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FINAL REPORT

ON

EXPLORATORY RESEARCH ON FUNCTIONAL FLUIDS - 1955

Job No. 2-02-750.01-2921

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INTRODUCTION

This report deals with the evaluations of new materials for base stocks and suitable additives for functional fluids of potential commercial value. Shortage of raw materials and new industrial applications initiated an investigation to find new components for functional fluids, which could make Monsanto independent of the cresylic acid market and offer fluids possessing more desirable properties.

SUMMARY

Limiting the study to hydrocarbon systems, mixtures of diphenyl with HB-40, HB-20, Solvaloid C, naphthalene, Santodex, polystyrene and Paratone N were found to be unsatisfactory, as a functional fluid base stock, because of high melting points. Fluids of potential interest as functional fluids can be obtained by the alkylation of triphenyl phosphate. Various solid and liquid phosphate esters were dissolved in Aroclor in an effort to determine the effects of different functional groups on the viscosity indices of the resulting formulations. In an attempt to improve the color stability of tricresyl phosphate several reagents were tested as cooking agents for cresylic acid without accomplishing the desired results.

CONCLUSION AND RECOMMENDATIONS

Several alkylated triphenyl phosphates possessed good viscosity and viscosity index properties and are worthy of more extensive evaluation as functional fluids. A ternary of diphenyl, o-terphenyl and m-terphenyl melts below room temperature and further studies should be planned on this mixture.

PATENT STATUS

The direct alkylation of triphenyl phosphate and the utilization of aryl isopropyl ethers in the synthesis of phosphate esters is believed to be novel and has been disclosed to the Patent Department by Dr. M. W. Farrar.

REFERENCES

Following are the references utilized in this work and are hereby cited.

(1) Final Report, Job No. 2-02-750.01-3032 - Alkylation of Triphenyl Phosphate by M. W. Farrar (12-30-55).

(2) Final Report, Job No. 117-2380 - Functional Fluids by R. E. Hatton, May 21, 1953.

(3) Final Report, Job No. 117-2080 - Hydraulic Fluids and Synthetic Lubricants by R. E. Hatton, May 15, 1952.

EXPERIMENTAL AND DISCUSSION

A. Additives for Diphenyl

Some interest has arisen in diphenyl as a functional fluid base stock. It was desired to reduce the pour point, increase the viscosity index, and increase the flash point. The additives used were restricted to hydrocarbon materials.

Diphenyl has a crystallizing point of about 69°C. The first objective of the work was to try to reduce this crystallizing point. Mixtures of diphenyl and HB-40, HB-20, Solvaloid C (aromatic petroleum fraction), and naphthalene were studied. Data on crystallizing points are as follows:

	Crystallizing Point, °C.			
% in Diphenyl Mixture	HB-40	HB-20	Solvaloid C	Naphthalene
0	68.5	68.5	68.5	68.5
12.5				59.5
25	58.5	58	57	50.5
37.5				39.5
50	44	45	44	49.5
62.5				58
75	<10	11	<10	65
100				79.5

These data show that mixtures of diphenyl with HB-40, HB-20, or Solvaloid C crystallized above room temperature unless the diphenyl content was about 25% or less. With naphthalene, the lowest crystallizing point obtained was 39°C. with 37.5% naphthalene in diphenyl.

It was thought that maybe hydrocarbon polymers might be used to depress the melting point of diphenyl and give a good viscosity index to the resulting fluid. However, Santodex (alkylated polystyrene), polystyrene, and Paratone N (polyisobutylene) depressed the melting point but little in concentrations up to 15%.

The literature indicated that a ternary eutectic mixture of diphenyl, o-terphenyl, and m-terphenyl has a melting point of about 19°C. Such a mixture was made up to contain 52% o-terphenyl, 22% m-terphenyl, and 26% diphenyl. The resulting material was fluid at room temperature and had the following viscosities: 2.47 cs. at 210°F. and 18.97 cs. at 100°F. for a viscosity index of 270.

B. Evaluation of Alkylated Triphenyl Phosphate

Samples of various alkylated triphenyl phosphates were submitted by Dr. M. W. Farrar for evaluation as functional fluids. The results are as follows:

Sample	Reference	Viscosity, cs. + 210°F.	Viscosity, cs. + 100°F.	Viscosity Index
"Reaction Product, Ethyl Chloride and Triphenyl Phosphate"	A66007	4.61	28.85	+ 71
"Reaction Product, Ethyl Chloride, $AlCl_3$ and Triphenyl Phosphate"	A66039	5.45	38.01	+ 81
"Reaction Product, Propylene and Triphenyl Phosphate"	A-66040	4.39	34.72	- 33
"Isobutylene alkylated triphenyl phosphate"	A66046	4.80	33.52	+ 49
"Triphenyl Phosphate Reaction Produced with Isopropyl Chloride and $AlCl_3$"	A66043	5.70	48.80	+ 40
"Triphenyl Phosphate Alkylated with t-Butyl Chloride"	A66049	7.82	99.37	+ 12
Tri(isopropyl phenyl) phosphate (JDS-A71010) prepared from alkylated phenol	(M.W.F.-A70805)	3.82	23.69	+ 19
Tri(isopropyl phenyl) phosphate prepared from alkylation of phenol and esterifying with $POCl_3$	(M.W.F.-A70811)	5.96	62.25	- 2
Tri(isopropyl phenyl) phosphate	(M.W.F.-A70815)	5.41	46.88	+ 23
Tri(isopropyl phenyl) phosphate	(M.W.F.-A70824)	3.54	18.51	+ 64

