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DEVELOPMENT OF FIRE RESISTANT
WATER BASED HYDRAULIC FLUIDS

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ABSTRACT

Fire resistant, water based hydraulic fluid formulations have been evaluated for autoignition temperature, lubricity, static corrosion (determined from the liquid phase corrosion test) and for pump performance using a Vickers Vane Pump. In this report period, several large batches of alkanolamine borates and glycol borate condensates have been prepared for evaluation as well as a number of synthetic compounds containing boron and nitrogen.

INTRODUCTION

Synthesized boron-nitrogen and glycol borate condensates have not only improved the fire resistance of many water based hydraulic fluids but have also acted as corrosion inhibitors on metals present in hydraulic pumps. These compounds are being utilized as additives to a water based hydraulic fluid base blend or as a substitute for a material in the blend.

Presently, additional data are being obtained to show the effect of selected additives on the autoignition temperatures of the base fluid blends. This study should define compatibility and effective concentration of the additives.

Vickers Vane Pump tests have been run in order to determine lubricity characteristics as well as the corrosive effects of some of the fluids on various metals under the dynamic test conditions in the pump reservoir. A preliminary check of the static liquid phase corrosion test of MIL-H-19457 specification has been run to obtain comparative data.

SYNTHESIS OF IGNITION INHIBITORS

During the past several months, a complete series of alkanolamine borates have been prepared which have been screened as components of hydraulic fluids. The materials synthesized are polymeric in nature and water soluble for the most part. These compounds do not appreciably alter the viscosity of a finished water-glycol lubricant and only a few substantially increase fire resistance. The physical properties of the synthesized compounds are listed in Appendix Table I.

Our efforts are presently directed towards incorporating the alkanolamine esters into a water based hydraulic fluid which will meet all of the proposed target specifications. When 10 percent of the most promising candidate is added to an available commercial water glycol hydraulic fluid, the autogenous ignition temperature of the end product is increased by 75 to 100°F. Concentrations of inhibitor below 10 percent of the total fluid do not appear to be effective. The following table summarizes appropriate data.

AUTOIGNITION INHIBITION OF A COMMERCIAL WATER GLYCOL HYDRAULIC FLUID

	<u>AIT, °F</u>
A - Commercial Water Glycol Hydraulic Fluid	765-775
A + 5% DEAB	775-780
A + 10% DEAB	860-870
10% Polyalkylene Glycol A 35% Polyalkylene Glycol B 10% DEAB 45% Water	875-895
10% Polyalkylene Glycol A 35% Propylene Glycol 10% DEAB 45% Water	930-950

Alkanolamine borates, glycol borates and various other additives are being screened for compatibility and autoignition inhibition

properties in a promising hydraulic fluid base blend. Appendix Table II summarizes the evaluation. As brought out before, about 100°F increase in autoignition temperature is the greatest increase observed.

Vickers vane pump tests summarized below indicate that direct substitution of a glycol borate condensate for one of the polyalkylene glycols used in blend A produces a fluid (designated Blend J) which is deficient in lubricating properties. When only a partial substitution of the polyalkylene glycol in base A with the glycol borate condensate was effected, the resulting fluid had better lubricating qualities. This formulation is coded as base K. Further lubricity improvement in base K may be effected upon inclusion of appropriate antiwear additives. This phenomenon is demonstrated by the addition of a small amount of Benzotriazole and sodium benzoate (refer to results under Blend L). Blend L shows a vast improvement in lubricity characteristics over Blend J which is a similar formulation without wear additives.

	<u>Wear Rate, Ring</u>
Base A	1.2 mg/hour
Base J	3000 mg/hour
Base K	17 mg/hour
Base L	16.6 mg/hour

Complete wear and formulation data are presented in Appendix Table III.

The effect of both lubricity and autoignition depressant additives on the pump performance of several water glycol hydraulic fluid bases is presented below. The addition of up to 8 percent of the synthesized P-Glyco Bor additive improves the lubricity characteristics of the resultant formulation.

