St. Louis Research Report No. 1281

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FINAL REPORT

ON

SCREENING TESTS ON MONSANTO AND COMPETITIVE PLASTICIZERS - 1954

PART I: THE INTENSIVE EVALUATION OF SECONDARY PLASTICIZERS INCLUDING THE AROCLORS

Job No. 2-02-750.01-2821-I

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INTRODUCTION

A project of evaluating secondary or extender plasticizers has been undertaken with a two-fold purpose. The first is to learn the good points and the limitations of secondaries currently offered to the trade. The second purpose is to study the properties of Monsanto Aroclors (chlorinated biphenyls) and in turn attempt to find a place for them in the secondary market.

There are currently two main classes of secondaries: the chlorinated paraffins and the aromatic hydrocarbons, products of oil fractionation. Both classes of compounds offer advantages in price when compared to the primary plasticizers, but they also have serious limitations of use in vinyl formulations. This report, then, is a study of those advantages and disadvantages, and includes a study of the Aroclors.

SUMMARY

So far nineteen secondaries, including the Aroclors, have been evaluated in relation to their performance and permanence as the sole plasticizer and in combination with a primary plasticizer.

Preliminary evaluations were made on the secondaries at 67 and 50 PHR and at 1:1 DOP and 1:2 DOP. In addition, heat and light stability, flammability, soapy water extraction and electrical tests were made on the secondaries at the compatibility-limit point.

CONCLUSIONS

The Conclusions section is divided into two parts. Part I compares the chlorinated paraffins to the Aroclors and HB-20, since they are competitive in performance and price, selling at 15 to 22 cents per pound. Part II is a report on the other secondaries studied to date, those which sell from 5 cents per gallon to 15 cents per pound.

Part I

Test results indicate that:

1. The Aroclors and HB-20 are more compatible and are faster fusing than the chlorinated paraffins. The limits of compatibility with DOP for the Aroclors and HB-20 is 1 part secondary to 3 parts DOP. For the chlorinated paraffins the limit is 1 part chlorinated paraffin to 6 parts DOP. Table I, Part I.

2. The Aroclors are more heat stable, less sensitive to extraction by kerosene and slightly more flame retardant than the chlorinated paraffins.

3. The two classes of compounds are essentially equivalent in light stability, flexibility, water sensitivity and in electrical properties. Tables II, III and III.

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4. The chlorinated paraffins are superior to the Aroclors and HB-20 in these respects: they are much less volatile, are less extractable by soapy water, fume less while milling and produce compositions with less odor in kind and degree. Table I and II.

5. The vapors given off while roll-milling a composition containing a liquid Aroclor are pungent and toxic. The products, therefore, should not be used in a room that is not well ventilated or evacuated.

6. Both HB-20 and the liquid Aroclors seem to have a beneficial effect on viscosity-stability in plastisols by slowing down viscosity buildup. Table III.

Part II

The chief attribute of the aromatic hydrocarbons, when used in vinyls, is a low price.

Except for Cabol 100 (G. L. Cabot Co.), they will not form a sheet on the roll mill and have very limited compatibility when mixed with DOP - 1:6.

Generally, they are very dark in color and fume heavily while being roll-milled. The fumes given off are extremely pungent.

Since they are dark-colored, their heat and light stability are poor and they are limited in use to compositions of dark brown or black color. Table I, Part II.

RECOMMENDATIONS

The program of evaluating secondaries should be continued because more compounds in that category are appearing on the market and because Monsanto, with its Aroclors, HB-20 and HB-40, has a stake in the secondary market.

PATENT STATUS

Nothing of a patentable nature has been discovered as a result of this project.

EXPERIMENTAL WORK

Preliminary evaluation tests were run on formulations of the secondaries at 40% and 50 PHR concentrations and at 1:1 DOP and 1:2 DOP, the latter two ratios being at 40% concentration. The rest of the testing was done at the particular compatibility limits for each secondary.

The preliminary evaluation results in Table I, Part I indicate the following:

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1. That HB-40, HB-20 and the Aroclors are much more compatible (via the Loop Test) than the chlorinated paraffins. HB-40 is compatible at 1:1 DOP and HB-20 and the Aroclors are compatible at 1:3 DOP, whereas the chlorinated paraffins are compatible at only 1:6 DOP.

2. That the Aroclors and HB-40 alone, or when mixed with DOP, are faster fusing than HB-20 and the chlorinated paraffins.

3. That the Aroclors are less extractable by kerosene than HB-20, HB-40 and the chlorinated paraffins.

4. That the Aroclors and HB-20 when incorporated in plastisols do an adequate job of slowing down the buildup of viscosity. This element of low viscosity buildup should be of importance to the user of plastisols for glove dipping and some cloth coating.

