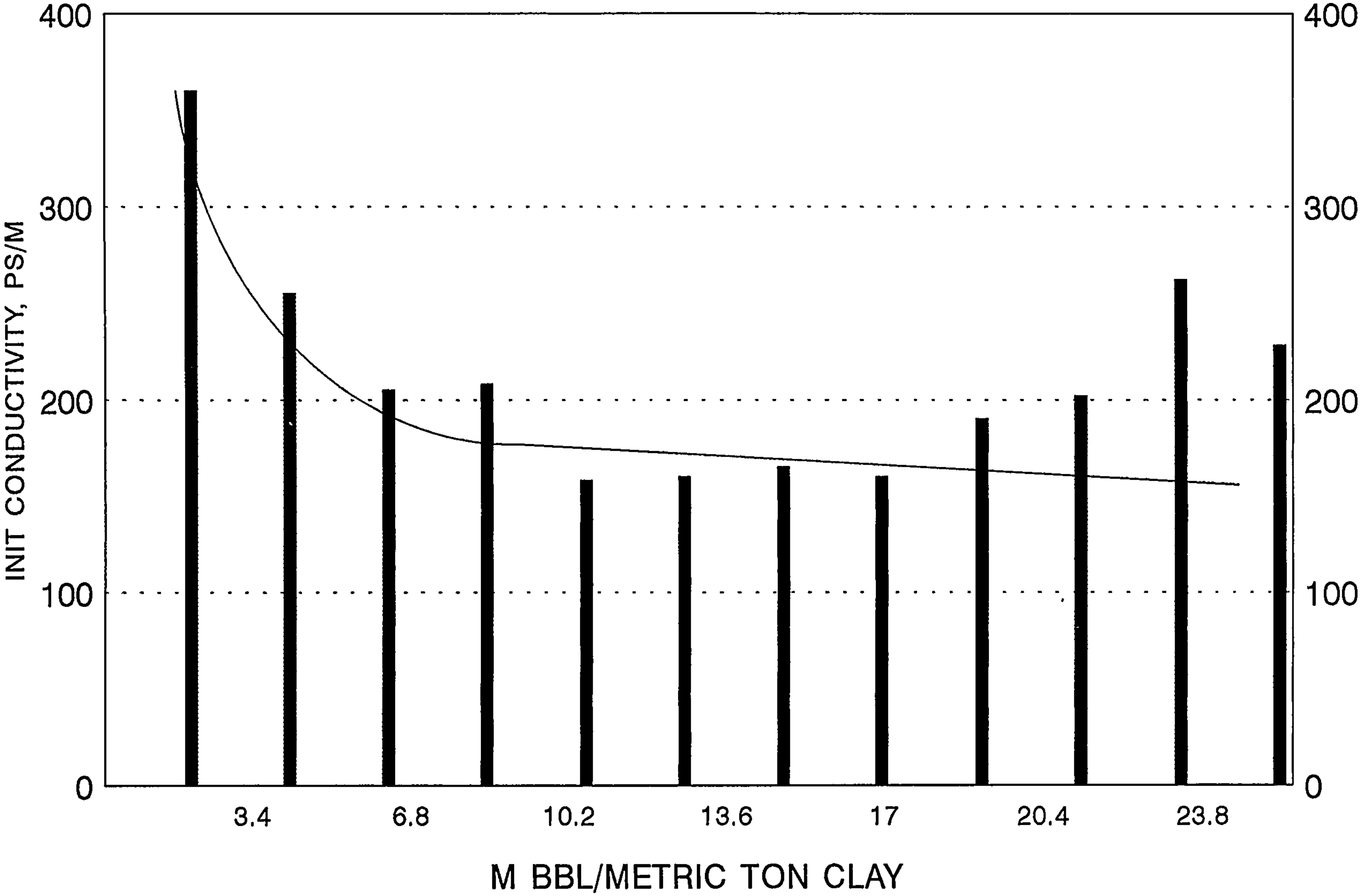
CMF = 21

CMF < 4 = PROBLEMS

FIGURE 5

MEROX FUEL THROUGH CLAY COLUMN

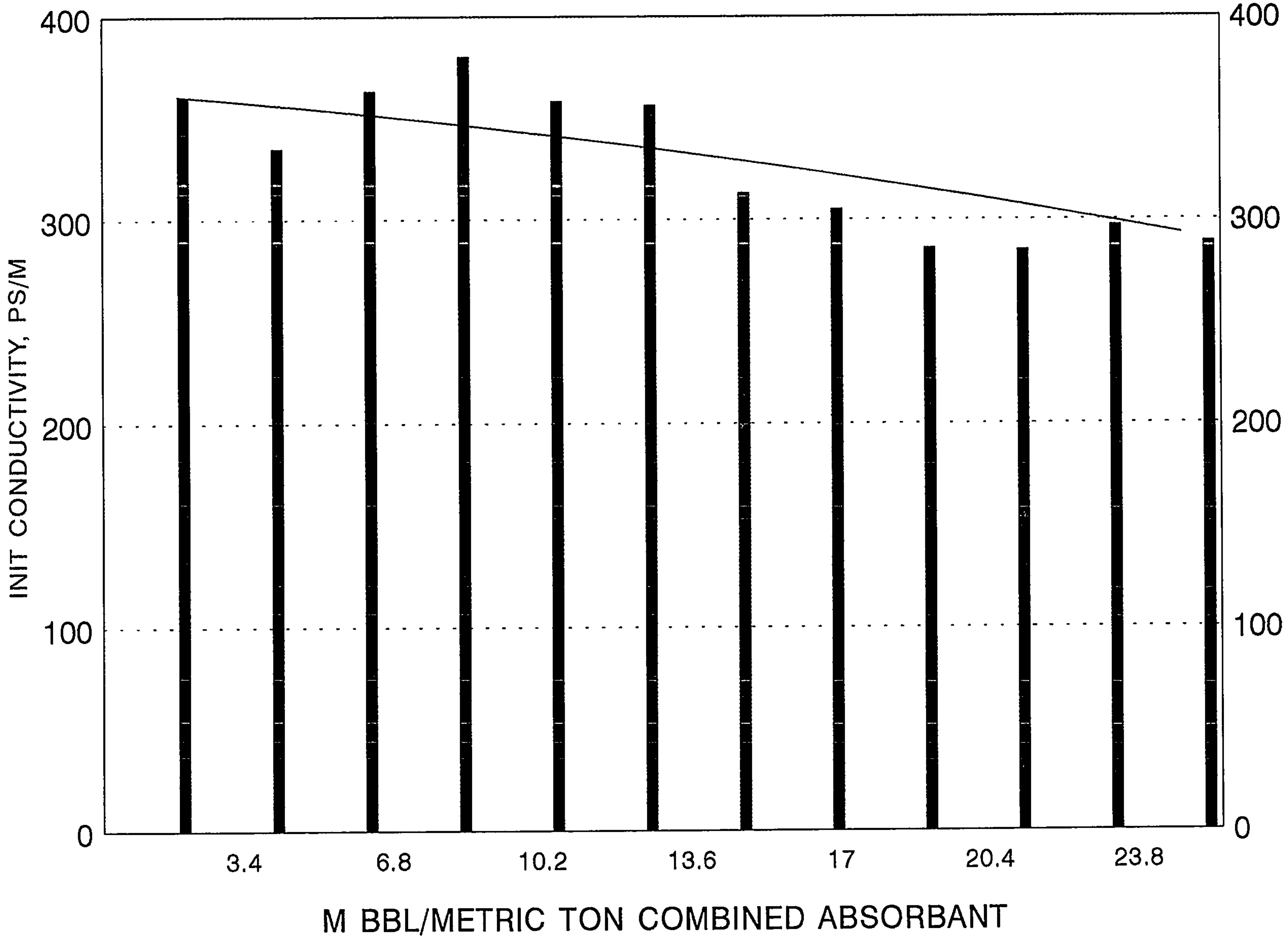
FUEL NOT CLAY TREATED AT REFINERY



15 G CLAY, 1.5 X 13.5 CM COLUMN
AVE FLOW RATE 5 ML/MIN --> 4 ML/MIN
INITIAL AMINE ABS. 0.33

FIGURE 6

CLAY + 20% ALUMINA COLUMN

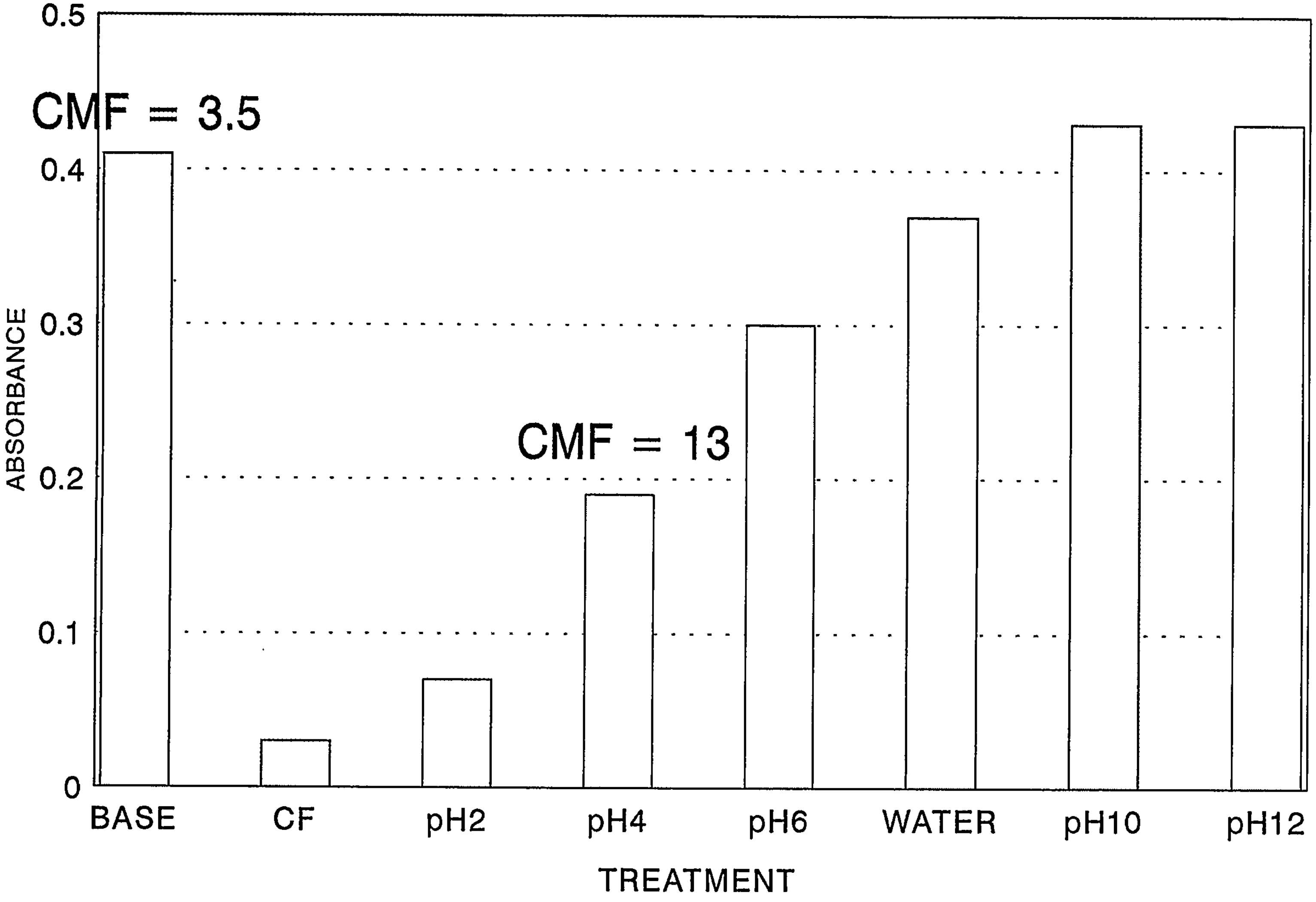


12 G CLAY, 3 G 60 MESH BASIC ALUMINA
AVE FLOW RATE 3 ML/MIN

FIGURE 7

SURFACTANT AMINE IN P92-682 JET A-1

EFFECTS OF CLAY FILTRATION AND WASHING



WASH WITH PH SOLUTION THEN 3X WATER WASH

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

FACTORS AFFECTING THE SILVER CORROSION PERFORMANCE OF JET FUEL FROM THE MEROX PROCESS

Carl L. Viljoen [1], Sibbele Hietkamp [2], Boshoff Marais [3] and Johannes J Venter [3] *

[1] Sasol Oil R & D, PO Box 1, Sasolburg, 9570, South Africa
[2] CSIR, PO Box 395, Pretoria 0001, South Africa
[3] National Petroleum Refineries of South Africa, (Pty) Ltd, PO Box 234, Sasolburg 9570, South Africa.

ABSTRACT

The Natref refinery at Sasolburg, South Africa, which is 63,6% owned by Sasol and 36,5% by Total, is producing Jet A-1 fuel at a rate of 80 m^3/h *by means of a UOP Merox process. A substantial part of the crude oil slate is made up from crudes which have been stored for considerable times in underground mines. Since the 1970's, Natref has experienced sporadic non-conformance of its treated jet fuel to the silver corrosion (IP 227) test. Various causes and explanations for the sporadic silver corrosion occurrence have been put forward but a direct causal link has remained obscure. The paper addresses these possible causes for silver corrosion and some of the process changes which have been made to alleviate the problem. Emphasis is placed on the most recent