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ORGANIC
CHEMICALS DIVISION
RESEARCH
Report

Special Report No. 2918

CONFIDENTIAL
RESTRICT CIRCULATION

MCS 153
Transfer Report

Transfer to Organic Development

Job No. 4013

January 7, 1963

Written by: J. D. Sullivan

Monsanto

ST. LOUIS, MO.

MONS 021090

MONSANTO CHEMICAL COMPANY
ORGANIC CHEMICALS DIVISION
ST. LOUIS RESEARCH DEPARTMENT

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A. INTRODUCTION

This report is an attempt to bring together in one place all of the pertinent technology on the preparation and use of MCS 153. The publication of this report will formally transfer the responsibility for this product from the Research Department to the Organic Development Department.

Although OS 81, Monsanto's synthetic steam turbine lubricant, has served as a suitable gas turbine fluid, the lower viscosity MCS 153 is desirable to facilitate start-ups at low temperatures. MCS 153 is a shear stable functional fluid having the following formulation:

Aroclor 1242	75.31%
Aroclor 1232	12.84%
Tricresyl phosphate (TCP)	10.00%
Poly(Oxybutylene-MDI) Diol (FH-139)	1.80%
N-Phenyl-α-Naphthylamine (PAN)	0.05%
DC-200 Silicone	50 ppm

FH-139 is a shear stable viscosity index improver prepared by the reaction of polyoxybutylene diol (B-2000) with methylene di-p-phenylene isocyanate (MDI). This is a "long sought after" development in functional fluid research and its utility may be visualized beyond the current gas-turbine application. Shear stability is imperative for hydraulic fluids of the Aroclor and the Pydraul series and would prove extremely advantageous in the Skydrol fluids used in the aircraft industry.

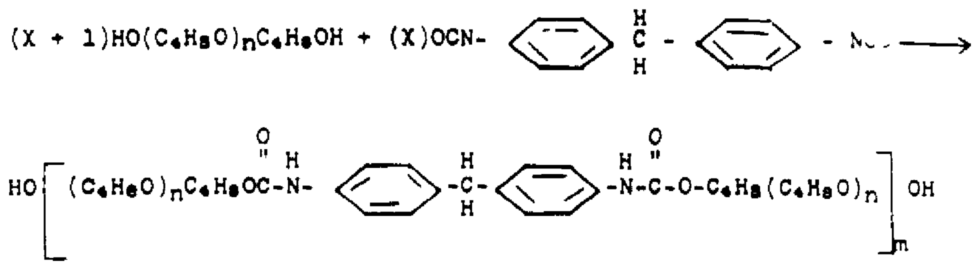
An intensive effort was made to design a shear stable viscosity index improver which did not cause emulsification when the formulation was mixed with water. Non-emulsifying fluids are not a requirement for the gas-turbine application but it is an important property for fluids which could be contaminated by water by mechanical failures such as in steam turbine or shipboard installations. Water washing followed by dehydration, is becoming a popular method for recovering used hydraulic fluids and increasing emphasis is being placed on formulations which will not emulsify in contact with water.

Of the viscosity index improvers prepared and tested, the most effective polymers, which also gave non-emulsifying fluids upon formulation, were ones prepared from polybutylene glycols (B-2000) and MDI. However, this polymer (FH-139) prepared in the plant from production size lots of B-2000 and MDI caused the resulting MCS 153 formulation to emulsify in contact with water. This emulsifying tendency was traced definitely to a contaminant, other than moisture and free acid, in the polybutylene glycol. Purifying this diol by customary techniques, prior to polymerization, failed to give non-emulsifying formulations.

MCS 153 was marketed as a gas-turbine lubricant but this problem will have to be resolved before FH-139 can be used in formulations whose applications require non-emulsifying fluids.

B. CHEMISTRY

The general equation for the preparation of FH-139 is as follows:



The reaction temperature for the polymerization is 70° to 85°C.