5. That all of those compounds listed in Part I are essentially equivalent in flexibility and water sensitivity.

6. That the chlorinated paraffins are less volatile and they fume less upon milling than the Aroclors, HB-20 and HB-40. The fuming and high degree of volatility are the major drawbacks to the use of the Aroclors and HB-20.

7. That the chlorinated paraffins produce compositions with less odor than those of the Aroclors and HB-20. HB-40 is nearly median in that instance.

Test results in Table II indicate that:

1. The Aroclors are slightly more flame retardant than the chlorinated paraffins and much more than HB-20 and HB-40.

2. The Aroclors and HB-40 are more heat stable than the chlorinated paraffins and HB-20.

3. They are generally equivalent in light stability; however, HB-20 is very poor in this respect. They are also roughly equivalent in electrical properties.

4. The chlorinated paraffins are much less extractable by soapy water than are the Aroclors.

Preliminary data in Table I, Part II indicate that the aromatic hydrocarbons suffer from:

1. Poor initial color and odor.

2. Poor viscosity properties.

3. Poor compatibility as determined by the Loop Test. This is not true of Cabol 100. It seems to be compatible at 1:1 DOP.

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4. A high degree of fuming while milling and the fumes given off are rather noxious.

However, they are inexpensive and probably do find use in low-grade, black formulations where their deficiencies are less noticeable.

In summation then, the Aroclors, HB-20 and HB-40 do show several distinct advantages over the chlorinated paraffins and the aromatic hydrocarbons which should recommend them to users of secondary or extender plasticizers. However, the incorporation of the Aroclors and HB-20 in vinyls must be limited by their fuming, their volatility, and the toxicity of the Aroclor fumes.

DISCUSSION

To give the reader an idea of the wide range of selling prices the following is quoted from the price lists of the companies concerned:

HB-40	22¢/lb.
Aroclors	18¢/lb.
Chlorinated Paraffins	16-17.5¢/lb.
HB-20	15¢/lb.
Aromatic Hydrocarbon	0.05¢/lb.
Aromatic Hydrocarbon	0.05¢/gal.

The range of prices shown above and the evaluation data found in this report gives the potential formulator an extremely wide choice of extenders for his particular use. It becomes necessary then for the buyer/user to select a secondary carefully and for the seller to approach the buyer equipped with all data showing the abilities of the secondary with sufficient warning about its deficiencies. A user could easily get into difficulties of major severity if he employed some of these secondaries indiscriminately.

ANALYTICAL PROCEDURES

All testing in this report was done according to the "Standard Test Methods of the Plasticizer Application Laboratory."

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TABLE I - PART I

EVALUATION OF SECONDARIES

	Milling Results					Hardness		Water Sensitivity		Kerosene Extraction % Plas. Lost	Comp. Exud. Test
	Fuming	Odor	Fusion	Flow Test	Volatility % Plas. Lost	Before Vol.	After Vol.	% Sol. Matter Lost	% Absorption		
[illegible]	heavy	strong	rapid	+2.7	40.3	[illegible]	100+	1.45	0.06	7.0	No exudation
[illegible] PHR	heavy	strong	rapid	-1.7	25.5	91	100+	0.66	0.05	3.8	No exudation
[illegible] DOP	heavy	strong	rapid	-30.0	41.2	[illegible]	95	1.98	0.06	13.4	Slight [illegible]
[illegible] DOP	heavy	strong	rapid	-33.4	30.9	77	84	0.92	0.07	15.8	Very [illegible]
[illegible]	heavy	strong	rapid	-3[illegible]	29.0	90	100+	0.55	0.09	8.2	No exudation
[illegible] PHR	heavy	strong	rapid	+11.0	14.9	95	100+	0.19	0.07	3.6	No exudation
[illegible] DOP	heavy	strong	rapid	-26.7	37.5	93	100+	0.40	0.10	14.6	Mod. exudation
[illegible] DOP	heavy	strong	rapid	-33.6	30.7	78	100+	0.28	0.17	29.4	Slight [illegible]
[illegible]	heavy mod.	strong	mod.	+4.3	18.9	94	100+	0.26	0.05	5.8	No exudation
[illegible] DOP	heavy mod.	strong	mod.	+18.8	10.4	100+	100+	0.13	0.07	2.8	No exudation
[illegible] DOP	mod.	strong	mod.	-22.2	28.7	96	100+	0.14	0.12	12.8	Slight [illegible]
[illegible] DOP	Sl.mod.	strong	mod.	-29.2	23.9	91	94	0.10	0.13	10.2	Very [illegible]
[illegible]	Sl.mod.	strong	slow	+18.4	9.1	100+	100+	0.09	0.07	2.6	No exudation
[illegible] PHR	Sl.mod.	strong	slow	+25.0	[illegible]	100+	100+	0.07	0.06	1.7	No exudation
[illegible] DOP	Slight	strong	slow	-19.3	12.4	[illegible]	[illegible]	0.04	0.11	12.2	Very [illegible]

