ORGANIC CHEMICALS DIVISION RESEARCH *Report*

St. Louis Research Report No. 2488

FINAL REPORT
ON
APPLICATION WORK ON PRESENT PLASTICIZERS-1959-PART I
****
Job No. 2-02-750.01-3793-I

March 21, 1960

Written by: N. W. Touchette

Monsanto

ST. LOUIS, MO.

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Monsanto Chemical Company
Organic Chemicals Division
St. Louis Research Department

St. Louis Research Report No. 2488

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TABLE OF CONTENTS

		Page
I.	INTRODUCTION	1
II.	SUMMARY	1
III.	CONCLUSIONS	1
IV.	RECOMMENDATIONS	3
V.	PATENT STATUS	3
VI.	REFERENCES	4
VII.	EXPERIMENTAL WORK	4
	A. Color Stability Heat Tests on DOP	4
	B. Extended Volatility Test for Patent Purposes	5
	C. Polyolefins	5
	1. Light Stability of Polyethylene Containing Antioxidants	5
	2. Flameproofing Low-Density Polyethylene	6
	3. Flameproofing High-Density Polyethylene Polypropylene	9
	D. Stifflex Curves on S-409, Monoplex S-90 and di-(2-ethylhexyl glycolyl) phthalate	9
	E. Plasticizers for Nylon	12
	F. Water Dispersion Floor Polishes	12
	1. Screening Tests	12
	2. Emulsification of Plasticizers	13
	3. Gel Test on Polyelectrolyte	13
	4. Preparation of Plasticized Polystyrene Emulsion	15
	5. Evaluation of Complete Polish Formulation	15
	6. Industry Test Program	15
	G. Non-Fogging Plasticizer for Automotive Upholstery	16
	1. Methods Employed in the Industry	16
	2. Monsanto Infrared Test	17
	3. Contamination by Glycerine	17
	4. Infra-red Test Results	18
	5. Numerical Rating of Fogging	18
	6. Oil Immersion Test Procedure	19
	7. Temperature, Plasticizer, Concentration and Time Effects Upon Fogging	22
	8. Test Results on Monsanto and Competitive Plasticizers	24
	9. Testing of Plasticizers and Resin per se	24

TABLE OF CONTENTS - Cont.

		Page
10.	Fog Value of DOP From Several Manufacturers	27
11.	Evaluation of Various Samples of S-409 from Plant Production	28
12.	Evaluation of Chrysler and Ford Specimens	29
13.	Ford's Fade-Ometer Test	30
14.	Ford Program	30
15.	Evaluation of Stabilizers and Lubricants	34
16.	Composition of Santicizer 169 (X-6060)	34
17.	ADM's Admex 747	35
18.	Study of the Ford Test	36
19.	Fogging Characteristics of Mixtures of S-169 and Admex 747	38
20.	Fogging as a Function of Resin	40
21.	Fogging Tests on Toscony Fabrics' Samples	42
22.	Fog Value on Decyl Tridecyl Phthalate	43
23.	Fogging as Related to Carbon Black, Bisphenol A, HB-40 and Volatility	44
VIII.	ACKNOWLEDGMENT	45
IX.	APPENDIX	45

DSW 622153

I. INTRODUCTION

Application work on existing plasticizers by the Plasticizer Application Group is a perennial program for maintaining and advancing Monsanto's position in the plasticizer field. Primarily, present products are tested for adaptation to new and varied applications. Secondly, new exploratory plasticizers which show promise in the screening evaluation are given a more intensive examination to determine possible marketability. Thirdly, direct comparison of Monsanto plasticizers with specific competitive products help determine a plan of action to meet this competition. Finally, the testing of samples for quality control as well as process modification research insures that Monsanto's position in the plasticizer industry is advanced.

Another segment of research on the specialized area of acrylic resin plasticizer in this general area of application work on present plasticizers will be reported as Part II on this job number.

II. SUMMARY

This report covers a variety of problems concerning the intensive evaluation of Monsanto's plasticizers, both commercial and potential commercial samples in present and projected uses.

Color stability upon heating of variously treated DOP samples was completed. The Patent Department requested extended volatility tests on several TEA prepared esters. Several projects on polyolefins including light stability studies and flameproofing of polyethylene and polypropylene were completed. Stifflex curves on several plasticizers were run.

An attempt was made to study plasticizers for nylon. The use of Monsanto plasticizers in polystyrene-based water dispersion floor polishes was investigated. The problem of non-fogging plasticizers for the automotive trade was studied.

III. CONCLUSIONS

The following conclusions were drawn from the details of the experimental work reported here.

1. Thermally esterified DOP has greatly improved color stability after high temperature heating and is nearly equivalent to competitive material.

2. Di(tridecyl glycolyl) phthalate prepared by the TEA process was found to have low volatility upon extended testing.

3. Polyethylene containing Santonox R as an antioxidant was found to discolor upon exposure to UV light. Continued exposure causes the yellow color to discharge. Several other antioxidants, Santowhite Powder Refined and di-t-butyl-p-cresol, offered antioxidant protection without the problem of yellowing upon UV light exposure.

Low-density polyethylene was successfully flameproofed using combinations of Aroclor 5460 and antimony oxide. The Aroclor 5460 offered an advantage over Chlorowax 70 in this application through better retention of physical properties of the flameproofed composition.

Aroclor 5460 and antimony oxide could not be used to flameproof high-density polyethylene (Marlex 58) or polypropylene (Profax). Chlorowax 70 was not successful with Marlex 50, however, a self-extinguishing formulation was obtained with Profax.

4. The slope of the stifflex curves for S-409, Monoplex S-90 and di(2-ethylhexyl glycolyl) phthalate are very similar in nature.

5. Based upon preliminary work, it appears that the only feasible way to plasticize nylon is by the extrusion technique in which the predried resin pellets are wet with the plasticizer prior to feeding to the extruder.

6. Santicizer 117 (methyl diphenyl phosphate) and dimethyl phthalate were found to be plasticizers for polystyrene-based water dispersion in laboratory tests. However, when presented to the industry both plasticizers were rejected due to poor leveling characteristics of S-117 and poor removability of dimethyl phthalate. Development Department contacts indicated that the formulation used here gave satisfactory performance but the industry has changed to other formulations which are more difficult to level.

7. Santicizer 169 has passed the Ford Fogging Test in a number of colors. Failure resulted when the samples were black and heavy, shades of green and blue.

In these applications, Admex 747, selling at 46 cents a pound, might be useful.

The fogging characteristics of a vinyl composition is not only related to the plasticizer system but also to the resin type, stabilizer and lubricant used in the formulation. The resin,stabilizer and lubricant system become increasingly important when used with a low-fogging plasticizer.

The Monsanto oil immersion test developed in our laboratory to give accurate and reproducible temperature control can be used to test the various components per se which make up the total formulation. The resin because of the high concentration is very critical; Opalon resins are fair with regard to fogging. Other resins vary; for instance, Geon 103EP is extremely good while Geon 121 fogs heavily. Based strictly on low fogging characteristics, the following formulation appears best: Geon 103EP or Marvinol VR-50, Santicizer 169 or Admex 747, Mark WS and Calcium Stearate.

The fogging characteristics of S-409 have improved from a fog value of about 20 to about 12. However, these are still higher than Paraplex G-54 at 6.

IV. RECOMMENDATIONS

It is highly recommended that this type of supporting application work on our present plasticizers be continued and that new and novel uses for Monsanto's present plasticizers continue to be explored.

In specific areas it is recommended that further work be done on the problem of plasticizers for polystyrene floor polishes. This work should not be restricted to attempts to improve the position of S-117 and di-methyl phthalate but the area of new compounds should also be investigated. In particular compounds of high water sensitivity should be prepared and evaluated.

It is recommended that close liaison be maintained with the Sales Department in the use of S-169 in the automotive trade.

V. PATENT STATUS

One disclosure (No. 2172) on S-117 in floor polish was filed from the Plasticizer Application Group as the result of the work reported here.

VI. REFERENCES

The Final Report on Job No. 2-02-750.01-3591-II, "Application Work on Present Plasticizers" by N. W. Touchette, (SL Research Report No. 2271, December 23, 1958) contains references to all prior reports concerning application work on present plasticizers.

Previous work on the fogging problem is contained in St. Louis Research Report No. 2276 on Plasticizer Test Method Development - Part I, Job No. 2-02-750.01-3598-I, December 1, 1958 by N. W. Touchette.

It is anticipated that one additional part of this report will be issued on the work done in plasticizing acrylic lacquers which is a specialized area of research.

VII. EXPERIMENTAL WORK

A. Color Stability Heat Tests on DOP

A series of specially prepared and/or treated DOP samples were tested for color development during per se heating at 205°C. for 2 hours. The results in Table I show that thermally esterified DOP is equivalent to Carbide's DOP and nearly equivalent to Eastman's product and to distilled and rewashed DOP (the only other means in the past to upgrade the color stability).

TABLE I

Color Stability of DOP During Oven Exposure
(110 ml of DOP exposed in air circulating oven at 205°C. for two hours)

	APHA Color Values
Eastman's DOP	15
Carbide and Carbon's DOP	50
Monsanto's standard DOP	350
DOP, Laboratory prepared, H_2SO_4 catalyzed	475-500
DOP, Laboratory prepared, TSA catalyzed	250
DOP, Esterified with Microcel C	125
DOP, Thermally esterified	45
DOP, ozone treated	550-575
DOP, Distilled and rewashed	35-40

B. Extended Volatility Test for Patent Purposes

The Patent Department requested additional tests on the volatility of several monomeric esters prepared by the TEA process and identified as follows: di(tridecyl glycolyl) phthalate (SL-16588), hexyl phthalyl hexyl glycolate (SL-16591), butyl 4-/bis(2-ethylhexoxy)phosphinyl/butyl phthalate (SL-16592), and tridecyl phthalyl tridecyl glycolate (SL-16595).

The results shown in Table 2 indicate the tridecyl derivative to be low in volatility.

Table 2

Extended Volatility Test

	% Plasticizer Loss		
	1 Day	2 Days	6 Days
SL-16588	1.8	2.3	3.2
SL-16591	2.8	4.6	10.0
SL-16592	1.9	3.1	6.1
SL-16595	1.1	1.5	2.1

C. Polyolefins

1. Light Stability of Polyethylene Containing Antioxidants

U. S. Industrial Chemicals reported poor light stability of polyethylene (PE) containing Santonox R. The problem was thought to be caused by high processing temperatures and laboratory work was undertaken to duplicate and explain the problem.