1. Degree of Polymerization

Although much higher molecular weights were attained in this polymerization reaction, limiting the chain lengths of FH-139 to the minimum viscosity requirements of gas turbine applications increased the chances of shear stability and non-emulsification of the resulting MCS 153. Difficulties would be encountered in the production of higher molecular weight polymers because of the low fluidity of the products and the selection of a suitable solvent or diluent which would not inhibit the polymerization. Since FH-139 was slated for a viscosity index improver in Aroclor type fluids, it was felt that high molecular weight polymers could be easily handled by reacting MDI and the diol in a solution of the appropriate Aroclor. However, Aroclor inhibits the polymerization and the reaction cannot be carried out in this medium without the aid of a catalyst. On the other hand, the polymerization proceeds smoothly in benzene without a catalyst. The use of polymerization catalysts in the reaction of MDI with the diol resulted in gel polymers which were insoluble in the fluid base stocks.

If the polymer contains terminal isocyanate groups, they will react readily when the fluid comes in contact with water and result in severe emulsions. Likewise, water must be excluded from the reaction of MDI with the diol since the resulting urea groups would serve as terminators for the polymerization. Acid impurities in the starting materials will inhibit the complete polymerization of MDI and the diol.

2. Addition of Reactants

   a. Stepwise Polymerization - In order to obtain the desired polymerization, the diol and MDI were added in definite increments to supply the required excesses of each reactant, for various time intervals, during the reaction period. Specifically, two moles of MDI were added to one mole of the diol to form a polyoxyalkylene diisocyanate. This diisocyanate was reacted with two more moles of the diol to form a poly(oxyalkylene urethane) diol. The cycle was repeated until a polymeric diol, having an approximate molecular weight of 10,000, was obtained.

   b. Batchwise Polymerization - If the total MDI and polyglycol required were added at the same time in a single reaction mixture, the desired order of polymerization cannot be attained even with prolonged heating. Under these conditions, the molecular weight of the polymer did not reach its maximum and optimum viscosity index improvement of the resulting formulation was not obtained.

C. PROPERTIES OF MCS 153

1. Fluid Properties

Table I lists the pour point, along with the viscosities of MCS 153 at various temperatures. Similar results are listed for OS-81, Monsanto's current steam turbine lubricant, for comparative purposes.

Table I

		MCS 153	OS 81
a. Viscosity (cs)			
	at 20°F	3,681.0	200,000
	at 40°F	468.6	3,200
	at 60°F	120.0	-
	at 100°F	22.6	34
	at 130°F	10.7	-
	at 175°F	4.9	5.5
	at 210°F	3.2	3.1
b. Pour Point		0°F	+20°F

In Table 1c are listed viscosities of numerous formulations in which the shear stable viscosity index improver (FH-139) was added to various Monsanto base stock fluids.

Table 1c

c. Viscosity Index Study

Monsanto's Base Stock Fluids	100°F Vis.	210°F Vis.	VI
Aroclor 1242, S-489	17.2	2.35	-273
" " + 4% FH-139	36.0	4.01	- 3 2
TCP	31.66	4.159	- 33 4
" + 4% FH-139	62.18	7 691	+ 95 3
Tetralkyl Urea	51.48	7.465	+114
" " + 4% FH-139	78.56	10.77	+121
FH-118	47.1	7.41	+125
" + 4% FH-139	81.58	11.97	+132
Santicizer 140	17.66	3.258	+ 28.0
" + 4% FH-139	34.05	6.379	+142.0
FH-102-2	10.91	2.960	+141
" + 4% FH-139	19.15	4.877	+184
Santicizer 141	9.955	2.431	+ 62.3
" " + 4% FH-139	20.07	4.487	+156 0
OS-59	6.791	2.254	+156
" + 4% FH-139	6.956	2.298	+158
Dibutyl Phenyl Phosphate	4.166	1.440	+ 86.8
" + 4% FH-139	8.472	2 708	+176
Diphenyl Sulphide	2.80	1.16	+121
" " + 4% FH-139	5.800	2.234	+199

Unfortunately, FH-139 is insoluble in hydrocarbon oil and cannot be utilized in that application.