approaches which were taken to identify the origin of the sporadic silver corrosion. An inventory of all the potential causes was made, such as bacterial action, elemental sulphur formation in storage, etc. and experiments designed to test the validity of these causes, are discussed. A statistical evaluation which was done of the historical process data over a 2 year period, failed to link the use of mine crudes directly to Ag-corrosion occurrence. However, a correlation between elemental sulphur and* H_2S *levels in the feed to the Merox reactor and Ag-corrosion was observed. Finally, the outcome of the experiments are discussed, as well as the conclusions which were reached from the observed results.*

1. INTRODUCTION

The Natref (National Petroleum Refiners of South Africa (Pty) Ltd) refinery at Sasolburg, South Africa, is 63,6% owned by Sasol and 36,4% by Total South Africa. A substantial part of its jet fuel is produced by means of the UOP Merox process. The refinery processes crude oil at a rate up to 570 m^3/h, while the feed to the Merox unit is 70-80 m^3/h. A substantial part of the crude oil feed frequently consists of crude which has been stored in underground mines for considerable time periods. Alternative sources of jet fuel at the refinery is from the diesel hydrotreating unit when it is on kerosene mode and by means of the distillate hydrocracker, as illustrated in Figure 1.

Since the late 1970's, Natref has experienced sporadic non-conformance of its Merox treated jet fuel to the silver corrosion test for aviation turbine fuels, the IP 227 test[1]. Although the sporadic occurrence of silver corrosion non-conformances on kerosene treated by the Merox process has received much attention over the years, the actual cause or set of causes have remained obscure.