Petrothene 205, supplied by USI, was roll milled at two levels of concentration with three antioxidants; Santonox R, Santowhite Powder Refined and DBPC. A portion of each sample was exposed in an air circulating oven at 250° for 10 minutes. These conditions caused significant yellowing of the control PE.

The heat treated specimens as well as unheated controls were exposed in the Fadeometer, Weatherometer and window.

The light stability test in the Fadeometer was stopped after 500 hours and the Weatherometer after 600 hours. Results in each unit were comparable.

The color generated in the heat cycle in the control PE was almost completely discharged in the first 50 hours of exposure. Thereafter, very little change took place. In the samples containing 0.02% Santonox R, the color formed during heating was not as strong and appears to be completely discharged again in 50 hours of light exposure. However, with 0.1% Santonox R, the first 50 hours of exposure caused a yellowing in both the control and heated PE. This yellowing diminished with further exposure and had completely gone by 500 hours.

Santowhite Powder Refined and DBPC were similar in their action in that the color developed upon heat treatment was less than the control and some bleaching action took place upon light exposure.

Window exposure did not show significant differences between any of the samples.

The above results confirm the fact that Santonox R treated PE is light sensitive regardless of previous heat history and that continued exposure to UV light bleaches this color.

The use of either Santowhite Powder Refined or di-t-butyl-p-cresol (DBPC) gave protection during heat treatment without the problem of darkening upon light exposure.

2. Flameproofing Low-Density Polyethylene

The evaluation of Aroclor 5460 as a flameproofing agent for low-density Polyethylene (DYNH) and comparison with Chlorowax 70 in this application was completed. The results indicated that at low concentrations (20%) the Chlorowax is a better flameproofing agent. However, the tensile strength is significantly reduced. At a higher concentration (30%), the flameproofness characteristics of the two are similar but the tensile reduction of Chlorowax-modified material is very evident. The addition of antimony oxide does not alter the above results. The heat stability of the Chlorowax-modified samples was found to be very poor.

The values of Melt Index, tensile properties and flameproof tests are given in Table 3.

The Melt Index and % Memory values were determined using Condition E of ASTM 1238-57T except that in all cases 9 grams of material was charged into the cylinder. For low melt index materials, about half the charge was extruded by hand pressure after 3 minutes.

The changes in Melt Index values with increasing amounts of additive are to be expected. The % Memory values do not show large changes except for the low value for 50 DYNH, 30 Aroclor 5460 and 20 antimony oxide. This particular mix was quite fluid as evidenced by the Melt Index and thus the % Memory probably does not mean too much.

Tensile properties were determined on minature specimens with the Instron with a jaw speed of 10 inches a minute. The yield strength shows little relationship to the amount or kind of additive. Elongation and tensile decrease with increasing amounts of additive with the Chlorowax causing the greatest changes.

The burning tests were conducted according to the procedure given in St. Louis Research Report No. 1727. In this test, strips of polyethylene, 1" x 4" with lines scribed 1/2" from each end, are hung in an asbestos cylinder 2-1/2" diameter x 5" length. A bunsen flame, 1" high, is used to ignite the specimen. When the flame reaches the first scribed mark, the bunsen flame is removed and the stopwatch started. The time to flame-out or burning to the second scribe mark is measured. From the charred area when the sample is self-extinguishing a burning rate in square inches a minute can be calculated. As shown in the table, all specimens except two containing Aroclor 5460 were self-extinguishing, however, the addition of the Aroclor did decrease the burning rate by half. The fact that a particular sample is self-extinguishing does not mean that the specimen is unaffected during the test. In some cases severe distortion plus melting took place.

Heat stability tests run in an air circulating oven at 190°C. show the Aroclor-modified polyethylene samples to have better heat stability than the Chlorowax samples. Earlier evidence of the poorer stability of the Chlorowax was noted in the molding operation where the Chlorowax samples darkened appreciably.

Since this work was completed we have been informed that an article has appeared concerning the use of Chlorowax 70 in PE. The addition of 3.3% butyl rubber to the flameproofed compositions supposedly overcomes the losses of elongation and tensile properties. This lead has not been explored in our laboratories.

The ultimate utility of the Aroclor-Modified PE is questionable since the composition really does not resemble PE in physical properties. It is possible that other compositions could equally fill the requirements intended for modified PE.

DSW 622160

TABLE 3

PROPERTIES OF LOW-DENSITY POLYETHYLENE (DYNH) MODIFIED WITH AROCLOR 5460 AND CHLOROWAX 70

	Melt Index[1]	% Memory	Tensile Properties[2] % Elong	Tensile Properties[2] Tensile	Tensile Properties[2] Yield	Burning Tests Rate (in^2/min.)	Burning Tests Drips Flame	Burning Tests Self Extinguishing
Control (DYNH)	1.96	57.2	655	2130	1395	7.1	Yes	No
80 DYNH 20 Aroclor 5460	5.86	59.0	690	2020	1320	3.0	Yes	No
80 DYNH 20 Chlorowax 70	5.9	61.5	585	1640	1450	-[3]	Yes	Yes
70 DYNH 30 Aroclor 5460	11.2	51.5	647	1850	1320	-[3]	Yes	Yes
70 DYNH 30 Chlorowax 70	10.5	67.2	130	1175	1195	-[3]	Yes	Yes
80 DYNH 10 Aroclor 5460 10 Antimony Oxide	3.8	57.2	650	1895	1300	4.0	Yes	No
80 DYNH 10 Chlorowax 70 10 Antimony Oxide	3.6	59.0	655	1905	1445	-[3]	Yes	Yes
50 DYNH 30 Aroclor 5460 20 Antimony Oxide	19.1	18.2	270	1185	1570	-[3]	Yes	Yes
50 DYNH 30 Chlorowax 70 20 Antimony Oxide	13.0	63.9	Too Brittle for Test Under These Conditions			-[3]	Drips, no flame	Yes

1 Procedure "A" (190°C./2160 grams)
2 Jaw separation - 1/2", speed 10 inches a minute
3 Did not support flame after removal of burner.

DSW 622161

3. Flameproofing High-Density Polyethylene Polypropylene

The addition of Aroclors to both polypropylene (Profax) and linear polyethylene (Marlex 50) did not cause a significant reduction in the burning rate as had been previously experienced with low-density polyethylene.

Samples were prepared using Aroclor 5460 at 20, 30 and 40% plus several combinations of Aroclor 5460 and antimony oxide. When tested for flameproofness using the asbestos chimney test, the Profax-Aroclor 5460-antimony oxide (50/30/20) combination showed a 40% reduction in burning rate but the sample still dripped flame. Low density polyethylene in this formulation was self-extinguishing. When Chlorowax 70 was substituted for Aroclor 5460, the resulting formulation was self-extinguishing. Furthermore, substitution of Aroclor 1268 gave similar results to the Aroclor 5460.

The results in Marlex 50 were much the same except that not even Chlorowax 70 produced a self-extinguishing formulation. The reduction in burning rate was less than 10%.

Due to the poor showing with regard to flameproofing exhibited by the Aroclors, no attempt was made to obtain physical properties of the various formulations. However, it is estimated that the properties were greatly reduced.

D. Stifflex Curves on S-409, Monoplex S-90 and di-(2-ethylhexyl glycolyl) phthalate

Stifflex curves were determined on S-409, Monoplex S-90 and di-2-ethylhexyl glycolyl phthalate at a concentration of 100 phr in Opalon 300 using the Tinius Olsen Flex Tester. The procedure (ASTM D1043-51) used nominal 65 mil specimen which were cooled below -60°C. for the initial reading. The angle of deflection was obtained at five degree intervals after conditioning the specimen for three minutes. The torque was changed to maintain a deflection angle between 20 and 200 degrees of arc. From the torque and deflection angle, the modulus of rigidity was calculated and plotted on semi-log paper vs. temperature to give the range from -60 to +15°C. as shown in Figure 1. The curves for the three plasticizers are very similar in slope and displaced only about 5-7°C.