	<u>Wear Rate, Ring</u>
Blend B (including 1% sodium benzoate)	4.0 mg/hour 0.2 mg/hour
+ 1% P-Glyco-Bor	0.2 mg/hour
+ 4% P-Glyco-Bor	0.1 mg/hour
+ 8% P-Glyco-Bor	0.2 mg/hour

More detailed data are presented in Appendix Table IV

A preliminary check of the corrosivity of several fluid blends was conducted by examining the pump parts after test runs at 120° and 140°F. Blends J, K and L, all containing the synthesized P-Glyco-Bor additive, caused no visible corrosion to the pump parts. Blend C, which contains a commercial fire resistant, water soluble, phosphate additive, caused heavy corrosion to the steel pump parts. Blends A and B, both containing various percentages of several polyalkylene glycols in a water formula, cause moderate to heavy corrosion to the steel pump parts.

WATER GLYCOL BASE STOCKS RATED FOR CORROSIVITY
DURING VICKERS VANE PUMP RUNS

<u>Blend</u>	<u>Rating*</u>
A	4
B	6
C	10
J	1
K	1
L	1

* Ratings - 1 = Very good condition - No visible corrosion of pump parts

10 = Very poor condition - Rust and corrosion of pump parts is evident

A series of pump tests were conducted in order to show the effect of the formulated, water based hydraulic fluids on some of the metals. It is noted here that the addition of the P-Glyco Bor additive to Base Blend B containing sodium benzoate, lessens the attack of zinc plate. Data confirming this statement is presented in Appendix Table V.

A preliminary check of the static liquid phase corrosion test of MIL-H-19457 specification was run to obtain comparison data to the dynamic corrosion tests. It is again noted that the Zinc panel is clean and bright which is definitely due to the addition of the P-Glyco Bor additive added to the Base Blend B. These observations can be detailed in Appendix Table VI.

The following data represent initial studies of foam tendencies of three experimental fluids. Tested at 75°F and 140°F in order to determine what degree of foam can be expected from higher viscosity fluids specified in the proposed target requirements. The most promising hydraulic fluid formulation having the lowest foam tendency

will be considered the most acceptable. These data indicate that the P-Glyco Bor additive in conjunction with the high molecular weight glycol presents no foaming problem.

FOAM TENDENCY OF FLUIDS @ 75°F AND 140°F

		<u>Tendency ml of foam after 5 min aeration</u>	<u>Stability ml of foam after 10 min of collapse time</u>
Base A + 1% sodium benzoate	75°F	550	190
	140°F	580	None
Base A + 1% sodium benzoate 0.1% benzotriazole	75°F	550	190
	140°F	540	None
Base L	75°F	230	10
	140°F	510	20

STATUS AND FUTURE PROGRAM

Ignition inhibitors, both the commercial and the experimental materials, have been screened for this project. Two types of compounds, glycol borates and alkanolamine borates, show the most promise for this application. These materials are now being prepared in sufficient quantities for the formulation and evaluation tests listed in the target specification.

The AIT apparatus, described in ASTM D 1255 T, has been constructed and will be used to confirm data we have determined by the procedure listed in ASTM D 286.

APPENDIX TABLE I

Name	Appearance	Neut No.	PH-20% in H ₂ O	Visc @ 100°F CS	Visc @ 100°F 20% in H ₂ O CS	R I ND/20°C	Flash Pt (COC)	Fire Pt (COC)	AIT°F
50 HB 660-Het	Dark, Brown Liquid	21.2 Acid	2.7	271.0	separation	1.4673	450°F	500°F	750-775
Tri-THFB	Sample separated into 2 layers on standing-24 hours	3.36 Base	6.0				250°F	290°F	<700
E-Glyco Bor	Water wt. liquid	78.5 Base	8.4	79.4	1.17	1.4422	240°F	260°F	950-970
P-Glyco Bor Batch 1	Clear, amber liquid	81.3 Base	8.4	300.0	1.27	1.4400		220°F	
P-Glyco Bor Batch 2	Clear, amber liquid	71.6 Base	8.4	78.2	1.27	1.4331		280°F	>1000
P-Glyco Bor Batch 3	Clear, amber liquid	70.0 Base	8.1	131.75	1.262	1.4351		280°F	
P-Glyco Bor Batch 4	Cloudy fluid	60.6 Base	8.3			1.4310			
D-Glyco Bor Amine in P-G	Yellow to Brown semi solid	267.5 Base	10.0					130°F Recheck 120°F	