2. **Quality Tests**

These tests are analytical determinations for trace contamination.

		MCS 153	OS 81
a.	Neutralization Number (typical)	0.07	0.07
b	Water, % by weight, maximum	0.10	0.10

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3. Physical Properties

The following table lists the densities of MCS 153 at various temperatures along with the specific heat of this fluid at 77°F.

a. Density

Temperature	Gm/ml
20°F	1.3663
60°F	1.3452
100°F	1.3247
210°F	1.2674

	MCS 153	OS 81
b. Specific Heat at 77°F, BTU/lb./°F	0.30	0.31

4. Electrical Properties

Table II lists dielectric constants, power factors and specific resistivities for MCS 153, OS 81, DTE Oil 797 and Cellulube 220.

Table II

	MCS 153	OS 81	DTE 797	Cell. 220
a. Dielectric Constant at 25°C				
at 60 cps	6.52	5.95	2.22	-
at 1000 cps	5.94	5.84	2.24	6.91
b. Power Factor (%) at 25°C				
at 60 cps	52.0	17.6	0	-
at 1000 cps	3.45	1.08	0	17.5
c. Specific Resistivity (ohm-cm)				
at 25°C	1.7×10^{10}	5.0×10^{10}	1.4×10^{13}	2.0×10^{8}
at 100°C	2.0×10^{8}	3.3×10^{8}	3.9×10^{11}	8.6×10^{7}

Dielectric constants and power factors were measured at 60 and 1000 cycles per second at room temperature (25°C) Specific resistivity measurements were made at 25°C and 100°C with a megohm bridge.

5. Flammability

The following flammability tests show that MCS 153 is fire retardant despite the incorporation of FH-139 into the formulation.

		MCS 153	OS 81
a.	AIT	1130°F	1260°F
b.	Flash Point (C.O.C.)	360°F	385°F
c.	Fire Point (C.O.C.)	560°F	660°F
d.	High Pressure Spray Test (AMS 3150B)	Does not flash or burn	Does not flash or burn
e.	Hot Manifold Test (AMS 3150B)	Intermittent flashing on tube, does not carry flame to pan (1300°F)	No flashing at 1300°F
f.	Molten Metal Ignition Test	Intermittent ignition, self-extinguishing. Flashes by spark, self-extinguishing.	Does not ignite. Flashes by spark, self-extinguishing.

6. Lubricity

The following table compares the lubricating properties of MCS 153 to OS 81.

		OS 81	MCS 153
a.	Four-Ball Wear at 167°F, 1 Hr. 626 RPM		
	Steel on Steel 4 Kg.		0.21 mm
	Steel on Steel 10 Kg.	0.27 mm	0.23 mm
	Steel on Steel 40 Kg.	0.55 mm	0.53 mm
	Stell-on-Brass 10 Kg.	1.25 mm	0.92 mm
b.	Timken P.S.Z.	30 lbs. Passed 11,350	40 lbs. Passed 11,760

c. Shear Stability

FH-139 in formulations of Aroclor and/or tricresyl phosphate are exceptionally shear stable. After twelve (12) passes through the Diesel Injector, the viscosity of the fluid is decreased by only 0.5%.

7 Performance Tests

a. Oxidation-Corrosion Test

For purposes of comparison, MCS 153 is compared to the 7808 type fluid specifications along with OS 81 and WS-3777, an Esso candidate for a 9236 type fluid. The following table lists the results of comparable oxidation and corrosion tests after a 72 hour retention time at 347°F per Mil-L-7808C.

	Viscosity Initial		Viscosity Change %		Acid	Metal Attack					Wt. Loss
	100	200	100	210	Change	Mg	Al	Fe	Cu	Ag	%
OS 81	34.5	3.15	17.9	1.9	0.14	.01	.03	.03	-.11	-.01	3.4
MCS 153	22.9	3.28	-4.9	-13.7	0.15	.02	.02	.02	-.34	-.10	8.1
WS-3777	52.3	10.4	-4.3	- 5.9	0.54	.02	.02	.03	∓02	.01	2.3
7808C	11.	3.	-5 to +15		2.0	±.2	±.2	±.2	±.4	±.2	-

No sludge or coking was observed in the MCS 153 formulation after the test was terminated.