DSW 620871

These viscosity data show that the alkylation of triphenyl phosphate results in fluids which are of potential value as functional fluids.

C. Evaluation of Solid Phosphates in Aroclor

Samples were prepared of tri (tert.-butyl phenyl) phosphate (A71008) and tri (α phenyl ethyl phenyl) phosphate (A71009) for evaluation as plasticizers and functional fluid constituents. They were tacky solids and very difficult to isolate and purify. Viscosities were run on 25% solutions of these solid phosphates in Aroclor 1242 and compared with similar solutions of fluid phosphate esters in an effort to determine the effects of the various functional groups on the viscosity indices of the resulting formulations.

The following table lists the viscosities of various solid and liquid phosphate esters dissolved in Aroclor 1242.

Tris Phosphates 25% Soln. in Aroclor 1242	Viscosities of 25% Solutions (c.s.)						
	Notebook Numbers	Job #2080-1952			Job #2921-1955		
		100°F.	210°F.	V.I.	100°F.	210°F.	V.I.
Triphenyl		13.72	2.34	-127			
Cresyl diphenyl		15.65	2.47	-151			
Tri Cresyl	A71018	20.12	2.73	-201	22.14	2.85	-214
Tri (tert.-butyl phenyl)	A71017				36.71	3.75	-228
Tri(α phenyl-ethyl-phenyl)	A71018				60.33	4.52	-295
Tri(para-tert-butyl phenyl)	A71017				40.20	4.37	-105
Tri(para-cresyl)	A71014				20.50	2.76	-200
Cyclohexyl di-phenyl	A71014				19.29	2.74	-170
Tri xylenyl	A71015				40.05	3.02	-635
$CH_3PH(OC_6H_5COOCH_3)_2$	A71016				49.00	3.80	-430
2 Ethyl hexyl diphenyl	A71015				14.20	2.40	-120

In general, based on data preliminarily obtained, the trialkyl phosphates have the highest viscosity indices and the V.I. decreases as the alkyl groups are replaced by aromatic substituents. Adding side chains to the alkyl or aryl groups correspondingly lowers the VI's of the phosphate esters. The viscosity index of any given triaryl phosphate (A71017-18) increases as the amount of the para isomer (A71014-A71017) is increased. Phosphonates (A71016) in Aroclor 1242 drastically lowers the viscosity index compared to similar solutions of TCP or Santicizer 141.

D. Cooking Agents for Cresylic Acid

Various cooking agents for cresylic acid were exploited in an effort to improve the color stability of the distilled cresylic acid and the quality of the finished product in the phosphate ester process.

(1) Fumaric Acid -

The distilled cresylic acid "B" was yellowish after cooking it with fumaric acid at 125°C. to 150°C. for one hour before the vacuum take-over distillation (A71034).

(2) Manganese Dioxide -

Cooking cresylic acid "B" with MnO_2 for 2.5 hours at 150°C. and 300 mm. gave a colorless distillate, except for a small yellow fraction at the end of the take-over distillation. Condensing this cresylic acid with $POCl_3$ processed nicely but resulted in a very dark finished product (A71035).

(3) Zinc Treatment -

The color of the phosphate ester, made from phosphoric acid cooked cresylic acid "B", was only slightly improved by treatments with metallic zinc, using hydrochloric acid or acetic acid as a catalyst (A71036).

E. Miscellaneous Exploratory Results

For the sake of completeness the following miscellaneous results are recorded under this heading.

(1) A sample of tetra (2 ethyl-hexyl) hexane 2,5 diphosphate (Dayton-A71019) gave a viscosity index of +148. Following are the viscosities at the indicated temperatures:
at 100°F. = 16.44 c.s. at 210°F. = 3.84 c.s.

(2) The direct chlorination of triphenyl phosphate (A71013) with chlorine at 50° to 60°C. gave only a 10% chlorine efficiency.

(3) A sample of isopropyl biphenyl (A71012) gave the following viscosity:
at 100°F. = 5.26 c.s. at 210°F. = 1.57 c.s.

ACKNOWLEDGMENT

The functional fluid group is indebted to Dr. M. W. Farrar for the preparation of numerous alkylated triphenyl phosphates which he submitted for evaluation during this investigation.

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