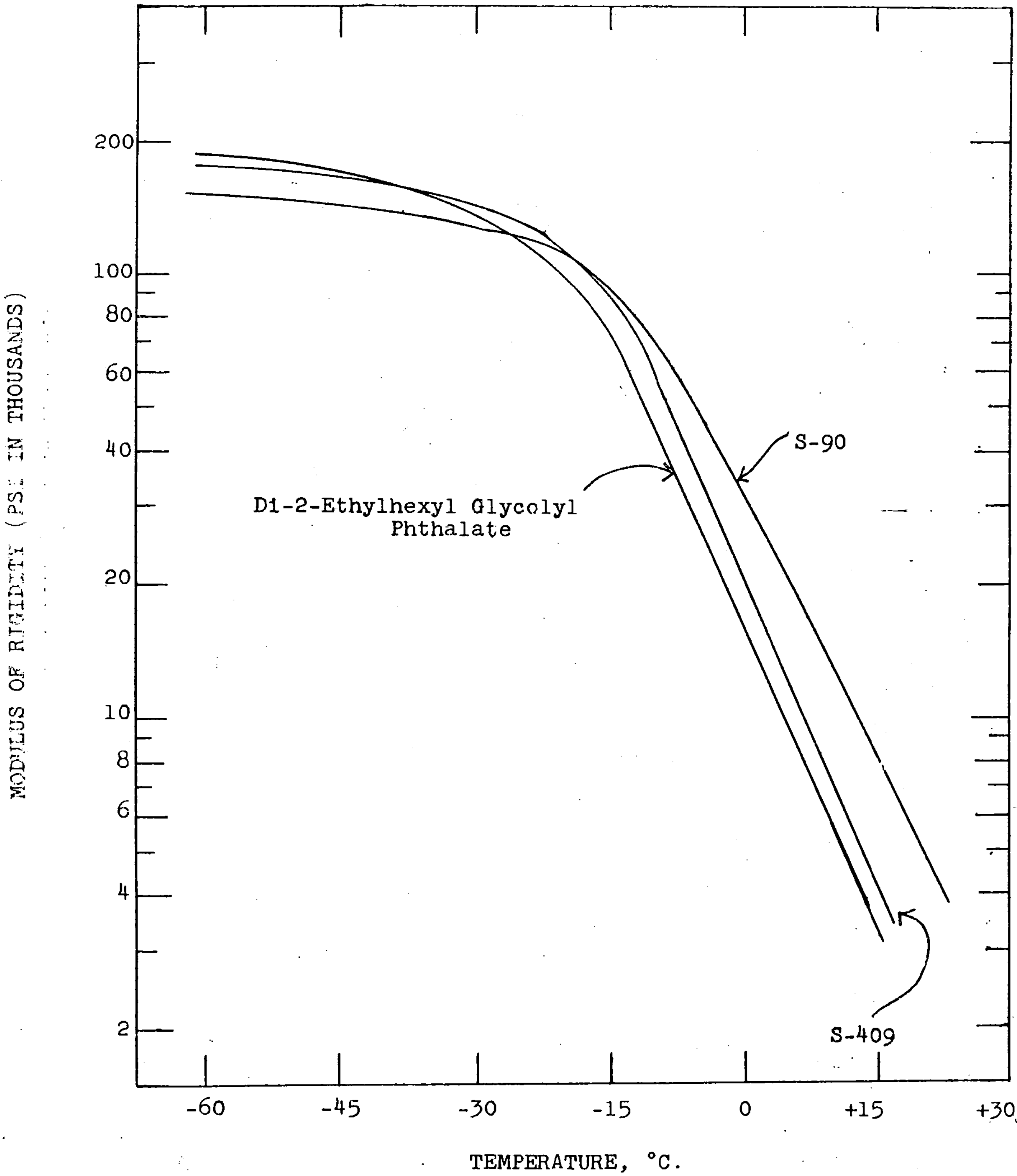


Figure 1. Stiffness versus temperature of poly (vinyl chloride) plasticized with 100 phr S-409, Monoplex S-90 & di-2-ethylhexyl glycolyl phthalate.

E. Plasticizers for Nylon

The technology of nylon resins has advanced to the stage where previous evaluations of Monsanto plasticizers in nylon can no longer be applied to the present resin, type 6/6. A program was undertaken to reevaluate various plasticizers in duPont's Zytel 101.

Attempts to use the steam heated roll mill were unsuccessful due to insufficient temperature to soften the resin pellets. Addition of plasticizer to the pellets caused additional problems due to increased lubricity.

The use of the oil heated roll mill at 500°F. resulted in sheet formation but discoloration took place quickly probably due to oxidation. Plasticizer addition had no effect upon the discoloration. Micro-techniques of hot plate milling developed by Dr. Sears also resulted in extreme discoloration.

One test run was made at Dayton using their 1" vent extruder on Zytel 101 plus 2% Santicizer 8. In this test the pellets were wet with the plasticizer prior to extrusion. No difficulty was encountered in feeding during the run. However, the stock bubbled excessively at both the vent and the die such that a suitable product could not be obtained. The bubbling was believed a result of high moisture content of the resin since nylon is fairly hydroscopic and the resin had not been predried. Time did not permit another run to be made.

It is expected that extrusion is the proper way to handle nylon resin. It also appears that mixing in the extruder in either one or two passes would be satisfactory.

TABLE 4

Evaluation of Plasticizers in Floor Polishes
(Plasticized U-2003 - 31.7; Polyethylene emulsion - 11.7; Durez 15546 Solution 7.0)

Plasticizer	Leveling	Glass
S-151	Poor	--
DIDA	Poor	--
S-160	Good	Good
Methyl benzyl phthalate	Good	Good
Butyl cellosolve dicresyl phosphate	Good	Good

F. Water Dispersion Floor Polishes

DSW 622164

1. Screening Tests

Previous work in this area (St. Louis Research Report No. 1933) had indicated that S-160 and S-141 could perform satisfactorily in the field of water dispersed floor polishes based on polystyrene latex. However, reports from the trade indicated that these plasticizers used singly or in combination reduced the gloss of the floor polish. This one property loss could not be tolerated by the industry.

Work was continued evaluating various plasticizers in a two-step program. The first was a test for compatibility with the polystyrene resin by mixing 6 parts of plasticizer and 100 parts cold resin, diluting with 200 parts water and allowing to stand 24 hours. The plasticizers which formed two layers and thus were incompatible after this time period were Santolite MS, S-8, M-17, and M-17/Santolite MHP (1.7/1).

The plasticized resin was then compounded with a leveling agent and wax emulsion for tests of the finished formulation for gloss and leveling. Table 4 records the results on additional plasticizers in total floor polish formulations.

2. Emulsification of Plasticizers

The apparent limited compatibility of S-M-17 and S-8 could have possibly resulted from incomplete mixing during addition to the polystyrene dispersion. It was thought this problem could be overcome by pre-emulsification of the plasticizer prior to the mixing operation.

Limited work was done on attempts to emulsify using oleic acid-morpholine systems. All samples prepared separated into two distinct layers after standing overnight but could be redispersed by shaking. No further work was performed in this area.

3. Gel Test on Polyelectrolyte

Based on Springfield's recommendation, a gel test was run using the plasticizer and polyelectrolyte which is added to the polystyrene latex. This suggestion was based on their belief that the plasticization of the polyelectrolyte was more critical than plasticization of the polystyrene.

A test similar to the polystyrene gel test was run in which 5 grams of the polyelectrolyte (DX-873-styrene maleic anhydride copolymer half butylated) are mixed at room temperature with 10 grams of plasticizer. Observations on the resulting mixture are made after 24 hours. It was found that three conditions prevailed at this time: clear gel, cloudy gel and two layers. The clear gel indicated a swelling type plasticizer and one which would be compatible. Cloudy gel indicated limited swelling and compatibility while two layer formation was the result of non-swelling and gross incompatibility. It was determined that the plasticizers which formed clear gels were worthy of further consideration as floor polish plasticizers. The results of evaluation of various plasticizers by the gel test are given in Table 5.

TABLE 5

Plasticizer Evaluation for Floor Polishes by the Gel Test on the Polyelectrolyte

Swelling Type (Clear Gel)

Methyl Diphenyl Phosphate
Dimethyl Phenyl Phosphate
Ethyl Diphenyl Phosphate
KP-140
P-600
Methox
Dimethyl Phthalate
Tributyl Phosphate
Diethylene Glycol
Dibutyl Phenyl Phosphate
DEG /S-8 (1:1)

Swelling (Cloudy)

Triacetin
Butyl Cellosolve Diphenyl Phosphate (S-143)
Benzyl Cresyl Phthalate
S-8
S-141/KP-140 (1:1)
S-131-A-15
Diethyl (1-Hydroxypropyl) Phosphonate Diphenyl Phosphite
Butyl Diphenyl Phosphate
DEG/S-141 (1:1)
Methyl Benzyl Phthalate
DEG/Methyl Benzyl Phthalate

Non-Swelling (Two Layer)

DEP, DBP
S-160, S-141
S-151, M-17, B-16
TOF, S-140, S-191, DIDA
Aroclor, 1221, 1232, HB-40
CC-55, TPP, S-409
Di(2EH glycolyl) Phthalate

It will be noted that a number of plasticizers which formed clear gels are those recommended in the trade literature as plasticizers for floor polishes. This fact enhances the reliability of the test. Several potential plasticizers were indicated: dimethyl phthalate, methyl and ethyl diphenyl phosphate and dimethyl and dibutyl phenyl phosphate.

The gel test was extended for use with other components of the floor polish. The polystyrene emulsion (U-2003) was carefully air dried to duplicate actual use conditions and ground by hand into a fine light yellow crystalline powder. A few crystals of the ground U-2003 were added to various plasticizers on watch glasses. After standing 24 hours noticeable degrees of change had taken place as shown in Table 6. None of these plasticizers appear to be exceptional plasticizers for the polystyrene.

The compatibility with the wax was determined in the same manner as the gel test (1 gram wax to 10 grams plasticizer) except the containers were heated to melt the wax. The results shown in Table 7 indicate a decided advantage in favor of KP-140 as a plasticizer for the wax.

TABLE 6

Compatibility of Various Plasticizers
with Dried Polystyrene Emulsion (U-2003)

Plasticizer	Resin Appearance After 24 Hours
KP-140	Slightly swollen, white
DIDA	No change
MDPP	Clear, with some lumps
DMP	Clear, with some lumps
DBP	Clear, with some lumps
S-160	Partially clear
S-141	Overall cloudy
S-143	Overall cloudy

TABLE 7

Compatibility with Wax (Bareco Petunaula D)
(Heated and Stirred Together and Allowed To Cool)

KP-140	Homogeneous, soft mixture
DMP	Two layers
MDPP	Two layers
S-160	Homogeneous, hard mixtures (became grainy upon stirring)
S-143	Grainy Mixture

KP-140 and MDPP were both tested by the gel test with polystyrene (Luster 601 Powder) and the leveling agent (Shanco L-1090). Both plasticizers reacted similarly and produced either a clear gel with polystyrene or a clear solution with Shanco L-1090.

4. Preparation of Plasticized Polystyrene Emulsion

A series of plasticizers were incorporated in U-2003 at the 6 point level as previously described. The plasticizer systems evaluated were: KP-140, MDPP, KP-140/S-160 (1/1), MDPP/S-160 (1/1), KP-140/DBP (1/1), MDPP/DBP (1/1), S-151 and DMP.

After standing overnight, the above solutions were compounded with the leveling agent (RSS-0149L) and coated onto black rubber floor tile. After drying very little difference could be noted except that dimethyl phthalate gave better gloss. The difference between KP-140, MDPP and S-151 which was noted in the gel test could not be detected here.

5. Evaluation of Complete Polish Formulation

The plasticized U-2003 containing KP-140, MDPP and DMP was compounded into a complete polish formulation as follows:

Plasticized U-2003	-	31.7
Polyethylene emulsion (MCT-0804-2)	-	11.7
Durez 15546 Solution (RS-C3C-1A)	-	7.0

These were evaluated on black rubber floor tile and oven stability. The properties on floor tile appear comparable except for dimethyl phthalate which gave noticeably better gloss and depth. In oven stability tests, DMP gelled in three weeks while KP-140 and MDPP were satisfactory for two months at which time the test was stopped.

6. Industry Test Program

Both DMP and MDPP (now called S-117) were sent to selected customers for evaluation. Reports from Johnson, Simoniz,Franklin Research and UBS all stated that S-117 was comparable to KP-140 in all properties except leveling. This property as we have stated before is extremely critical with the wax people. Our contact groups reviewed the formulation we used with Simoniz and were told it was satisfactory.