In April 1993, a research project was undertaken by Sasol in conjunction with chemists from the CSIR (Council for Scientific and Industrial Research) to identify the causes of silver corrosion occurrence in treated kerosene. It was believed that the cause would firstly have to be established and proven by experiments before the subsequent elimination thereof could be considered.

2. HISTORICAL BACKGROUND

Over the past 20 years, adherence to the silver corrosion specification has cost Natref a considerable amount of money in terms of limiting refinery flexibility, enforced sub-optimal production options, capital investments, reprocessing costs and management time.

Various changes to the Merox plant have also been made in an attempt to eliminate the intermittent non-conformance of the product to the Ag-corrosion test. The most noteworthy of these was the installation of a clay filter in 1984 and the installation of a Merichem contactor (Napfiner) upstream of the pre-wash in February 1992. Although the quality of the rundown has improved due to these process changes, the sporadic occurrence of off-specification Ag-corrosion ratings (values of 2 or higher) has persisted.

In the past, the use of crude oil which has been stored for a number of years in underground mines, has often been blamed for silver corrosion problems in the Merox treated rundown. High elemental sulphur, S°, levels in the feed to the process could be correlated to the use of mine crudes in 1992. Also, very high S° levels in the rundown could be correlated to the occurrence of non-zero Ag-corrosion. However, statistical analysis of the historical data of 1992 and 1993 could not link the use of mine crudes directly to non-zero Ag-corrosion in the rundown.