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EVALUATION OF SECONDARIES

	Milling Results					Hardness		Water Sensitivity		Kerosene Extraction & Plas. Loss	
	Fuming	Odor	Fusion	Flex. Temp. T°f	Volatility % Plas. Lost	Before Vol.	After Vol.	% Sol. Matter Lost	% Absorption		
[illegible] DOP	slight	strong	slow	-25.7	16.8	93	96	0.02	0.16	14.5	Very sl. exud.
[illegible]	heavy	strong	mod.	+3.0	Incompatible - exuded overnight						
[illegible]	heavy	strong	slow	+10.2	12.0	99	100+	0.26	0.40	2.1	Heavy exud.
[illegible]	heavy	strong	mod.	-34.2	31.2	82	91	1.13	0.07	7.1	[illegible]
[illegible] DOP	heavy	strong	rapid	-37.6	27.3	77	83	0.65	0.09	48.2	Very [illegible]
[illegible]	mod.	strong	slow	-4.2	24.0	96	99	0.92	-0.32	6.5	Mod. exudation
[illegible]	mod.	strong	slow	+4.3	15.0	98	100+	0.26	-0.01	1.7	Slight exud.
[illegible]	mod.	strong	rapid	-29.3	31.0	78	86	0.13	0.07	44.3	Very [illegible]
[illegible]	mod.	strong	rapid	-32.7	23.7	75	93	0.14	0.09	31.8	No exudation
[illegible]	nil	v.sl.	Incompatible - exuded after molding								
[illegible] PHR	nil	v.sl.	Incompatible - exuded after molding								
Cheraflex [illegible] DOP	v.sl.	sl.	mod.	-28.2	3.2	92	98	0.07	0.02	24.7	Heavy exudation
Cloranil [illegible] DOP	sl.	sl.	rapid	-33.6	3.6	98	97	0.04	0.11	28.1	Mod. exudation
Cloranil [illegible]	v.sl.	sl.	Incompatible - exuded after molding								
[illegible] PHR	v.sl.	sl.	Incompatible - exuded after molding								

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EVALUATION OF SECONDARIES

	Milling Results					Hardness		Water Sensitivity		Kerosene Extraction % Plas. Lost	Ext. Compatibility
	Fuming	Odor	Fusion	Flex Temp. T_f	Volatility % Plas. Lost	Before Vol.	After Vol.	% Sol. Matter Lost	% Absorption		
Chlorafin 40 – 1:1 DOP	sl.	sl.	mod.	-35.2	4.0	83	78	0.06	0.03	53.9	Heavy exudation
Chlorafin 40 – 1:2 DOP	sl.	sl.	rapid	-37.2	4.2	79	73	0.01	0.06	43.2	Mod. exudation
Chlorafin 42 – 40%	nil	v.sl.	Incompatible - exuded after molding								
Chlorafin 42 – 50 PHR	nil	v. sl.	Incompatible - exuded after molding								
Chlorafin 42 – 1:1 DOP	v.sl.	sl.	mod.	-28.9	2.8	82	81	0.03	0.14	21.5	Heavy exudation
Chlorafin 42 – 1:2 DOP	sl.	sl.	mod.	-34.0	3.9	79	74	0.01	0.13	31.0	Mod. exudation
Chlorafin 42 – 40%	v.sl.	sl.	slow	Incompatible - exuded after milling							
Chlorafin 42 – 50 PHR	v.sl.	sl.	slow	+ 0.2	1.0	100+	100+	0.14	0.06	1.5	Mod. exudation
Chlorowax 40 – 1:1 DOP	sl.	sl.	mod.	-24.4	3.1	81	82	0.00	0.19	21.5	Heavy exudation
Chlorowax 40 – 1:2 DOP	sl.	sl.	rapid	-30.3	3.7	80	75	0.01	0.17	23.8	Heavy exudation
Chlorowax 40 – 40%	nil	sl.	slow	Incompatible - exuded after milling							
Chlorowax 40 – 50 PHR	nil	sl.	slow	Incompatible - exuded overnight							
Chlorowax 70 – 1:1 DOP	sl.	sl.	mod.	-27.5	3.3	83	83	0.02	0.15	31.1	V. heavy exud.
Chlorowax 70 – 1:2 DOP	sl.	sl.	rapid	-31.2	3.7	80	78	0.05	0.19	31.3	Heavy exudation
Chlorowax 70 – 40%	nil	sl.	slow	+25+	-6.3	100+	100+	0.00	0.03	7.4	No exudation