Appendix Table I continued

Name	Appearance	Neut No.	PH-20% in H ₂ O	Visc @ 100°F CB	Visc @ 100°F 20% in H ₂ O CB	R I ND/20°C	Flash Pt (COC)	Fire Pt (COC)	AIT°F
75 H 450 Bcr	Brown liquid	2.52 Base	7.2	141.4	2.368	1.4645	500°F	610°F	760-775
PHPC	Clear, amber liquid	8.9 Base	9.75	90.96	1.356	1.4481			960-975
PPCB-A	Cloudy solid		5.15		separated in H ₂ O				790-810
MEAB-A Batch 1	Cloudy, viscous polymeric type	740 Base	10.1		1.497				835-855
MEAB-A Batch 2	Viscous- polymeric type	700 Base	10.5		1.574	1.4885			970
MEAB Batch 1	Viscous- polymeric type	605 Base	9.6			1.4994			875-890
MEAB Batch 2	Viscous- polymeric type	435 Base	9.9						970
DEAB-A Batch 2	Viscous- polymeric type	523 Base	9.6		1.824	1.4990			
DEAB-A Batch 3	Viscous- polymeric type	504 Base	9.7		1.515	1.4955			775

Appendix Table I continued

Name	Appearance	Neut. No.	PH-20% in H ₂ O	Visc @ 100°F in CS	Visc @ 20% in H ₂ O in CS	R I ND/20°C	Flash Pt (COC)	Fire Pt (COC)	AIT°F
DEAB Batch 2	Viscous-polymeric type								
DEAB Batch 3	Viscous-polymeric type	202 Base	6.2	1.239	1.4734				925°+
DEAB Batch 4	Viscous-polymeric type	252 Base	8.2	1.19	1.4760				970
MIPAB-A	Viscous-polymeric type	645 Base	10.5						
NIPAB	Viscous-polymeric type	365 Base	9.5	1.09	1.4686				
DIPAB-A	Viscous-polymeric type								
DIPAB	Viscous-polymeric type	224.4	7.9	1.098	1.4616				825°
TIPAB-A	Viscous-polymeric type	126.2	8.8	1.359	1.4678				
TIPAB	Viscous-polymeric type	112.2	8.8	1.270	1.4592				

Solidified during reaction - discontinued

APPENDIX TABLE II

AUTOIGNITION INHIBITION OF A GLYCOL BASED
HYDRAULIC FLUID THROUGH ADDITIVE TREATMENT

Selected Base Fluid

16% Polyalkylene Glycol (a)
39% Polyalkylene Glycol (b)
45% Water

<u>Additive Treatment</u>	<u>AIT°F</u>
1. None	830
2. 4% Potassium Diethyl Phosphate	805
3. 4% GB DEA Complex	840
4. 4% DEAB - Batch 1	870-935
5. 4% E. Glyco-Bor - Batch 1	845
6. 4% DEAB-A - Batch 1	815
7. 10% DEAB-A - Batch 3	<825
8. 10% MEAB - Batch 2	825
9. 4% Urea	830
10. 8% Urea	<840
11. 5% MIPAB	<805
12. 10% DIPAB-A	810
13. 20% DIPAB-A	895
14. 30% DIPAB-A	835
15. 40% DIPAB-A	<800
16. 10% DIPAB	<810
17. 20% DIPAB	800
18. 10% TIPAB-A	785
19. 20% TIPAB-A	760
20. 30% TIPAB-A	835
21. 40% TIPAB-A	845
22. 10% TIPAB	760
23. 20% TIPAB	925
24. 40% TIPAB	875