3. DESCRIPTION OF THE PROBLEM

At this refinery, the rundown from the Merox process is monitored two times per day for silver corrosion by means of a standard 4 hour IP 227 test. All the jet fuel tanks, transit as well as final product tanks, are monitored for silver corrosion on a daily basis. The rundown seldom shows anything other than zero Ag-corrosion. For example, during the period May 1991 to May 1993 only 5,3% of the time Ag-corrosion results of 1 were obtained, with only two results (0,3%) being rated as 2 (off specification). The tanks, however, test sporadically positive to silver corrosion. This leads to costly reprocessing or re-routing of the kerosene to the diesel pool.

Sometimes distinct deterioration of the jet fuel is observed upon storage. Conventionally the assumption would be that this is caused by microbiological processes, such as sulphate reducing bacteria (SRB). However, this phenomenon has also been observed in freshly cleaned tanks, from which water is drained meticulously, and in which no SRB's and other micro-organisms were found. Since silver corrosion is mainly caused by H_2S and elemental sulphur, the measurement of these compounds received much attention and procedures have been developed for their analysis at parts per billion levels. However, analytical difficulties are experienced in the measurement of H_2S and S° at p.p.b. levels in the presence of total sulphur at p.p.m. levels. Since the Merox process converts mercaptans to disulphides, it does not decrease the total sulphur level in the kerosene.

4. RECENT APPROACH

A comprehensive study was made of all the various possible causes which have been postulated regarding the sporadically occurring Ag-corrosion at the Natref refinery. The theories were grouped together and prioritized in an order of decreasing importance, as follows.

4.1 H_2S as Cause of Ag-Corrosion

The most corrosive compound towards silver is hydrogen sulphide. The silver surface is also much more sensitive (in terms of discolouration) towards H_2S than towards elemental sulphur. It has been shown that 100 p.p.b. of H_2S will cause off-specification Ag-corrosion[2].

H_2S can be formed in kerosene by the following mechanisms:

4.1.1 H_2S from sulphides by a decrease in pH

H_2S can be liberated from sulphides such as NaHS and Na_2S by a decrease in pH. This decrease in pH can be due to: (a) acidification by metabolic products from aerobic bacteria, e.g. acetic, lactic acids, (b) acidification by atmospheric contamination e.g. CO_2, (c) by separation of alkaline water upon storage and cooling of the kerosene; and (d) by acidifying chemical reactions.

4.1.2 H_2S from sulphate reducing bacteria

Anaerobic bacteria are capable of reducing any sulphates to H_2S. It has been shown that they can still be active at relatively high oxygen concentrations of a few parts per million[3].

4.1.3 H_2S from FeS

H_2S can be generated by the hydrolysis of iron sulphide under neutral conditions and more easily under acidic conditions:

$$\mathrm{FeS} + 2\mathrm{H_2O} \rightarrow \mathrm{H_2S} + \mathrm{Fe(OH)_2}. \qquad 1)$$

Iron sulphide can be formed due to the action of H_2S on the steel under the corrosive conditions at the top of the crude distillation unit. It can also be generated in the storage tanks due to either bacterial or chemical corrosive action.

4.1.4 H_2S from mercaptan and/or elemental sulphur chemical reactions

Mercaptan and/or elemental sulphur reactions that may produce H_2S or generate H^+ are expected to take place under reducing conditions. Examples are:

$$2\ \mathrm{RSH} \rightarrow \mathrm{H_2S} + \mathrm{R_2S} \qquad 2)$$

$$2\ \mathrm{RSH} + \mathrm{S}^\circ \rightarrow \mathrm{R\text{-}SS\text{-}R} + \mathrm{H_2S}. \qquad 3)$$

These reactions are believed to be unfavourable under the relatively mild conditions and short times that kerosene is in storage. The thermal decomposition of disulphides to olefins and H_2S is also unlikely under these conditions.

4.2 Elemental Sulphur as a Cause of Ag-Corrosion

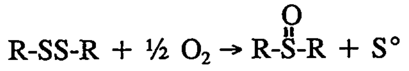
The corrosive action of elemental sulphur (S°) in kerosene upon silver has been studied intensively[4,5,6]. The synergistic effect between H_2S and S° has been universally accepted, since various investigators have found that mixtures of very low concentrations of S° and H_2S are more corrosive to the IP 227 test than the separate components[2,7].

Since S° (and H_2S) levels are determined daily in samples from the Merox treated rundown, reactions which could generate S° upon storage were considered. These are:

Oxidation of mercaptans:

$$\mathrm{RSH} + \tfrac{1}{2}\,\mathrm{O_2} \rightarrow \mathrm{ROH} + \mathrm{S}^\circ \qquad 4)$$

Oxidation of disulphides:



$$\mathrm{R\text{-}SS\text{-}R} + \tfrac{1}{2}\,\mathrm{O_2} \rightarrow \mathrm{R\text{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}\mathrm{\text{-}R} + \mathrm{S}^\circ \qquad 5)$$

or

$$\mathrm{R\text{-}SS\text{-}R} + 2\mathrm{O_2} \rightarrow \mathrm{R_2SO_4} + \mathrm{S}^\circ \qquad 6)$$

Oxidation of H_2S:

$$H_2S + \tfrac{1}{2} O_2 \rightarrow S^\circ + H_2O. \qquad 7)$$

It will be noted that most of these reactions are an overoxidation of the central Merox reaction which could be caused by an excess of oxygen in the reactor.