The following table lists the results of oxidation-corrosion tests on MCS 153 and OS 81 at 250°F for 168 hours.

	OS 81	MCS 153
Metal Attack, Mg/cm:		
Mg	0	-0.01
Al	-0.01	-0.01
Fe	-0.01	0
Cu	-0.05	-0.04
CD/Fe	-0.04	-0.01
Viscosity:		
100°F Initial	34.51 cs.	22.55 cs.
100°F Final	35.48 cs.	24.71 cs.
% Change	+2.8	+9.6
210°F Initial	3.15 cs.	3.24
210°F Final	3.11 cs.	3.31
% Change	-1.3	+2.1

	OS 81	MCS 153
Acidity:		
Initial, TAN	0.07	0.07
Final, TAN	0.09	0.05

b. Foam Tests (ASTM D892)

The following table lists the foaming characteristics of MCS 153 and OS 81.

		MCS 153	OS-81
75°F	Tendency (foam after 5 min. air blowing)	100 ml.	10 ml
	Stability (time to collapse)	200 sec.	10 sec.
200°F	Tendency	0 ml.	0 ml.
	Stability	--	--
75°F after 200°F			
	Tendency	50 ml.	20 ml.
	Stability	40 sec.	20 sec.

c. Rust Tests (ASTM D665)

The cylindrical specimens removed from these tests were equivalent for MCS 153 and OS 81. Furthermore, both of these were comparable to coupons exposed to an uninhibited petroleum oil under similar test conditions.

d. Emulsion Tests (ASTM D1401)

The emulsification properties of a fluid is measured by the ability of the formulation to separate from an equal amount of water, in a half an hour at 135°C, after the mixture has been thoroughly agitated for five minutes at that temperature. Both OS 81 and MCS 153 are rated as non-emulsifying fluids by this test.

OS 81			MCS 153		
Emul.	Fluid	H_2O	Emul.	Fluid	H_2O
0	40 ml.	40 ml.	0 ml.	44 ml.	36 ml.

Although most additives, especially viscosity index improvers, increase the tendencies of synthetic formulations to emulsify with water, FH-139 is rated as a non-emulsifying, shear stable, viscosity index improver.

8. Heat Stability

Laboratory tests showed that large molecular weight polymers (20,000 to 30,000) made from MDI and polyalkylene glycols degraded when heated for prolonged periods above 200°F. On the other hand, lower molecular weight (approximately 10,000) polymers are still effective viscosity index improvers and are more thermally stable. In addition to shear stability and non-emulsification, this thermal characteristic of the polymer was another reason for limiting the chain length of the FH-139 going into the MCS 153 formulation. Table III (see page 10) lists the changes in viscosity and acidity in MCS 153 and OS 81 after long retention times in a severe (static) oven test at 300°F.

It will be noted that the acid build-ups and viscosity increases were only moderate at temperatures well in excess of the operating temperatures of a gas turbine.

9. Toxicity

The toxicity of MCS 153 is unknown at present, but it is anticipated that this fluid will prove to be relatively non-toxic and non-irritating to the skin.

10. Patent Status

A disclosure (No. 2451) has been filed by the Organic Division to cover the use of polymers, made from polyglycols and diisocyanate, as shear stable, non-emulsifying viscosity index improvers for various fluid base stocks.

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TABLE III

	Original			After 120 Hrs.					After 168 Hrs.				
Fluid	100° F	210° F	NN	100° F	% Change	210° F	% Change	NN	100° F	% Change	210° F	% Change	NN
MCS 153	22.6	3.24	.07	21.1	-6.6	2.98	-8.1	.09	20.7	-6.0	2.96	-8.7	0.10
OS 81	34.5	3.15	.07	35.3	+2.2	3.13	-0.6	.07	35.2	+2.0	3.23	-0.9	0.09

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