APPENDIX TABLE III

SCREENING PUMP TESTS OF FLUID BLENDS

Vickers V-104-A-10 Pump

Pressure 900 psi
 Vol. output 5 GPM
 Operating Temp 115-125; 130-145°F

		<u>Hours</u>	<u>Wear, mg</u> <u>Ring</u>	<u>Vanes</u>
<u>Blend J</u>				
Polyalkylene Glycol (a)	21%			
P-Glyco Bor Batch 2	34%			
Water	45%	3	9050	942
<u>Blend K</u>				
Polyalkylene Glycol (a)	16.5%			
Polyalkylene Glycol (b)	29.5%			
P-Glyco Bor Batch 3	8.0%	18	183	24
Water	45 %	22	89	33
Sodium Benzoate	1.0%	65	19	12
<u>Blend L</u>				
Polyalkylene Glycol (c)	16.0 %			
P-Glyco Bor Batch 4	35.95%			
Water	45.0 %			
Sodium Benzoate	1.0 %	16	273	1
Benzotriazole	0.05%	23	383	0

APPENDIX TABLE IV

EFFECT OF ADDITIVE MATERIALS ON THE
PUMP PERFORMANCE OF THE BASE FLUIDS

Fluid	Hours	Wear, mg		
		Ring	Vanes	
Blend B + 1% Sodium Benzoate Test Stand No. 1	18	47	41	
	22	39	25	
	Test Stand No. 2	18	9	8
		65	2	4
Blend J + 1% EFH Additive	18	213	4	
	9	150	3	
Rerun of above fluid	19	377	1	
	21	397	2	
Blend J + 2% EFH Additive	24	432	NWL	
	22	423	4	
Blend B + 1% Sodium Benzoate + 1% P-Glyco bor Batch 3	19	5	1	
	Blend B + 1% Sodium Benzoate + 4% P-Glyco bor Batch 3	65	8	7
Blend B + 1% Sodium Benzoate + 8% P-Glyco bor Batch 3		18	3	2

APPENDIX TABLE V

STUDY OF METALS CORROSION IN LIQUID PHASE
IMMERSION TESTS DURING PUMP OPERATION

Immersion @ 140°F in reservoir of hydraulic pump stand
Test panels - 1x1x1/16; Zinc plate 1x2x1/16

Fluid - Blend B + 1% Sodium Benzoate
Duration - 20 hrs

	<u>Weight Change, mg</u>
Aluminum	-0.2
Copper	+0.4
Bronze	None
Steel	+0.2
Zinc plate	-2.8 evidence of attack
Zinc plate	-0.3 on Zinc plate

Fluid - Blend B + 1% Sodium Benzoate
+ 1% P-Glyco bor Batch 3
Duration - 20 hrs

Aluminum	+0.1
Copper	+0.4
Bronze	+0.7
Steel	+0.2
Zinc plate	-1.2
Zinc plate	None

Fluid - Blend B + 1% Sodium Benzoate
+ 4% P-Glyco bor Batch 3
Duration - 65 hrs

Aluminum	-0.8
Copper	+0.1
Bronze	-0.3
Steel	+2.7
Zinc	-0.6

APPENDIX TABLE VI

STATIC CORROSION LIQUID PHASE CORROSION TEST

MIL-H-19457

Duration - 1 week
Test Temp - 130°F

Fluid - Blend B + 1% Sodium Benzoate

<u>Metal</u>	<u>Weight Change, mg/mg/cm²</u>	<u>Appearance</u>
Aluminum	-0.3/0.009	Clean and bright
Bronze	+0.4/0.012	Hazy film
Steel	-0.5/0.015	Clean and bright
Copper	+1.9/0.056	Dulling film - bronzed
Zinc	-2.3/0.067	Dulled surface

Fluid - Blend B + 1% Sodium Benzoate
+ 4% P-Glyco bor Batch 3

Aluminum	-1.0/0.030	Scattered gray black staining
Bronze	-1.0/0.030	Clean and bright
Steel	-0.8/0.021	Slightly dulled surface
Copper	+1.1/0.032	Dulling film - bronzed copper
Zinc	-1.6/0.047	Clean and bright

Fluid - Blend B + 1% Sodium Benzoate
+ 8% P-Glyco bor Batch 3

Aluminum	-0.2/0.006	Gray-black staining slightly more than in fluid above
Bronze	-0.4/0.012	Clean and bright
Steel	-0.4/0.012	Clean and bright
Copper	+1.1/0.032	Dulling film; bronzed
Zinc	-1.7/0.050	Clean and bright