4.3 Process Related Causes for Ag Corrosion

These are incidents of contamination due to process upsets or physical contamination due to leaking valves, the sharing of pipes, pumps etc. Another cause may be operator errors, since these would be able to explain the irregular occurrence of the Ag-corrosion problems. Since the refinery is operated and maintained under strict guidelines, both these causes are considered to be of lower probability.

4.4 Ag-Corrosion Caused by Specific Corrosive Compounds

A literature search yielded no information on sulphur compounds other than S° and H_2S whose presence in kerosene can cause silver corrosion. In fact, experimental evidence suggests that most of the other sulphur compounds in kerosene seem to have inhibiting effects on Ag-corrosion.

4.5 Ag-Corrosion Due to Absence of Natural Corrosion Inhibitors

It is possible that the occasional absence of some inhibiting compound, which is normally present in the jet fuel, might cause the sporadic Ag-corrosion non-conformances. It is known that most anti-tarnishing compounds used in commercial silver polishes are C_{16} to C_{18} mercaptans or mercaptan derivatives. Examples are octadecyl thioglycolate and octadecyl mercaptan. Under certain process conditions it may be possible that too much of these are removed from the kerosene.

5. STATISTICAL ANALYSIS

A first Ag-corrosion cause analysis approach was to do a statistical analysis of the Merox process data for a 2-year period (May 1991 to May 1993) by means of a statistics software package named SAS. Correlations between the key process parameters and the occurrence of non-zero Ag-corrosion on the rundown were sought. For this purpose, the percentage of each crude in the slate for a specific day was also viewed as a process parameter.

A correlation was found between elemental S° in the feed to the process and Ag corrosion of the product. No correlation was found between feed rate to the process versus Ag-corrosio, or between crude type and Ag-corrosion.

Unfortunately, a correlation could be obscured by inherent flaws in the data being gathered at the refinery. Most process data are spot measurements of the parameter which is taken once every 24 h and is then assumed to depict the value of that parameter for the full period. The feed rate, for example, is the average value over the 24 h period. All fluctuations in feed rate have been lost from the data. The same is true for most of the other parameters. It is therefore not surprising that the statistical evaluation of the process data yielded somewhat inconclusive results.

6. EXPERIMENTS

Laboratory and plant experiments were designed and carried out in order to prove or disprove the different theories, where possible. A simplified scheme of these, together with some implications of positive results on the process, is shown in Figure 2.

7. RESULTS FROM EXPERIMENTS

7.1 H_2S Liberation by Addition of Acid

The results of the experiments to determine the liberation of H_2S as a function of pH, are presented in Table 1. During October 1993 the untreated kerosene feed had a low elemental sulphur content and during February 1994 the sulphur content was high. Even with excessively large amounts of acetic acid only small amounts of H_2S were liberated during October. However, during February, significantly more H_2S was released and in July even more. The maximum amount obtained (85 μg/kg) after the addition of 1 ml acetic acid, would suffice to make the product off - specification. The amount of acetic acid used was however so large that it is highly unlikely that bacteria could release similar amounts of acids. Although we have shown that acidification of the product does release H_2S, the amount is normally small and excessive quantities of acid are required. In another experiment, investigating H_2S liberation by acidification due to CO_2, no H_2S was liberated by purging kerosene samples with CO_2 for a period of 4 hours. The experiment to investigate acidification due to aerobic bacteria also yielded negative results. No microbial activity could be detected over a 7 day period. Tests for SRB's were also negative.

7.2 H2S precursors in Spent Reactor Caustic

The reactor spent caustic was titrated with strong acid to a pH of 4 while the H_2S liberated during the titration was measured, as shown in Table 2. The maximum amount of H_2S that was liberated was 200 p.p.b. This low amount contradicts the theory that the spent caustic contains a substantial amount of H_2S precursors which may be transferred to the kerosene. Also no substantial difference was found between the October experiments (kerosene feed with low S° content) and the February experiments (kerosene feed with high S° content).

A qualitative GC-MS analysis of the organic components of the reactor spent caustic solution was also done. A large number of phenolic compounds were identified. The main components were:

- phenol
- 3-methyl phenol
- 4-methyl phenol
- 3,4-dimethyl phenol
- 3-ethyl phenol

- 3-ethyl-5-methyl phenol
- 2,5-dimethyl phenol
- 4-ethyl-2-methyl phenol
- 3,5-diethyl phenol
- 2-methyl-6-propyl phenol
- 2-methyl-5-(1-methylethyl) phenol

No sulphur containing compounds such as mercaptans and disulphides could be identified, nor any naphthenic or carboxylic acids. None of these were present at levels high enough for detection by the instrument (100 p.p.m.). The results do not substantiate the theory that organic sulphur compounds, acting as H_2S precursors, may be present in the reactor spent caustic. The high phenolic content of the reactor caustic will lead to contamination of jet fuel with phenolates, unless optimum performance of the salt and clay filters are ensured. Phenolates are strongly hygroscopic and therefore the water content of the fuel will increase when the phenolate concentration increases.

7.3 H_2S Generation by Hydrolysis of FeS

This experiment showed that no H_2S was formed by the hydrolysis of FeS in the kerosene/water system over a period of 3 hours. An acidic environment is apparently required to liberate H_2S from FeS in the storage tanks. Even if the hydrolysis reaction does not take place in the kerosene system, FeS should still be considered as a H_2S precursor. Thus iron sulphide should not be allowed to contaminate kerosene and maintenance and cleaning of tanks should receive appropriate attention.

