PDR #6

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TO: C. W. THEOBALD

FINISHES FROM FLUORINATED POLYMERS

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INTRODUCTION:

This study was initiated at the request of Research Management (Ref. -1) to help determine the best method by which the Du Pont Company could optimize its earnings from the use of fluorinated polymers in finishes. More specifically, answers were sought relative to (1) what route should be adopted for commercialization of fluoropolymer finishes, (2) which department should install commercial fluoropolymer facilities, (3) what prices are needed for the fluoropolymer finishes to earn an adequate return on a rolled-up Company basis.

Five departments are actively engaged in activities concerned directly or indirectly with the development of fluoropolymer finishes:

1. The Fabrics and Finishes Department is seeking new paint products of superior durability based in fluoropolymers.

2. The Organic Chemicals Department is trying to promote use of its fluoromonomers and is developing solvent-soluble VF_2/TFE* copolymers which may be suitable for long-life finishes.

3. The Film Department is marketing its Tedlar® polyvinyl fluoride film in direct competition with liquid finishes. Also their extensive PVF manufacturing facilities may be suitable for the production of other fluoropolymers.

4. The Electrochemicals Department is trying to develop polymeric binders based on fluoropolymers for direct sales to the paint industry.

5. The Central Research Department is synthesizing a variety of new fluoropolymers of potential use in finishes.

In addition, the Plastics Department with its basic position in tetrafluoroethylene and hexafluoropropylene is developing new outlets for its fluorocarbons by synthesizing fluorinated epoxides and ethers usable as comonomers. The Elastomers Department also has an interest in elastomeric fluoropolymers for its products.

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*See Appendix D for definition of abbreviations.

SUMMARY AND CONCLUSIONS:

Research Status:

The assignment of an estimated 38 men to fluoropolymer research projects (F&F, Orchem, Plastics, Elchem, Central Research, and Elastomers -- exclusive of work on "Tedlar" and Teflon®) is indicative of the wide interest in this area throughout the Company. At an average expenditure of $4,000 per man month, an estimated $1.8 MM per year is being spent currently to support fluoropolymer research. About two thirds of this work is of interest, directly or indirectly, to the F&F Department. The Organic Chemicals Department which is doing major scouting and process research on solvent-soluble fluoropolymers of interest to F&F had spent an estimated $1.0 MM by the end of 1963, and is currently spending at the rate of $55,000 per month.

The F&F Department has four men assigned to fluoropolymer research, including the writer, and one man on loan to the Organic Chemicals Department. Work is proceeding in areas of polymer synthesis, polymer evaluation, the development of formable fluoropolymer finishes, and this venture analysis. It is estimated that F&F fluoropolymer research expenditures have totaled $190,000 at the end of 1963, and will continue at the rate of about $18,000 per month.

Approximately 40 fluoropolymers based on VF, VF_2, or TFE have been examined in F&F as potential vehicles for finishes. Of these the following compositions hold the greatest promise:

VF_2/TFE with adhesion promoting and plasticizing monomers
TFE/isobutylene with adhesion promoting monomers
TFE/ethyl vinyl ether/vinyl glycidyl ether
VF/hexafluoroacetone
TFE/perfluorovinyl ether
VF/vinyl chloride

But, to date, only one new polymer family with obvious adaptability to finishes has been uncovered by F&F screening. These are solvent-soluble VF_2/TFE/BCEVP - 80/20/1 polymers, made by Orchem and formulated by F&F into a post-formable stripcoating finish. They have exhibited superior outdoor durability (color and gloss retention based on accelerated weathering) in combination with outstanding formability. These finishes have been successfully applied on aluminum in field tests on commercial coating equipment.

The potential market for VF_2/TFE/BCEVP polymers is currently restricted to factory-applied finishes where the substrate can tolerate the relatively high baking temperatures required to form a satisfactory film. Fluoropolymer systems suitable for air-drying finishes (by solvent evaporation) have not been found so far. The screening of fluoropolymer samples for finishes is continuing, and work is also in progress on stripcoating finishes based on polyvinyl and polyvinylidene fluoride.