Following receipt of these results, additional samples of polish were prepared as given in Section 5 using S-117 and KP-140. These were evaluated on black rubber tile, green asphalt tile, tan vinyl asbestos tile and yellow flexible vinyl tile. Neither formulation would level on the flexible tile. However, on the remaining tile, both polishes looked comparable.

In an effort to determine the reason our results did not correlate with other laboratory samples of the above polishes and the formulations were sent to UBS Chemical for their evaluation. They replied that in the two polishes submitted, leveling and other properties were comparable. However, UBS stated that almost any plasticizer would perform satisfactorily in this formulation and they suggested several formulations for use in evaluating plasticizers. No further work has been done to check out this latest information from UBS. Since the reports from all customers who evaluated S-117 are much the same, we feel certain the cause of the trouble has been explained.

G. Non-Fogging Plasticizer for Automotive Upholstery

During the summer of 1958, the vinyl coated fabric industry received complaints from their customers in the automotive trade that vinyl coatings in the cars were causing "fogging". This fog appears as a condensation or haziness upon the windshields after cars are exposed in a closed condition to the hot summer sun. The condensate has been described as sticky, tacky and difficult to remove.

The automotive companies were quick to conclude that vinyl coatings in upholstery and crash pads were at fault. One of the major reasons for this belief was the simultaneous appearance of the fogging problem and a large increase in the use of vinyl coating for automotive interiors. However, the coaters were not fully convinced that the vinyl coatings were the trouble-makers.

Another serious drawback to the investigation of the problem resulted from the random appearance of the fog. As far as could be discovered there was no pattern to the fogging nor could the fogging be connected with any particular auto type or region of the country.

1. Methods Employed in the Industry

Various methods were reported from the trade as duplicating the heating conditions to cause fogging. The method receiving widest apparent usage was the Chrysler test. Beakers containing the black vinyl specimens are placed on a turntable rotating at 2-3 rpm and covered with plate glass. Infra-red heat lamps are positioned above the beakers to give a temperature of 190° F. as measured by a thermocouple embedded in the vinyl sample.

After 16 hours the plate glass is removed and examined for fogging.

This basic method was modified by use of flasks or petri dishes in place of beakers but no change of major importance was noted.

2. Monsanto Infrared Test

The initial laboratory test here used 1-liter Erlenmeyer flasks placed on a Rotosho turntable which was covered with black cardboard. The speed of the turntable was 2-3 revolutions a minute. Watchglass covers were used. The vinyl samples containing carbon black were 3-inch disks cut from 40-mil press polished sheets. A thermocouple was embedded in one sample and connected to a potentiometer for temperature measurement. The flasks were rotated under two 375-watt infra-red lamps for 16 hours maintaining a sample temperature of 190-195°F. The amount of fogging on the watchglass cover was evaluated visually.

In the early experiments all vinyl specimens were plasticized to equal Shore "A" hardness. To facilitate sample preparation a master batch of the dry ingredients was mixed in the following proportions:

Opalon 300	- 100 parts
Dyphos	- 3 parts
DS-207	- 0.6 parts
Kosmos BB	- 1.5 parts

The individual plasticizers and masterbatch were hand mixed, fluxed on the two-roll mill and press polished.

3. Contamination by Glycerine

The first results obtained by the above method did not distinguish between various plasticizers. That is, all plasticizers gave equal and heavy fogging. By replacing the flasks with tall Berzelius beakers and using 4-1/2" squares of plate glass, the fog was condensed on the glass. The fog was removed from the glass plate by scraping with a razor blade, for subsequent I.R. analysis. The fog from various plasticizers and resins was analyzed and in each case the fog was found to be predominately glycerine.

The plasticizers per se and the individual dry ingredients were tested but no source for the glycerine contamination was found.

Since the glycerine only appeared from compounded samples, the method of sample preparation was examined. From this study it was concluded that glycerine was being introduced into the samples from the cellophane which is normally used in the molding operation to prevent sticking of the sample to the molds. Cellophane when subjected to the fogging test produced heavy fogging. Samples of various plasticizers molded without cellophane gave vastly different results from previous samples.

4. Infra-red Test Results

The following visual results were obtained on new samples molded without cellophane:

Degree of Fogging

None	Slight	Moderate	Heavy
Harflex 300	DIDP	Adipol ODY	DOP
Plastolein 3049-S	S-409		S-160
Monoplex S-90	G-54		S-141
Di-2-ethylhexyl glycolyl phthalate	TCP		DIDP/S-160 (2/1)
	DIDP/S-90 (1/1)		S-140
	TCP/S-90 (1/1)		
	G-62		
	DIDP-E		

In addition two samples of coated fabric obtained from Textileather were tested. A white sample gave slight fogging while a black sample gave heavy fogging. The apparent better performance of the white sample may have resulted from the heat reflective properties of the pigment and consequently lower temperature rather than an improved plasticizer system.

5. Numerical Rating of Fogging

The Photovolt Photoelectric Meter with reflectance attachment was used in an attempt to measure the fogging. However, no difference could be detected between a heavily and a slightly fogged surface. The 60° gloss attachment did show a difference in specular reflection of samples which visually appeared to be fogged to different degrees. The following procedure was established. The 60° gloss attachment was adjusted to read 100 with a clean plate glass backed by the black carrara glass. The specular reflection of the plate glass cover is taken before and after the fogging test. The difference between the two readings is the "Fog Value". It will be seen that a plate which reads 100 before and after the test has a Fog Value (FV) of 0 indicating no fogging.

The following table shows the comparison between the visual and Photovolt rating of fogging to indicate the correlation.

Plasticizer	Fogging Visual	Fogging Fog Value
DOP	Heavy	36
DIDP	Slight	4
S-90	None	0

The infra-red procedure was used to obtain fog values on various Monsanto and competitive plasticizers as shown in Table 8.

An experiment was designed to determine the precision of the test method. The experiment consisted of testing two plasticizers, DOP and DIDP, in duplicate in each of four runs. The detailed analysis is included as Appendix I and will be summarized here.

The overall precision, that is, variation resulting from between and within experiments, can be represented by a standard deviation (for a single determination) of 6.32 units of specular reflection while the 95% confidence limits for a single test is ± 12.64. Within a single experiment the precision is represented by a standard deviation of 3.71 and 95% confidence limits of ± 7.42.

From the detailed analysis it was noted that 65% of the total variation was due to differences between experiments. The major cause of this variation was thought to be lack of temperature control and reproducibility due to use of the heat lamps. The position of the lamps had to be changed from experiment to experiment to achieve the same temperature in the samples.

6. Oil Immersion Test Procedure

In an attempt to improve temperature control, a series of samples in beakers covered with plate glass were placed in an air circulating oven at a 90°C. for 16 hours. There was no change in specular reflection for the samples which were DOP, DCP, DNODP, and DIDP. As a result it was concluded that the temperature differential achieved by only heating the sample while the plate was at room temperature was essential to cause deposition of the fog.

TABLE 8

Fog Value of Monsanto and Competitive Plasticizers (Formulated to a Shore "A" of 80-82)

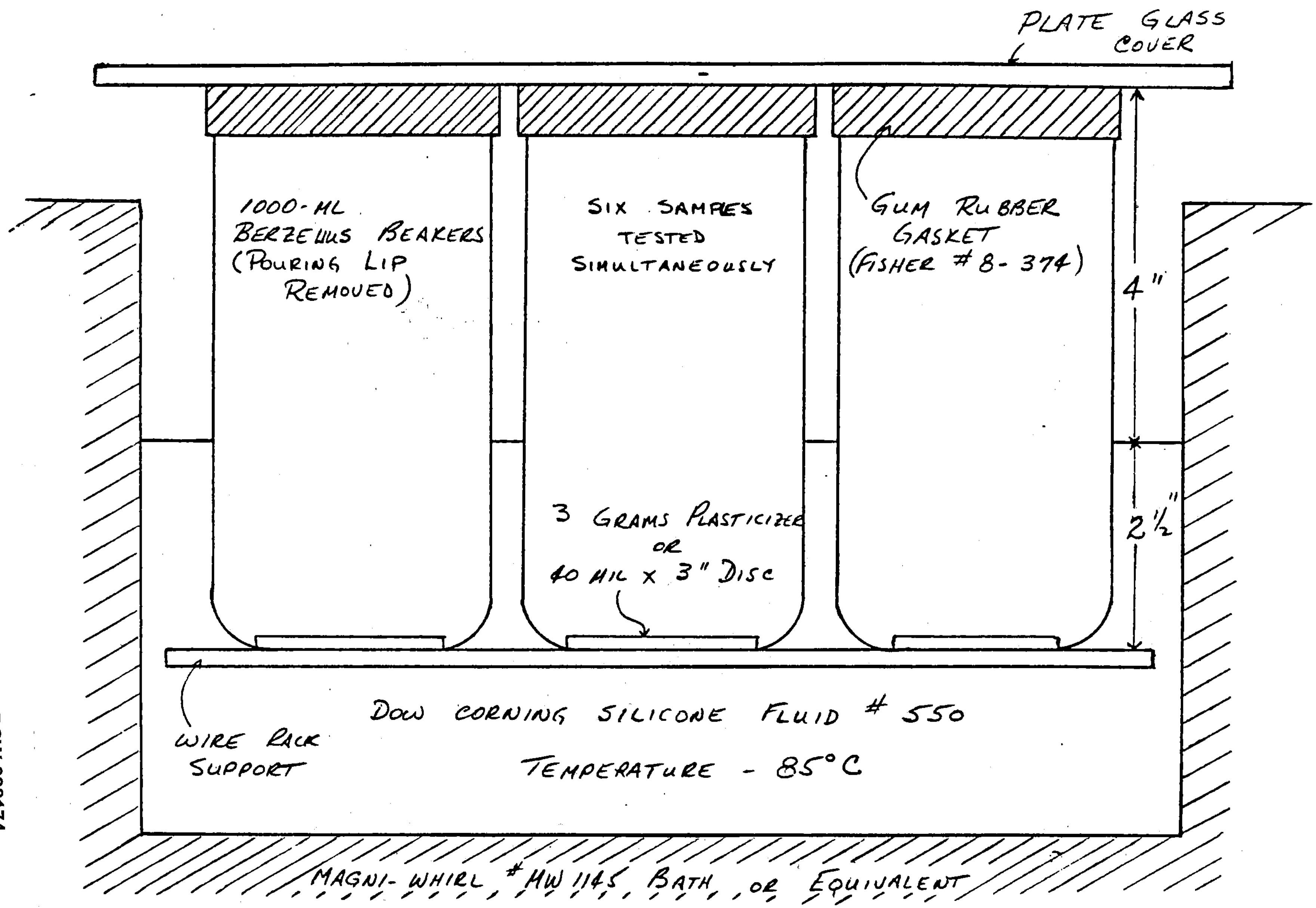
Plasticizer	FV	Plasticizer	FV
Bis (2-ethylglycolyl) phthalate	1	Paraplex G-62	1
S-405	1	Monoplex S-90	0
S-407	1	Monoplex S-90 (Opalon 410)	0
S-403	1	Paraplex G-54	6
S-409 (BPA before filtering)	3	Emery 3049-S	6
DIDP	6[1]	Eastman NP-10	13
DIDP-E	6[2]	Flexol 810	14
S-409	10	Hercoflex 150	15
TCP	10	Harflex 300	26
DNODP	16	Dicapryl phthalate	34[2]
S-636 (DIDP-E/DOP 1/1)	25	Flexol 380	46
DOP	36[1]	Textileather Coated Fabric	
S-606 (DIDP/S-160 2/1)	43	White	13
S-141	44	Black	80
S-613 (DIDP/S-160 1/2)	47		
Ford Special No. 2	46		
S-602	48		
S-160	59		