7.4 Formation of S° in Merox Reactor

The results in Table 3 show that no definite trend of elemental sulphur formation in the Merox reactor could be observed. However, it is not believed that this change in S° plays a major role in the occurrence of Ag-corrosion problems, since very high S° levels have historically been tolerated (2 000 p.p.b. and higher) in the merox rundown without causing problems. This observed formation of S° may only contribute to the problem at times when the S° content of the feed to the Merox reactor becomes very high. The experiment which investigated the formation of S° upon oxidation in storage, yielded only negative results. The scatter observed in the measured S° values made them statistically non-significant.

7.5 Ag-Corrosion Inhibition by Long Chain Mercaptans

The results of an experiment, testing the hypothesis that certain mercaptans may act as natural corrosion inhibitors, are shown in Table 4.

Octadecylmercaptan was used since it is commercially more freely available than the C_6 to C_{11} mercaptans which should actually be present in kerosene (Bp. 150° - 250 °C). The results obtained from Merox samples from the final jet fuel tank, F29597, which showed non-zero Ag-corrosion readings, indicated at first that the mercaptan did have a beneficial effect on Ag-corrosion. Unfortunately, no naturally off-specification samples of the Merox rundown were available during this period to test the effect of the long chain mercaptan on them.

In the samples which were made artificially corrosive to silver by the addition of either 1 000 p.p.b. S° or 80 p.p.b. H_2S (Ag-corrosion ratings of 2 and 1, respectively) the addition of 125 p.p.m. octadecylmercaptan had no visible inhibiting effect. It is unlikely that the shorter chain mercaptans (C_8 - C_{11}) would have an inhibiting effect at more realistic levels (20 - 30 p.p.m.). Of special interest are the results in which 80 p.p.b. H_2S was added to Merox rundown sample. In this low sulphur-containing product, this amount of H_2S was not enough to cause off-spec silver corrosion, but only a rating of 1. This means that low S^0 jet fuel may have a bigger tolerance or buffering capacity for H_2S than what was previously believed. At Natref it was assumed that 40-50 p.p.b. H_2S causes Ag-corrosion of 2 or higher. Unfortunately this experiment does not prove the hypothesis that long-chain mercaptans will improve Ag-corrosion ratings when they are present at permissible levels of 20-30 p.p.m.

7.6 Plant experiments

7.6.1 Effect of air reduction in the Merox reactor on the product quality.

The air flow rate to the Merox reactor was reduced from 0.12 Nm^3 air/m^3 kerosene feed to 0.012 Nm^3 air/m^3 kerosene. No effects on RSH concentration could be measured down to a flow rate of 0.053 Nm^3 air/m^3 kerosene feed. Below this value the RSH concentration increased and at 0,012 Nm^3 air/m^3 kerosene feed, this concentration exceeded the specification of 30ppm. It can therefore be concluded that the process parameters are not very sensitive to the air flow rate, while exceeding this minimum air requirement.

7.6.2 Effect of NaOH recirculation through the reactor on RSH levels.

During normal operation of the Merox reactor the caustic solution is cycled through the reactor once a day. The purpose of this experiment was to evaluate the quality of the jet fuel (RSH and H_2S content) depending on the time lapse after the last caustic circulation. During the circulation and in regular intervals before the next circulation, samples were taken before and after the reactor. In each sample the amount of H_2S, RSH and S° was determined. No significant differences were observed in concentrations of these three chemicals during the total time interval between two caustic circulations. It can therefore be concluded that the quality of the jet fuel is not affected by cycling the caustic solution through the reactor once a day.

8. CONCLUSIONS

The results of the experiments carried out in October 1993 and in February 1994 led to the following conclusions :

- Products derived from untreated kerosene feed with a higher S° concentration can liberate more H_2S with the addition of modest quantities of acetic acid than product derived from untreated kerosene feed with a lower S° concentration. The amounts were twice as large in February as during the October experiments. Provided acidification occurs, such amounts of H_2S can cause considerable silver corrosion. Although the amounts were still significantly smaller than expected, this cause can not be ruled out as the major cause for Ag Corrosion.

- The build up of H_2S precursors in the Merox reactor spent caustic is not significant and is independent of the S° concentration in the untreated kerosene feed. The expectations that the caustic would extract H_2S precursors from the product were not met.

- Significant amounts of phenolates did accumulate in the Merox reactor spent caustic. The phenols are not a cause of Ag-corrosion. Entrained phenolates in the product would however increase the water content of the treated product and may have a detrimental effect.

- When untreated kerosene high in S° is used as feedstock, it must be anticipated that the following systems will be contaminated sooner and therefore need rigid monitoring :

- a) spent reactor caustic
  It must be expected that other sulphur compounds accumulate in the caustic, thereby reducing its strength sooner compared with the use of low S° kerosene feeds.

- b) salt filter
  High S° kerosene feed is expected to lead to more entrainment of ionic species in the fuel. Such species will contain water, which depletes the salt filter.

- c) clay filter
  The clay filter removes probably more sulphur compounds, thereby decreasing its useful life expectancy.

- The plant experiments have shown that flexibility exists in the actual amount of air to be used for the Merox process. Furthermore it was shown that the process is tolerant to the frequency of the cycling of the caustic through the reactor.

This project has confirmed the complex and integrated nature of the link between the Merox process and the occurrence of Ag-corrosion. It also confirmed the synergistic value of a combined engineering and chemistry approach in addressing problems of this nature.