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EVALUATION OF SECONDARIES

	Milling Results					Hardness		Water Sensitivity		Kerosene Extraction % Plast. Lost	Comments
	Color	Odor	Fusion	Flex Temp.	Volatility % Plas. Lost	Before Vol.	After Vol.	% Sol. Matter Lost	% Absorption		
[illegible] PHR	nil	sl.	slow	+25	-7.9	100+	100+	0.00	0.13	7.5	No exudation
[illegible] DOP	nil	sl.	slow	+ 2.8	-10.2	96	97	0.00	0.13	22.7	Slight exudation
[illegible] DOP	sl.	sl.	mod.	-13.2	-10.6	89	88	0.02	0.15	30.5	Very slight exudation
[illegible]	nil	sl.	mod.	Incompatible - exuded after milling							
[illegible] PHR	nil	sl.	slow	Incompatible - exuded after milling							
[illegible] DOP	v.sl.	sl.	mod.	-34.6	4.2	78	81	0.02	0.06	52.2	Mod. exudation
[illegible] DOP	sl.	sl.	rapid	-37.1	4.9	75	78	0.01	0.08	53.0	Slight exudation

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TABLE I - PART II

EVALUATION OF SECONDARIES

Plasticizer	Milling Results			Flex Temp. T°f	Volatility Plas. Lost	Hardness		Water Sensitivity		Kerosene Extraction % Plas. Lost	Compatibility Loop Test
	Fuming	Odor	Fusion			Before Vol.	After Vol.	% Sol. Matter Lost	% Absorption		
Paraplex RG-40%		Incompatible - no sheet on the Roll Mill									
Paraplex RG-50 PHR		Incompatible - no sheet on the Roll Mill									
Paraplex RG-1-1 DOP	mod.	sl.	slow	-24.4	[illegible]	[illegible]	[illegible]	0.45	0.0[illegible]	55.7	Slight exudation
Paraplex RG-1-1:2 DOP	sl.	sl.	rapid	-2[illegible].7	[illegible]	[illegible]	[illegible]	[illegible].30	0.0[illegible]	57.[illegible]	Slight exudation
Cabol 100 - 40%	heavy	strong	mod.	+14.[illegible]	[illegible]6.0	100+	100+	0.06	0.0[illegible]	[illegible].0	Very sl. exud[illegible]
Cabol 100 - 50 PHR	mod.	mod.	mod.	+25+	[illegible]5.6	100+	100+	0.05	0.0[illegible]	1.5	Very sl. exud[illegible]
Cabol 100 - 1:1 DOP	mod.	mod.	rapid	- [illegible].[illegible]	16.[illegible]	[illegible]1	[illegible]0	0.17	0.04	10.[illegible]	Very sl. exudation
Cabol 100 - 1:2 DOP	mod.	sl.	rapid	-24.4	14.[illegible]	[illegible]5	[illegible]1	0.11	0.06	16.7	Very sl. exudation
Solvaloid C-40%	heavy	strong	rapid	- 3.4	30.[illegible]	[illegible]3	100+	0.43	0.10	3.2	No exudation
Solvaloid C-50 PHR	heavy	strong	rapid	+11.1	22.[illegible]	96	100+	0.10	0.10	3.0	No exudation
Solvaloid C-1:1 DOP	heavy	strong	rapid	-20.9	3[illegible].1	75	[illegible]2	0.31	0.14	5.6	No exudation
Solvaloid C-1:2 DOP	heavy	strong	rapid	-27.2	17.4	75	94	0.24	0.15	19.3	No exudation
Solvaloid K-40%	Incompatible - no sheet on the Roll Mill										
Solvaloid K-50 PHR	Incompatible - no sheet on the Roll Mill										
Solvaloid K-1:1 DOP	Incompatible - no sheet on the Roll Mill										