1. Average of 12 determinations

2 Average of 4 determinations

Therefore, a Magni Whirl Utility Oil Bath (Model MW-1145) was fitted with a rack and supports to hold six beakers. A liquid level (Dow Corning 550 fluid) was maintained so that the beakers were immersed 2-1/2 inches in the liquid. A cross-sectional drawing of the test apparatus is shown in Figure 2.

Several runs were completed and a bath temperature of 93°C. was established as giving comparable temperatures to the test using the heat lamps. In addition, since the carbon black was no longer needed to adsorb heat, it was removed from the formulation.



NOT TO SCALE

FIG. 2. CROSS SECTIONAL VIEW OF BEAKER ARRANGEMENT FOR THE MONSANTO FOGGING TEST

NWT 8/59

DSW 622174

A statistical experiment similar to the one previously described was performed using the oil bath at 93°C. with 2-1/2 inch immersion of the beakers. The plasticizers, DOP and DIDP, were tested in triplicate in each of four runs. The detailed analysis, given in Appendix II, show that the between experiment standard deviation was 3.1 and 95% confidence limits ±6.48. The within experiment standard deviation was 2.75 while the 95% confidence limits were ± 5.84. It will be noted that the between experiment variation was reduced by a factor of two through the use of the new method. In addition the within experiment precision shows a vast improvement.

7. Temperature, Plasticizer Concentration, and Time Effects Upon Fogging

a. Effects of Temperature Upon Fogging

The temperature of the oil bath was varied to determine the effect of this variable upon fogging using DIDP, DOP, S-409, G-54 and G-50 as the plasticizers. The results shown in Table 9 indicate a fogging dependence upon the test temperature. The DOP data appears to change rapidly in the range of 75-90°C. and may be leveling off at each end. DIDP levels off at 75-80°C. The polymerics are approaching a FV of 0 at 70°C. This work indicates the temperature to be very critical and as a result a test temperature for the oil immersion method was established at 85°C. At this temperature the values for the various plasticizers correlate well with results obtained by the infra-red heating methods.

TABLE 9

Temperature Dependence of Fogging

Temp., °C.	Fog Value DOP	Fog Value DIDP
93	65[1]	24[1]
88	56, 54, 55	17, 12, 14
82	38, 35, 38	6, 4, 6
76	31, 33, 25	6, 4, 3
71	20, 22, 22	4, 2, 2

Temp., °C.	S-409	G-50	G-54
93	36, 35	25, 32	29, 26
86	24, 17	20, 17	14, 19
81	15, 16	17, 14	5, 7
76	4, 6	1, 1	0, 5

[1] - average of 12 determination from statistical study.

DSW 622175

b. Effect of Plasticizer Concentration Upon Fogging

Polyvinyl chloride samples plasticized with three plasticizers at three levels of plasticizer concentration were evaluated for fogging in the oil bath method at 93°C. The results given in Table 10 show little difference in fog value between 40 and 50% concentrations. At low concentrations, the fog value was higher. As a result, future tests were run at 40% plasticizer concentration.

TABLE 10

Plasticizer Concentration vs. Fogging

Plasticizer	Plasticizer Concentration, %		
	25.8	40	50
	Fog Value *		
DIDP	39	26	27
Santicizer 409	47	39	36
Paraplex G-54	37	35	39

*Average of two determinations

c. Continued Testing of Same Specimens

A series of polymeric plasticizers, Santicizer 409, Paraplex G-50 and G-54, were tested three times using the same samples to determine the effect upon fogging of repeated heating. The samples were then heated in open beakers at the test temperature in an effort to drive off volatile constituents.

The results shown in Table 11 indicate very little change in the samples as a result of continued and repeated testing or preheating of the samples in open containers.

TABLE 11

Repeated Testing of Samples
(Oil Immersion at 93°C. for 16 hours)

Plasticizer System	Specular Reflection[1]			
	Test No. 1	2	3	4[2]
S-409	64	63	63	60
G-50	71	61	70	66
G-54	72	76	78	74

1- Average of two determinations.
2- Samples heated 16 hours at 93°C. in open beakers between Test No. 3 and Test No. 4.

8. Test Results on Monsanto and Competitive Plasticizers

Table 12 gives the fog values obtained on Monsanto and competitive plasticizers when tested at 40% concentration in Opalon 300 using theoil immersion procedure at 85°C. It will be noted that range of fog values from 0 to 50 representing no fogging to heavy fogging are given.

TABLE 12

Fog Values by the Oil Immersion Method
(40% Plasticizer Concentration in Opalon 300)
(Test Temperature 85°C.)

Plasticizer	Fog Value
Paraplex G-62	0
Emery 3049-S	2
Decyl tridecyl phthalate	4
Santicizer 405	4
Monoplex S-90	5
Elastex 37-R	6
S-407	6
Harflex 375	9
Harflex 300	9
DIDP	12
DIDP-E	12
Admex 761	13
Harflex 305	14
S-403	14
Paraplex G-54	16
S-409	24
DNODP	34
DOP	50

9. Testing of Plasticizers and Resin per se

Following receipt of a call report in which a customer stated that plasticizers per se would not fog by the Chrysler test, it was believed that the oil immersion methods would prove useful due to an external heat source. Samples of DOP and DIDP tested per se at 85°C gave comparable results with those obtained on plasticized PVC samples. The test was extended to cover a number of additional plasticizers and resins as shown in Tables 13 and 14.

It will be noted that the only serious crossoven is Paraplex G-54 which gave a fog value of 16 when tested in PVC while the per se fog value was 3.

TABLE 13

Fog Values of Plasticizers Per Se
(85°C. in oil immersion test)

Plasticizer	Fog Value
Paraplex G-62	0
Paraplex G-25	0
Admex 747	0
Paraplex G-40	1
Harflex 375	1
Harflex 305	1
Elastex 37-R	1
S-405	1
Monoplex S-90	2
Emery 3049-S	2
Ditridecyl phthalate	2
Paraplex G-54	3
Harflex 330	3
S-407	4
S-403	7
Paraplex G-53	10
DIDP, DIDP-E	12
Admex 770	12
Admex 761	16
Monoplex S-73	17
DOS	17
Paraplex G-50	18
Admex 746	19
TCP	20
Admex CL 748	20
DIDA	27
NP-10	36
DNODP	37
Plastolein 9058 (DOZ)	47
DNODA	52
DOP	56
DCP	57
Isohexyl benzyl phthalate (TEA)	58
DOA	59
Harflex 300-X	62
Isohexyl benzyl phthalate (carbonate)	68
Benzoflex 9-88M	72
S-141	73
S-160	78

DSW 622178

TABLE 14

Fog Values of Resins Per Se
(85°C. in oil bath)

Plasticizers		Fog Value
Opalon 300	(Rerun of sample 7)	18
Opalon 410	(Rerun of sample 10)	23
Opalon 505		8
Opalon 300 FM		30
Geon 101		25
Geon 203		1
Geon 121		77
Geon 103 EP		0
Marvinol VR-50		0
Pliovic VO		61
Pliovic AO		0
Vygen 105		4
Escambia PVC Pearls		26
Exon 654		79

A series of plasticizers and resins were tested per se by the oil immersion method at a bath temperature of 100°C. and the results are given in Table 15.

The conclusion reached upon examination of the data show that testing at 100°C. tends to resolve and separate those plasticizers which were grouped in the fog value range of 0-5 by testing at 85°C.

TABLE 15

Fog Value of Plasticizers and Resins
Per Se at 100°C.

Plasticizers	Fog Value
G-62	0
Ditridecyl Phthalate	25
G-50	60
DOP	69
DIDP-E	43
S-403	32
S-405	12
S-407	16
S-409	35
Plaskon 37- R	9
3049 S	1
Harflex 375	1
G-54	34
S-90	11
Opalon 330 FM	53
Geon 103-EP	11

DSW 622179

Since in the test on the plasticizer per se no allowance is made for losses of plasticizer due to milling and other processing, several polymeric plasticizers were heated for various times at 195°C. in open dishes in an effort to reduce the fog value. As shown in Table 16, some reduction in fog value is evident but the change is so low in magnitude that processing conditions would have little or no effect upon fog value. This work does not help explain the vast difference encountered in G-54 when tested in a compound versus per se testing.

TABLE 16

Effect of Preheating on Fog Values

Plasticizers	Precondition, hrs. at 195°C.			
	0	1/2	1	2
	Fog Values			
S-409	21	16	13	10
Paraplex G-54	5	9	10	7
S-409 + 10% G-62	-	16	16	10

10. Fog Value of DOP From Several Manufacturers

The oil immersion method was used to test DOP from various manufacturers for fogging characteristics. The results of two runs on the same samples are given in Table 17, which shows no appreciable difference among the suppliers.

TABLE 17

Fog Value of DOP from Several Manufacturers
(Per se measurements at 85°C. by oil immersion)

Manufacturer	Fog Value 1st Test	2nd Test
Carbide	63	62
Eastman	62	63
Goodrich	58	54
Monsanto	61	60

11. Evaluation of Various Samples of S-409 from Plant Production

A testing program was undertaken in an effort to help the plant reduce the fog value of S-409 by correlating fogging with a controllable property. The relationship of viscosity and fogging was determined as shown in Table 18. There appears to be no direct relationship of viscosity and fogging.