The experimental testing of the theories on the possible causes of Ag-corrosion has resulted in an improved understanding of the problem and, by reducing the number of possible causes, led to a more focused approach to the routine operation of the

Merox unit.

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FIGURE 1 : NATREF JET FUEL PROCESSING SCHEME

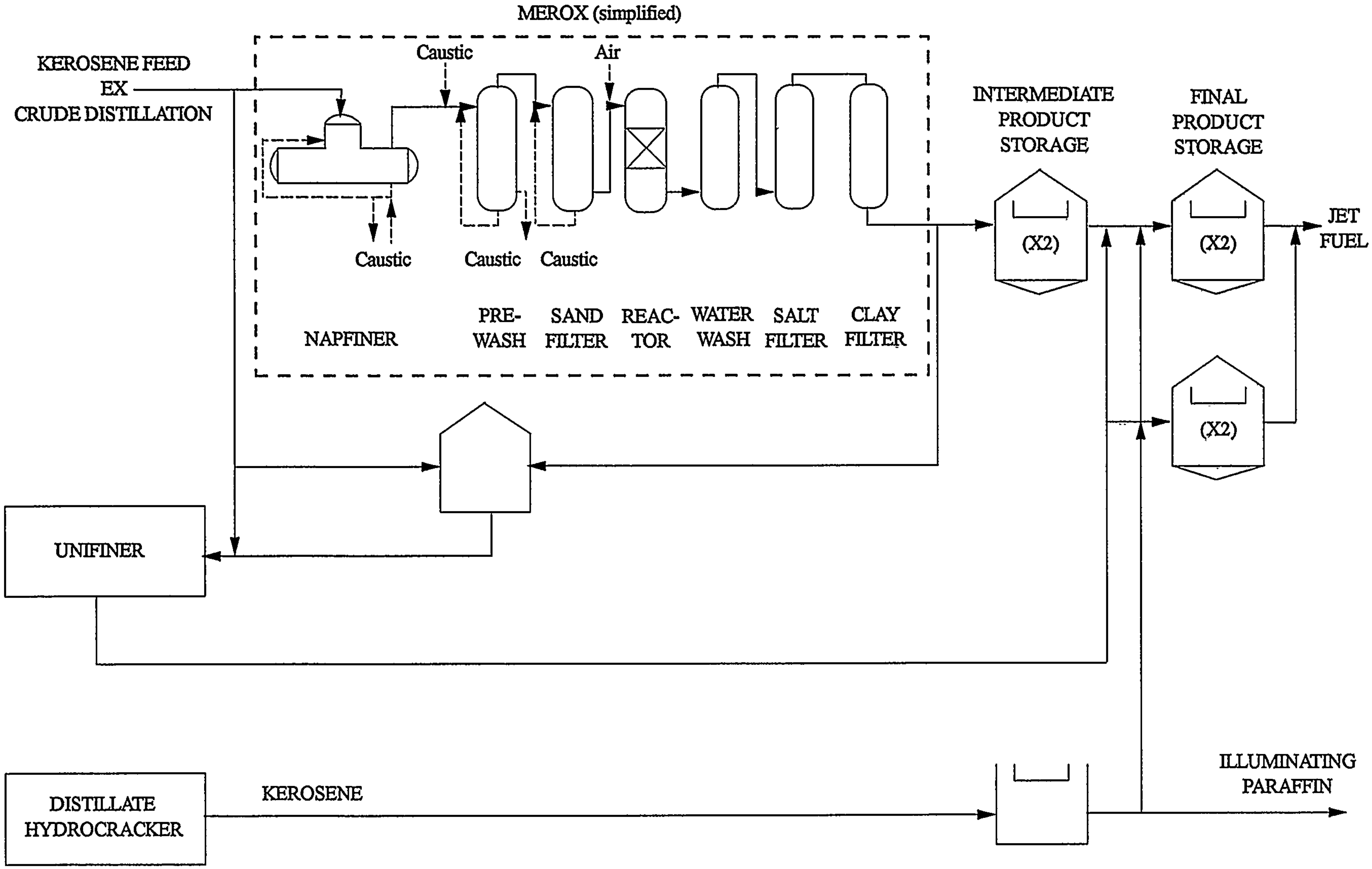

FIGURE 2: SCHEME OF EXPERIMENTS

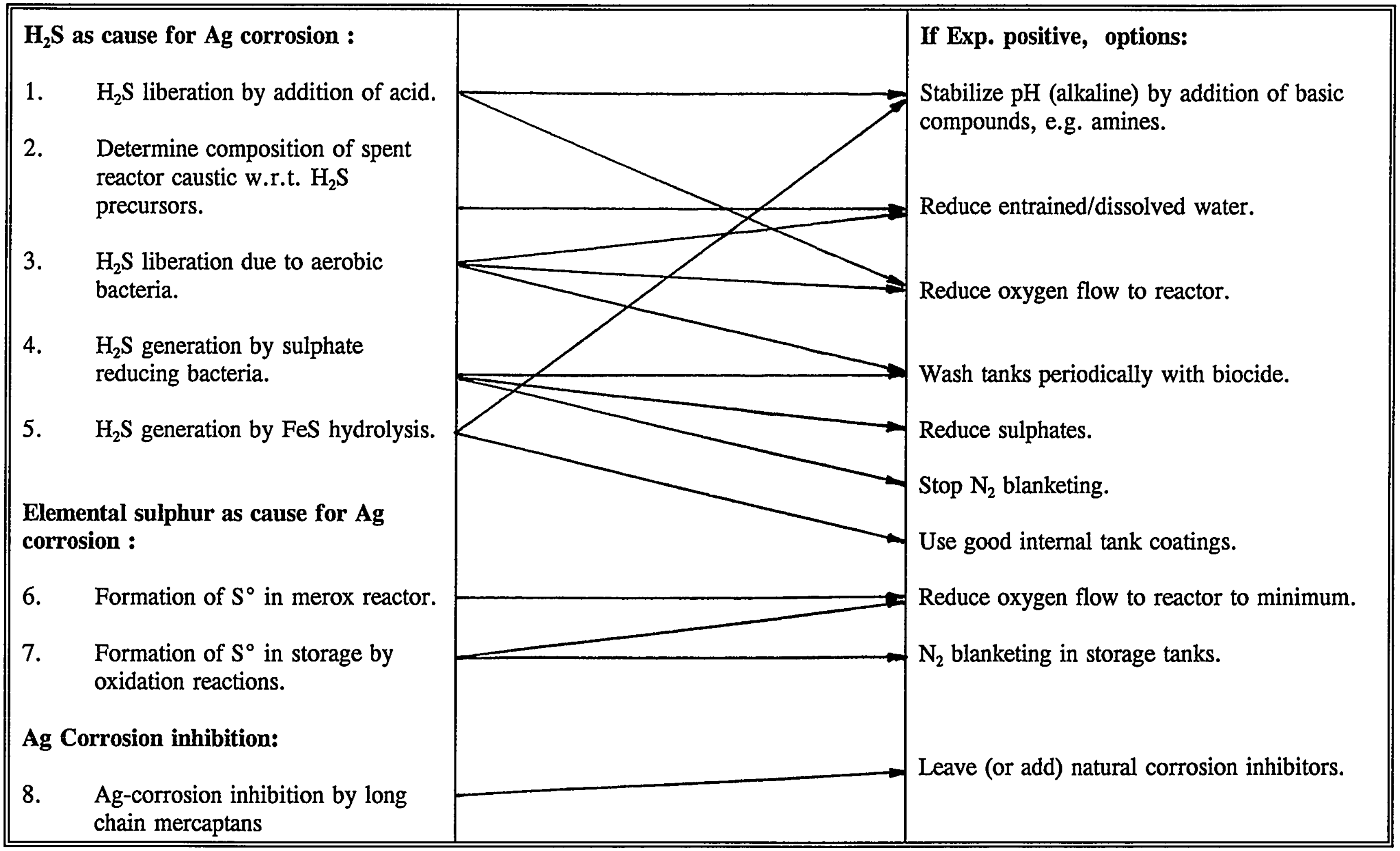

TABLE 1: H_2S liberation by the addition of acid to 500ml samples of treated kerosene

Date	Acetic Acid added	H_2S µg/kg	S° µg/kg
18/10/93	0	<4	39
	0,50 ml	8	39
26/10/93	0	<4	83
	1 ml	<4	88
03/11/93	0	<4	163
	0,25 ml	<4	234
	0,50 ml	25	237
	1,0 ml	25	229
	2,0 ml	25	232
22/2/94	0	<4	492
	0,25ml	15	525
	0,50ml	19	520
	1,00ml	38	560
25/2/94	0	<4	234
	0,10ml	15	300
	0,25ml	19	375
	0,50ml	30	400
	1,00ml	46	440
27/7/94	0	<4	645
	0,25ml	38	650
	0,50ml	67	660
	1,00ml	85	680

TABLE 2: Composition of Merox reactor spent caustic (100ml samples)

Date	Composition of spent caustic	Final pH	H_2S liberated (μg/kg)