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EVALUATION OF SECONDARIES

	Milling Results					Hardness		Water Sensitivity		Kerosene Extraction % Plas. Lost	Comments Loss (CO)
	Fuming	Odor	Fusion	Flash Temp. °F	Volatility % Plas. Lost	Before Vol.	After Vol.	% Sol. Matter Lost	% Absorption		
[illegible] DOP	mod.	sl.	slow		Incompatible - exuded after milling						
Durrex 20 - 40%	mod.	strong	slow	+23.0	5.2	100+	100	-0.02	0.11	-8.3	No exudation
Durrex 20 - 50 PHR	mod.	strong	slow	+25+	2.2	100+	100+	-0.01	0.11	0.22	No exudation
Durrex 20 - [illegible] DOP	mod.	strong	slow	-13.0	6.2	85	94	0.01	0.15	19.8	Slight exudation
Durrex 20 - [illegible] DOP	mod.	strong	mod.	-24.2	7.0	78	80	0.02	0.15	25.4	Slight exudation
Durrex 25 - 40%	heavy	strong	slow	+28.4	9.0	97	100+	0.20	0.11	1.7	No exudation
Durrex 25 - 50 PHR	heavy	strong	slow	+25+	4.9	100+	100+	0.09	0.09	0.81	No exudation
Durrex 25 - [illegible] DOP	heavy	strong	slow	-20.9	14.5	79	92	0.15	0.14	22.9	Slight exudation
Durrex 25 - [illegible] DOP	heavy	strong	mod.	-25.6	12.3	77	87	0.11	0.15	26.6	Slight exudation

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TABLE II

Plasticizers		Soapy Water Extraction	Flame Out Time	Electrical Dry Slab Test	Compatibility Loop Test
Aroclor 1232	1:3 DOP 1:5 DOP	4.6%	31 sec.	No essential differences.	No exudation
Aroclor 1242	1:3 DOP 1:5 DOP	4.0	41		No exudation
Aroclor 1248	1:3 DOP 1:5 DOP	3.7	34		No exudation
Aroclor 1254	1:3 DOP 1:5 DOP	3.5	48		No exudation
Cloracin 40	1:5 DOP 1:6 DOP	1.7	60		V.Sl. Exudation No Exudation
Cloracin 40V	1:5 DOP 1:6 DOP	1.6	67		V.Sl. Exudation No Exudation
Cloracin 42	1:5 DOP 1:6 DOP	1.7	66		V.Sl. Exudation No Exudation
Cloracin 42S	1:5 DOP 1:6 DOP	2.0	40		V.Sl. Exudation No Exudation
Chlorowax 40	1:5 DOP 1:6 DOP	2.5	60		V.Sl. Exudation No Exudation
Chlorowax 70	1:5 DOP 1:6 DOP	3.5	57		V.Sl. Exudation No Exudation
Halowax 4004	1:5 DOP	1.6	97		No Exudation
Panaflex BN-1	1:5 DOP 1:6 DOP	3.6	75		V.Sl. Exudation No Exudation

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TABLE III

HEAT AND LIGHT STABILITY

General Formulation

Opalon 300	100
Plasticizer	66
(1 pt. secondary to 5 pts. DOP)	
DS-207	0.75

	Minutes to Degradation*	Hours to Degradation**
Aroclor 1232	60	300
1242	60	300
1248	60	400
1254	60	200
Clorafin 40	40	200
40V	40	200
42	40	300
42S	40	200
Chlorowax 40	40	300
70	40	300
Halowax 4004	40	50
Panaflex BN-1	20	50

*At 170°C., normal heat stability test.

**In the Weatherometer.

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APPENDIX

1. Aroclor - Chlorinated biphenyl, Monsanto
   1232 - 32% chlorinated
   1242 - 42% chlorinated
   1248 - 48% chlorinated
   1254 - 54% chlorinated

2. HB-20 - Partially hydrogenated polyethylbenzene from Texas City still drainings.

3. HB-40 - Partially hydrogenated terphenyls, Monsanto.

4. Clorafin - Chlorinated paraffins, Hercules Powder Co.
   40 - 40% chlorinated
   40V - 40% chlorinated
   42 - 42% chlorinated
   42S - 42% chlorinated, stabilized

5. Chlorowax - Chlorinated paraffins, Diamond Alkali Co.
   40 - 40% chlorinated
   70 - 70% chlorinated, a solid

6. Halowax 4004 - 40% chlorinated paraffin, Carbide & Carbon.

7. Dutrex - Aromatic hydrocarbons, Shell Chemical Co.

8. Cabol 100 - Aromatic hydrocarbon, Godfrey L. Cabot, Inc.

9. Solvaloid C & K - Aromatic hydrocarbons, Socony-Vacuum Oil Co.

10. Panaflex BN-1 - Aromatic hydrocarbon, Pan American Oil Refining Co.

Laboratory Notebooks

Pages A-96817-8 A-46842
A-46823 A-58454
A-46827 A-58455
A-46837 A-58458 in laboratory notebooks issued to R. M. Parks in 1954.

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