The evaluation of S-409 containing 0.2% charcoal at various stages of the finishing operation is shown in Table 19. In this case the steaming operation reduces the fog value a slight amount while addition of Bisphenol A had no further effect.

The results on several composite lots of S-409 are given in Table 20 along with a representative value for Paraplex G-54. It should be noted that S-409 appears to be improving slightly but still does not approach the low fogging of G-54.

TABLE 18

Comparison of Fog Value with Viscosity of S-409 (Plant Produced)

S-409	Viscosity (centistokes)	Fog Value (Per se at 85°C.)
Batch 64	175	13
Batch 65	164	9
Batch 67	144	8
Batch 76	125	21, 20, 19
Batch 77	121	10, 14
Batch 79	129	14, 15

TABLE 19

Fog Values of S-409 at Various Stages of Production

	Fog Value (Per se at 85°C.)			
S-409 Batch No.	Before Steaming	After Steaming	After BPA Addition	Filtered
87	13, 13	9, 10	9, 9	-
95	12	10	11	-
98	14	8, 14[1]	9	10
98 (lab filtered)	9	8	14	-

[1] - Double steaming time

DSW 622181

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TABLE 20

Fogging Results on Tank Cars of S-409

Lot No.	Fog Values (Per se test at 85°C.)
C-9	15
C-11	11
C-12	18, 21
C-15	10, 10, 10, 6
C-16	13, 14, 17, 18, 19
C-73 (W-Bldg.)	9, 10, 14
G-54	5, 6

12. Evaluation of Chrysler and Ford Specimens

The Development Department obtained several samples of fogging and non-fogging films from both Ford and Chrysler. These were tested by the oil immersion method at 85°C. for two consecutive runs with results as shown in Table 21.

It will be noted that excellent spread is obtained on the Ford samples while on the Chrysler sample the difference between fogging and non-fogging is not so great.

TABLE 21

Evaluation of Chrysler and Ford Specimens

	Fog Value at 85°C.	
	1st Run	2nd Run
Chrysler, Thermocouple Standard	19	13
Chrysler, non-fogging	62	36
Chrysler, fogging	72	72
Ford, non-fogging	34	28
Ford, fogging	70	41
Ford, fogging	71	59

13. Fords Fade-Ometer Test

Ford Motor Company developed a test method for determination of fogging using the Fade-Ometer as the source of ultra violet light and heat.

The samples are placed in glass dishes with the coated side down and held in place with a wire gauze rack. The dish is sealed with a clean glass plate and the assembly is supported on a Fade-Ometer holder. The unit is placed in the Fade-Ometer, coated fabric side toward the light source for 20 hours at a black panel temperature of 145°F. (maximum 150°F.).

The fog on the glass plate is measured with a Weston Foot Candle, taking four readings of light transmittance on each plate and reporting the average.

The minimum light transmission for an acceptable sample is 75.

14. Ford Program

A cooperative program was started with Ford to prepare samples here for testing by their Fade-Ometer test for possible acceptance by Ford. Acceptance by Ford of a plasticizer system would be of great benefit in attempting to sell Ford's suppliers.

a. Laboratory Prepared Samples

A series of nine formulations were milled and molded for fogging studies. These included Ford's standard plus others which would duplicate the standard in performance as shown in Table 22. It is interesting to note that the fog values of the various formulations also given in Table 22 can be related almost directly to the per se fog values of the plasticizers. Also that the fog value from plasticized PVC using a mixed plasticizer system is slightly more than the per se value of the highest fogging plasticizer. The differences obtained on per se measurements of the resins can be further shown in compounded sheets.

TABLE 22

Ford Formulations for Fogging

	Std.	2	3	4	5	6	7	8	9
Geon 103 EP	100	100	100	100	100	100	100	100	--
Opalon 300	-	-	-	-	-	-	-	-	100
Dicapryl phthalate	36.7	-	-	-	-	-	-	-	-
DIDP-E	-	40	40	40	40	40	40	40	40
Admex 746	7.8	7.8	7.8	7.8	-	-	-	-	-
Paraplex G-62	-	-	-	-	6	6	6	6	6
DOZ	12.5	12.5	-	-	-	-	14	-	-
DNODA	-	-	12.5	-	14	-	-	-	-
DIDA	-	-	-	12.5	-	14	-	-	-
DOS	-	-	-	-	-	-	-	14	14
Duranite	25	25	25	25	25	25	25	25	25
Mark M	3	3	3	3	3	3	3	3	3
Mark PL	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Stearic Acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Fog Value	72	58	66	35	64	31	40	27	34

b. Samples Prepared by Springfield for Fogging Analysis

Six samples of calendered film were prepared by Springfield for submission to Ford for testing by their test for possible acceptance. The plasticizer systems were a comparison of the Ford standard plasticizer system of dicapryl phthalate and dioctyl azelate with DIDP-E plus other flexibalizing plasticizers as shown in Table 23.

The test results by the oil immersion and Fade-Ometer test conducted here plus the results obtained by Ford using their Fade-Ometer test are also given in Table 23. The results by the oil immersion show more fogging than anticipated. Monsanto's results by the Fade-Ometer are very erratic while Ford's results agree somewhat with the oil immersion values.

Due to the additional work done on stabilizers and lubricants since the above formulations had been requested, it was felt that Formulation F could be compounded to meet Ford's Specification of 75.

TABLE 23

Formulations and Test Results on Calendered Film Prepared by Springfield

	A	B	C	D	E	F
Opalon 330-FM	100	100	100	100	100	-
Geon 103-EP	-	-	-	-	-	100
DCP	36.7	-	-	-	-	-
DIDP-E	-	40	40	40	40	40
Monoplex S-73	7.8	7.8	-	-	-	-
Paraplex G-62	-	-	6	6	6	6
DOZ(azelate)	12.5	12.5	-	-	-	-
DNODA	-	-	14	-	-	-
DIDA	-	-	-	16	-	16
DOS (sebacate)	-	-	-	-	14	-
Atomite	25	25	25	25	25	25
Mark M	3	3	3	3	3	3
Mark PL	0.25	0.25	0.25	0.25	0.25	0.25
Stearic Acid	0.50	0.50	0.50	0.50	0.50	0.50
Carbon Black	1.0	1.0	1.0	1.0	1.0	1.0
Monsanto Fog Value [1]	60	51	64	41	38	36
Monsanto Result using Ford TM[1]	57	67	70	71	64	68
Ford Results[2]	54	50	50	52	62	70

1- Fog Value where 0 indicates no fogging.
2- Transmission where 100 indicates no fogging.

c. Additional Films Prepared by Springfield

Four additional calendered film formulations were suggested to Springfield incorporating the low-fogging stabilizer and lubricant systems. Springfield added three other formulations giving a total of seven as outlined in Table 24. These seven films were tested by the oil immersion method at 85°C. with the results shown in Table 24 as was predicted. Five of these films were submitted to Ford for evaluation by their Fade-Ometer method. Ford's results were very discouraging since they would hardly distinguish between the fogging and non-fogging plasticizer systems. Actually sample No. 3 in this series was almost identical with a previous sample which had been rated at 70. The major difference was the change in stabilizer system.

DSW 622185

Ford was informed of this discrepancy and agreed to rerun sample No. 3. This was done with the following results: 54, 56, 56 and 59.

Thus, it appeared that S-169 would not be approved by Ford. However, during isolated runs in the past the tremendous difference between white and black samples or pigmented and clear samples when tested with heat lamps or the Fade-Ometer had been noted. It was hoped that possibly this difference could also be detected with various colors and, thus, avoid a flat rejection of S-169 by Ford (see Section 18).

The physical properties of several films were obtained to compare the performance of the DIDP-E/DIDA mixture with Ford's standard. The relationship was excellent.

A portion of each film sample submitted to Ford was returned and the fog value redetermined by the oil immersion method. The results were in close agreement with those previously obtained.

TABLE 24

Formulations and Test Results on Springfield Film

	1	2	3	4	5	6	7
Opalon 330-FM	-	100		100	100	100	100
Geon 103-EP	100	-	100	-	-	-	-
DCP	36.7	36.7	-	-	-	-	-
DIDP-E	-	-	40	40	40	45	23
Monoplex S-73	7.8	7.8	-	-	-	-	-
Paraplex G-62	-	-	6	6	5	-	-
DOZ (Azelate)	12.5	12.5	-	-	-	-	-
DIDA	-	-	16	16	16	16	16
Santicizer 409	-	-	-	-	-	-	22
Atomite	25	25	25	25	25	25	25
Mark WS	2	2	2	2	-	-	-
Dyphos	-	-	-	-	4	4	4
Calcium Stearate	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Kosmos BB(carbon black)	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Oil Immersion Fog Value	65	63	15	24	18	18	24
Ford Results	50	50	64	68	-	-	72
Ford Results	42	52	58	54	-	-	64
Ford Results	42	55	52	70	-	-	70
T_f	-43.4	-48.3	-41.3	-41.2			
Shore Hardness	75	73	80	80			
Loop Compatibility	OK	OK	OK	OK			

15. Evaluation of Stabilizers and Lubricants

The stabilizers and lubricants used in the standard Ford test plus others were tested for fogging as indicated in Table 25. It appears that proper choice of stabilizer and lubricant can produce low fogging systems. To check this in a complete formulation, Mark WS and Mark XI each were substituted in formulation No. 6, Table 22 with calcium stearate as a lubricant. The fog value was reduced from 31 to 21 with WS and 20 with XI. These results indicate the tremendous influence that small amounts of high fogging ingredients have upon the fogging characteristics of a finished formulation.

TABLE 25

Fog Value of Stabilizers and Lubricants
(Tested in Oil Immersion at 85°C. for 16 Hours)

DIDP-E	3	3	3	3	3	3	3
Mark M	0.2	0.2	-	-	-	-	-
Mark PL	4 drops	-	-	-	-	-	-
Stearic Acid	0.1	0.1	0.1	-	-	-	-
Calcium Stearate (Harshaw's 5-V-1)	-	-	-	0.1	-	-	-
Mark WS	-	-	-	-	-	0.1	-
Mark Xl	-	-	-	-	-	-	0.1
Fog Value	63	43*	23	14	12	17	14

*Fog condensed as large clear droplets. This condition although representing heavy fogging gives low readings.