15/10/93	Free NaOH :5,7% Tot. Alkal:6,3% Spent: 9,5%	4	130
22/2/94	Free NaOH : 22,8% Tot. Alkal:24,2% Spent: 5,8%	4	200
24/2/94	Free NaOH : 6,8% Tot. Alkal: 8,3% Spent: 18,1%	4	<30

TABLE 3: Formation of S° in reactor. The samples were taken before 1) and after 2) the Merox reactor.

Date		S° μg/kg	H_2S μg/kg	RSH mg/kg
13/10/93	1)	61	<4	54
	2)	91	<4	8
14/10/93	1)	78	<4	53
	2)	116	<4	9
28/2/94	1)	55	<4	79
	2)	150	<4	11
4/3/94	1)	311	<4	76
	2)	198	<4	14
6/3/94	1)	319	<4	71
	2)	190	<4	16

TABLE 4: Influence of added mercaptans on Ag Corrosion

Date	Sample (250 ml)	Ag Corr before treatment	Duration of 1st Ag Corr test	H_2S added p.p.b.	S° added (mg)	$C_{18}H_{17}SH$ added (mg)	Ag Corr after treatment	Duration of 2nd Ag Corr test
13/10/93	Product tank	1	4 hrs	nil	nil	25	0	4 hrs
20/10/93	Product tank	1	16 hrs	nil	nil	25	0	4 hrs
21/10/93	Untreated kerosene	2+	4 hrs	nil	1 000	25	2+	4 hrs
24/10/93	Treated kerosene	0 0	4 hrs 4 hrs	nil nil	1 000 1 000	nil 25	2+ 2+	4 hrs 4 hrs
25/10/93	Treated kerosene	0 0	4 hrs 4 hrs	nil nil	1 000 1 000	nil 25	2 2	4 hrs 4 hrs
04/11/93	Treated kerosene	0 0	4 hrs 4 hrs	80 80	nil nil	nil 25	1 1	4 hrs 4 hrs