16. Composition of Santicizer 169 (X-6060)

During a visit to Ford, they were informed of an experimental product, X-6060,which would pass the fogging requirements and still give satisfactory performance at a reasonable price. It was known that X-6060 would contain 40 parts DIDP-E and 16 parts DIDA.

In order to confuse any possible analysis it was felt that a small percentage of S-409 would be advantageous. Therefore, three mixtures were prepared containing the above proportions of DIDP-E and DIDA with 0, 5 and 10% S-409.

DSW 622187

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X-6060 was stored in the freezing compartment of a refrigerator for two weeks without visual change with regard to cloudiness or further haze formation.

TABLE 26

Fog Values of X-6060

	Fog Value per se at 85°C.
X-6060	20
X-6060 + 5% S-409	17-1/2
X-6060 + 10% S-409	24-1/2

17. ADM's Admex 747

Ford tested and approved Admex 747 as a non-fogging plasticizer for automotive uses. The fog value of Admex 747 is 0 and its only drawback is cost (46 cents a pound). As it later developed the cost factor was sufficient to prevent its wholesale adoption in automotive fabrics.

Based on Ford's approval, Admex 747 was investigated thoroughly by the oil immersion test alone and combined with various other plasticizers and lubricants. The results are given in Table 27.

The performance of Admex 747 is excellent in fogging. However, at 40% concentration, the material is incompatible in the loop test.

TABLE 27

Fog Values of Admex 747 and Combinations Containing Admex 747

	Fog Value (Oil Immersion, 85°C., 16 hrs.)
Admex 747	0
Admex 747/S-169 (1/1)	16
Admex 747/DIDP-E (1/1)	10
Admex 747/DIDA (1/1)	24
Admex 747/Mark WS[1]	3
Admex 747/Mark Pl[1]	70
Admex 747/Calcium stearate[1]	0
Admex 747/Mark M[1]	46
Admex 747/Stearic Acid[1]	18

[1]- 1/4 gram additive to 3 grams Admex 747.

DSW 622188

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18. Study of the Ford Test

a. Temperature Effect

The Ford Fade-Ometer Test was studied in an attempt to explain the lack of correlation between the two laboratories.

Sample dishes of the same dimensions as the Ford dishes were obtained. However, standard Fade-Ometer holders were used in place of the Ford holders. In addition, readings of the fog were taken on the Photovolt meter.

Due to the type of measurement used by Ford where high transmission indicates low fogging, our results by the Ford test were reported as specular reflection to have results in the same order of magnitude.

A previous study at a black panel temperature of 135°F. had indicated rather good correlation with the oil immersion method as shown in Table 28.

Tests conducted on three of the Springfield film samples at the low temperature gave fair agreement with the oil immersion test and showed a difference between high and low fogging samples. These results are given in Table 29.

As the black panel temperature was increased to the range of 140-145°F. as recommended by Ford, difficulty was encountered in reading the panels. It appeared that a gradation occurred in the fog from the top to bottom of the panel. This could not be eliminated and, thus, four readings of the fog value were obtained on each panel and the results averaged for the final value.

The temperature of the specimen was also obtained by means of a thermocouple embedded in a black specimen. It was found that the specimen temperature was related to the black panel temperature as follows:

Black Panel Temperature	Specimen Termperature
140-150°F.	182°F.
135-140	175
120-125	165

Another problem encountered was temperature variation and range from Fade-Ometer to Fade-Ometer. No method was discovered to effectively control this condition and the solution was the use of one Fade-Ometer for the study.

TABLE 28

Correlation between Oil Immersion and Fade-Ometer Results

Sample	Temp, °F.	Fog Value Fade-Ometer	Fog Value Oil Immersion
WS Formulation	135	16	21
Xl Formulation	135	15	20
40% DOP	"	61	50
40% DIDP	"	12	12
Ford F	"	33	38

TABLE 29

Fade-Ometer Tests on Springfield Film

Film No.	Fog Value (Fad-Ometer at 135°F. for 20 hours)
2	74,75
3	39,41
4	34,44

Six of the Springfield films were tested by the Fade-Ometer method with results shown in Table 30. In this case the reported values are specular reflection so that the comparison with Ford's results is simpler. The results show some agreement with Ford's but the variation on each plate is high.

TABLE 30

Fade-Ometer Results on Springfield Film

Film No.	Ford's Results[1]	Fade-Ometer Specular Reflection[2]
1	42,42,50=45	24,27,26,24 = 25
2	50,52,55=52	24,23,24,25 = 24
3	64,58,52=58	61,48,57,76 = 61
4	68,54,70=64	57,49,59,66 = 58
5	-	66,46,63,67 = 60
6	-	69,68,65,77 = 70

1Result of three tests.
2Four readings from one plate from one test.

b. Specimen Color Effect

Upon several occasions the vast difference in fogging between white and black samples when tested in the Fade-Ometer has been noted. If this difference can also be noted between various colors, S-169 could still conceivably find a market.

A series of S-169 plasticized compositions in various colors (Table 31) were prepared and when tested by the Fade-Ometer test most of the colors seemed to pass the Ford Specification.

Samples were submitted to Ford and the white, blue, red and yellow passed their specification by a good margin in all cases except yellow (Table 31).

The effect of color was tested upon two series of compounds in white, yellow and blue with two plasticizer systems; the Ford standard and S-169. The results shown in Table 32 indicate with the Ford standard plasticizer system that the fogging is still great and apparently not influenced by the color of the sample while with S-169 these colors show little fogging, except for the phthalacyanine green and blue. It appears that these pigments act much like carbon black in their adsorption and heat build-up. The phthalacyanine green pigmented sample showed no difference in fogging when the pigment concentration was reduced to one-fourth the original concentration. Under these same conditions, the blue showed some improvement but the fogging was still heavier than the ultramarine blue.

The sample temperature inside the cell was determined by placing a thermocouple between two specimens and taking a reading after equilibrium had been reached. The differences between the various colored specimens was not as great as expected but the correlation with fogging characteristics appears to be good as indicated in Table 33.

19. Fogging Characteristics of Mixtures of S-169 and Admex 747

In an effort to determine if small amounts of Admex 747 added to S-169 would produce formulations which would meet the Ford test, a series with varying mixtures were tested by both test methods. The formulations and results given in Table 34, indicate little improvement in fogging is noted when a black specimen is tested in the Fade-Ometer until most of the S-169 is replaced. In the oil immersion method, the fogging decreases gradually as the concentration of Admex 747 is increased.

TABLE 31

Effect of Color Upon Fogging

Geon 101	18	18	18	18	18	18
S-169	12	12	12	12	12	12
Mark WS	0.3	0.3	0.3	0.3	0.3	0.3
Calcium Stearate (5-V-1)	0.1	0.1	0.1	0.1	0.1	0.1
Atomite	5	5	5	5	5	5
Bon Dark Red (RL-586-D)	-	1/16	-	-	-	-
Chrome Yellow (Y-433-D)	-	-	1/8	-	-	-
Ultra Marine Blue	-	-	-	1/16	-	-
Phthalocyanine Green	-	-	-	-	1/16	-
Carbon Black	-	-	-	-	-	0.3
Monsanto Fade-Ometer Test	92	88	90	95	72	54
Ford Fade-Ometer Test	91	92	82-5	96	-	-

TABLE 32

Effect of Color on Fogging of Two Different Plasticizer Systems

		Specular Reflection	
Color	Plasticizer System	Fade-Ometer	Oil Immersion
White	DCP and S-73	50	36
White	S-169	93	80
Ultra Marine Blue	DCP and S-73	45	40
Ultra Marine Blue	S-169	90	80
Yellow	DCP and S-73	42	38
Yellow	S-169	92	75
Phthalacyanine Green	DCP and S-73	45	36
Phthalacyanine Green	S-169	69	80
Phthalacyanine Blue	DCP and S-73	31	35
Phthalacyanine Blue	S-169	74	77

DSW 622192

TABLE 33

Specimen Temperature of Various Colored Specimens in Fade-Ometer
(Black Panel Temperature 145°F.)

Color	Concentration,%	Specimen Temp.,°F.
White	0.1	170
Yellow	0.1	170
Ultra Marine Blue	0.05	175
Phthalacyanine Green	0.05	180
Phthalacyanine Green	0.01	178
Phthalacyanine Blue	0.05	178
Phthalacyanine Blue	0.01	175
Black	0.05	185

TABLE 34

Study of Mixtures of Admex 747 and S-169
(55 phr plasticizer in Geon 103 EP)

	Specular Reflection			
	Fade-Ometer		Oil Immersion	
% Admex 747 in S-169	White	Black	White	Black
0	94	74	87	89
18	96	67	85	86
36	96	71	86	88
54	95	68	91	89
73	97	74	93	91
100	97	92	99	98

20. Fogging as a Function of Resin

A series of compositions in both white and black containing different resins were evaluated in the Fade-Ometer test. The formulations as shown in Table 35 was run with Geon 101 , Opalon 300 and Geon 103 EP. These resins were tested since they represented a range of fog values when tested per se.

It was found (Table 35) in black that the fogging characteristics of the plasticized composition can be related to the per se fog value of the resins. In white formulations this is not so evident although in this case the fogging of all samples was low.

In another experiment, three plastisol grade resins: Opalon 410, Geon 121 and Marvinol VR-50, were formulated with S-169 and Admex 747 at two concentrations to determine if the resin fogging characteristics influenced the fogging of the plasticized composition. The formulation contained plasticizer at 65 or 100 phr: G-62, 5 phr; Mark WS, 1.5 phr; and Atomite, 25 phr.

TABLE 35

Fogging Characteristics Based on Resin Type

(56 phr Admex 747, 6 phr G-62, 2 phr Mark WS, 0.2 phr calcium stearate, 25 phr Atomite)

Resin Type	Specular Reflection Fade-Ometer White	Black
Geon 101	97	87
Geon 103 EP	97	94
Opalon 300	95	89

The results, shown in Table 36, give a direct correlation between per se resin fogging characteristics and composition fogging. That is, Geon 121 is high fogging when tested both ways, Opalon 410 is next while Marvinol VR-50 fogs the least. It was also found that plasticizer concentration has little or no effect upon fogging characteristics.

TABLE 36

Effect of Plasticizer Concentration and Resin Type on Fogging

Resin	Color	Plasticizer	Specular Reflection Fadeometer PHR 65	100	Oil Bath 65	100
Opalon 410	Black	S-169	44	48	69	69
Geon 121	Black	S-169	24	24	30	24
Marvinol VR-50	Black	S-169	55	48	66	70
VR-50	Black	Admex 747	82	92	97	97
410	White	S-169	79	73	68	71
121	White	S-169	28	23	37	32

A number of per se samples of Opalon 330 FM were fogged by the oil immersion method to obtain sufficient fog to be scrapped from the plate glass and analyzed by infra-red.

The majority of the samples of scrappings was found to be a fatty acid similar to but not stearic acid. A second minor component was identified as most likely ammonium chloride.

21. Fogging Tests on Toscony Fabrics' Samples

Thirteen samples of film and coated fabric were received from Toscony Fabrics for evaluation of fogging characteristics. The samples represented components of a coated fabric such as film, cotton, sheeting, adhesive layer and top coating. The results are given in Table 37.

It is interesting to note that the difference between DOP and DIDP is washed out when the films are laminated to fabric with S-624 as the adhesive (No. 3 and No. 4). Top coating does not help this condition.

When TCP/DIDP are used in the adhesive formulation, the low fogging characteristics of DIDP again are shown. Top coating again apparently has only a slight effect upon fogging.

The only apparent cross-over appears with No. 12 and No. 13 where the two adhesive formulations are coated on cotton sheeting. Since Geon 121 is a high fogger (fog value of 77), we felt the resin could be overshadowing the plasticizer differences. Therefore, a plastisol similar to the adhesive formulations in No. 12 and No. 13 was prepared using Marvinol VR-50 (fog value of 0). The plastisols were coated on glass and fused 10 minutes at 175°C. Fog values were determined: 68 for S-624 and 16 for TCP/DIDP. Thus, we feel the resin accounts for the similar results between No. 13 and No. 13.

Samples No. 1 and No. 2 were also tested by the Ford Fade-Ometer test with very little fogging. This is due to the white color of the samples wherein insufficient heat was generated to cause fogging since DOP gave a fog value of only 20 and DIDP gave a reading of zero.

TABLE 37

Fogging Results on Toscony Fabrics Samples

Sample	Film Plasticizer	Adhesive Plasticizer	Top Coat	Fog Value
1	DOP	--	No	62
2	DIDP	--	No	25
3	DOP	S-624	No	77
4	DIDP	S-624	No	62
5	DOP	S-624	Yes	69
6	DIDP	S-624	Yes	66
7	DOP	TCP/DIDP	No	60
8	DIDP	TCP/DIDP	No	32
9	DOP	TCP/DIDP	Yes	60
10	DIDP	TCP/DIDP	Yes	27
11	Cotton Sheeting	--	-	34
12	Cotton Sheeting	S-624	No	81
13	Cotton Sheeting	TCP/DIDP	No	77

22. Fog Value on Decyl Tridecyl Phthalate

Several laboratory prepared samples of decyl tridecyl phthalate were evaluated by the oil immersion method . Each run yielded results difficult to interpret due to the presence of a crescent shaped pattern of heavy fogging. This heavily fogged area covered approximately one-quarter of the exposed glass and was generally toward the outer or cool side of the beaker, leaving the impression that a highly volatile component was condensing. A retest of the same plasticizer sample gave a fog value of 5 with a normal appearance. The test was repeated with several different samples and the same result was obtained each time.

A sample of decyl tridecyl phthalate was heated in an open container in the air circulating oven at 175°C. for 30 minutes. Following this treatment the sample was tested for fogging by the oil immersion method at 85°C. The fog value was 2.

An equal molar mixture of DIDP and ditridecyl phthalate was tested in the oil immersion test and found to have a fog value of 6. This result is surprising since generally the fog value of mixtures approached that of the most highly fogging component.

A sample of decyl tridecyl phthalate which had been sent to Springfield was returned and a portion was given additional steaming by M. W. Farrar in which a small amount of volatile material was taken off. Three samples of each material were tested with the specular reflection values of 94, 94 and 94 for the returned sample and 94, 95 and 95 for the old steamed sample. The uniform fogging and lack of a crescent shaped curve on the returned material leads us to believe it must be from a different lot than previously tested.

23. Fogging as Related to Carbon Black, Bisphenol A, HB-40 and Volatility

a. Effect of Carbon Black on Fogging

Carbon black was removed from the formulation when it was no longer needed to give good heat absorbing qualities to the plasticized sheet. The question of possible stabilizing action of the carbon black was answered by an experiment comparing white and black samples in the oil immersion method. The results tabulated in Table 38 indicate that no stabilizing action is obtained from the carbon black.

TABLE 38

Carbon Black Effect Upon Fogging

Plasticizer	Fog Value
S-409 Black	63, 67 = 65
S-409 White	68
G-54 Black	77, 76 = 76.5
G-54 White	77

b. Effect of Bisphenol A Upon Fogging

The fogging characteristics of Bisphenol A per se and slight amounts added to Admex 747 were determined in the oil immersion method. This work was necessary due to the widespread usage of BPA in vinyl compounding as an antioxidant. BPA per se fogs excessively (FV = 88). However, when 1% BPA is added to Admex 747 and tested per se the fog value is 3 and when the concentrate of BPA is reduced to 0.25%, no fog can be measured. Therefore, at the normal concentrations BPA has little or no effect upon fogging.

c. Fog Value of Combinations of DOP and HB-40

J. K. Sears found that HB-40 exerted an antioxidant effect upon DOP. Therefore DOP containing 3% HB-40 was tested in the oil immersion test to see if this effect was noticeable in fogging. The results indicated it was not since the mixture had a FV of 74 and DOP alone has a FV of 56.

d. Relationship of Fogging to Volatility

Two samples of the Springfield film (Table 23) were run in duplicate in the activated carbon test with cages for 24 hours at 87°C. The results, tabulated in Table 39, indicate small differences between the two samples. However, it was believed that experimental error would tend to overshadow this difference.

TABLE 39

Volatility Versus Fogging
(Springfield Samples, Table 23)

Sample	Fog Value	Volatility, % loss of Total Wt.
A	60	0.81,0.77 = 0.79
F	36	0.72,0.63 = 0.68

VIII. ACKNOWLEDGMENT

The excellent cooperation of the Sales and Development Departments is gratefully acknowledged. We particularly appreciate the help of D. H. Bechtold, J. Glenn Hicks and Springfield personnel on the problem of fogging. W. W. Paris is to be thanked for his statistical help.

IX. APPENDIX

Notebook Pages

SL 6866
13459-60, 65, 67-75, 77, 87-88
20169-79, 81, 96-98, 200
24372, 80, 84
25703, 5, 7, 9-10, 15-17, 26-8, 30-4, 36, 41, 44-5, 48-9
31751-2, 54-8, 63, 65, 67-8, 70, 73-8, 81-7, 91-2, 95,98-800.
39252-3,56-61, 64-70, 72-3, 75, 78, 82, 84-7, 89-94, 96,98, 300.

J. R. Darby

hhm

N. W. Touchette

APPENDIX I

Windshield Fogging Test Precision

I. Experimental Data

The following replicated 2 x 4 factorial experiment was performed to determine the precision of the windshield fogging test using black samples and infra-red heat source.

Experimental Data

Experiment	Plasticizer	Specular Reflection
1	DOP	57, 64
	DIDP	88, 86
2	DOP	49, 48
	DIDP	81, 79
3	DOP	63, 61
	DIDP	89, 92
4	DOP	52, 47
	DIDP	82, 91

II. Analysis of Data

The above experiment was analyzed by a standard analysis of variance with the following results.

ANOVA Table

Source	Sums of Squares	D.F.	Mean Square	F	E(MS)(1)
Plasticizer	3,813.0625	1	3,813.0625	277.4***	$\sigma_e^2 + 8\sigma_P^2$
Experiments	355.6875	3	118.5625	8.63**	$\sigma_e^2 + 4\sigma_E^2$
Residual	151.1875	11	13.7443		σ_e^2
Total	4,319.9375	15			

(1) = Variances which the mean squares estimate
*** Significant at the 99.9% level
** Significant at the 99.0 level

The mean squares obtained in the analysis of variance can be separated into the components of the total variance which they estimate as follows:

Thus if,

σ_e^2 = variance due to experimental error

σ_E^2 = variance due to experiments

σ_P^2 = variance due to plasticizers

DSW 622199

APPENDIX II

Windshield Fogging Test Precision

I. Experimental Data

The following experiment was performed to determine the precision of the windshield fogging test using white vinyl discs and heated in an oil bath at 93°C.

Experiment	Plasticizer	Specular Reflection
1	DOP	40, 33, 33
	DIDP	78, 73, 78
2	DOP	35, 35, 42
	DIDP	81, 74, 78
3	DOP	32, 32, 35
	DIDP	76, 73, 73
4	DOP	37, 38, 37
	DIDP	76, 77, 78

II. Analysis of Data

The above data was analyzed by a standard analysis of variance with the following results.

ANOVA Table

Source	DF	Sums of Squares	Mean Squares	F	E(MS)
Plasticizer	1	9,841.5	9,841.5	***	$\sigma_e^2 + 12\sigma_p^2$
Experiment	3	59.33333	19.77777	3.05[1]	$\sigma_e^2 + 6\sigma_r^2$
Residual	19	123.16669	6,48246		σ_e^2
Total	23	10,024.0			

*** Significant at 99.9%
[1] Significant at 90% level of significance

For One Sample in Each Experiment:

Within experiment standard deviation = $S_w = \sqrt{6.48246} = 2.54607$

Within experiment 95% confidence limits = $\pm$ 5.32

Between experiment standard deviation = $S_b^2 = 6.48246 + 2.2159 = 8.69836$

$S_b = 2.9493$

Between experiment 95% confidence limits = $\pm$ 6.13

When Duplicate Samples are run:

$S_{\bar{x}} = \frac{S}{\sqrt{n}}$

$S_w\ \bar{x} = 1.800$ 95% limits = $\pm$ 3.76

$S_b\ \bar{x} = 2.0855$ 95% limits = $\pm$ 4.36

When Triplicate Samples are Run:

$S_{w\bar{x}} = 1.470$ 95% limits = $\pm$ 3.07

$S_{b\bar{x}} = 1.703$ 95% limits = $\pm$ 3.56

DSW 622201