<u>Polymer and Formable Finish Cost</u>

Detailed cost estimates were made for the VF_2/TFE/BCEVP polymer (solution process) and a white stripcoating finish made from it. The results obtained are summarized on the next page:

Resin Production (lbs./yr.)	140 M	1 MM	3 MM	5 MM
Percent of Resin Plant Capacity	Semi-Works	20	60	100
Finish Production (gal./yr.)*	30 M	220 M	650 M	1100 M
Resin Costs:				
Company Mill Cost ($/lb.)	6.51	1.67	1.07	0.90
Cost Plus 20% Return ($/lb.)	---	4.36	2.16	1.66
Finish Costs:				
Company Replacement Cost ($/gal.)	19.69	8.04	6.56	6.14
Cost Plus 20% Return ($/gal.)	---	18.46	12.30	10.94
Finish Costs to User Based on Sales Price, 1 mil Film Thickness and 310 ft^2/gal/mil Coverage (¢/ft^2)	---	6.0	4.0	3.5

*Assumes one half of the resin production is used in finish.

Major factors affecting the finish cost are the fluoropolymer solvent (butyrolactone at 35¢/lb.) and the relatively low per gallon coverage (310 $ft.^2$/gallon/mil). The use of a 20¢/lb. solvent could reduce finish cost to the user to 3.0¢/$ft.^2$ and a similar reduction could be achieved if coverage were increased by one third. A suitable VF_2/TFE/BCEVP polymer made by an aqueous process could lower the resin cost plus return to $1.46 per pound at commercial plant capacity, but the ultimate reduction of finish cost to the user would be quite small.

Organosol finishes based on polyvinyl or polyvinylidene fluoride would be substantially cheaper than those based on VF_2/TFE/BCEVP polymer because of lower raw material costs and potentially higher solids levels. However, PVF and PVF_2 lack versatility because of their relative insolubility in ordinary solvents.

<u>Markets:</u>

The opportunity for a post-formable fluoropolymer stripcoating finish has been substantiated in a market survey. The price to market opportunity relationship was explored for a finish having two to three times the currently best available outdoor durability (color and gloss retention):

	Total Market Opportunity* (Ref.-2)			
	At 2¢/ft.^{2}**		At 4¢/ft.^{2}**	
Year	$/year	gallons/year	$/year	gallons/yr.
1963	6.2 MM	1.00 MM	7.9 MM	0.64 MM
1968	9.9 MM	1.60 MM	12.5 MM	1.01 MM

If we assume that our sales would capture 25% of the above opportunity, then the fluoropolymer stripcoating finish, by itself, would not be adequate to justify construction of a commercial fluoropolymer plant.

There are indications that a substantial market for fluoropolymer maintenance finishes could develop for use in bridges and in the severely corrosive areas of some chemical plants and petroleum refineries, provided the product (1) will dry in a reasonable time without baking, (2) has outstanding resistance to chemical attack, (3) will protect the substrate against corrosion, and (4) is equivalent in application properties to existing maintenance finishes.

Patent Status:

Although Du Pont currently has a proprietary position in fluorinated polymers and copolymers of interest in this report, the pertinent patents will expire within the next two and a half years. Pennsalt has been licensed to make, use and sell polyvinylidene fluoride homopolymers, while Minnesota Mining is permitted to produce copolymers of trichlorofluoroethylene and vinylidene fluoride. There are no significant basic patents

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*The total market opportunity is defined as the portion of the market which the product could penetrate, taking into account properties and cost. The data assume absence of competitive fluoropolymer finish products.

**Finish cost to the user.

relating to fluoropolymer assigned to competition, although some specific ones exist.

The Organic Chemicals Department is seeking coverage for its VF_2/TFE polymers containing an adhesion promoting "hook."

Competitive Materials and Application Techniques:

"Tedlar" PVF film is the only known commercial material with weathering properties similar to the experimental formable fluoropolymer finishes. The anticipated cost to the user (film plus adhesive) of the currently available film thicknesses (1.7 and 2.0 mils) is between 5.7¢ and 7.0¢ per square foot compared to 3.5¢ per square foot for the formable finish at a large scale of resin production. A 1 mil thick "Tedlar" film under development, could be priced competitively with the liquid finish.

"Kynar" polyvinylidene fluoride suspensions and solutions are being sold by Pennsalt Co., and have appeared only in experimental finishes so far. Limited tests indicate that if properly formulated in low or medium gloss stripcoating finishes, polyvinylidene fluoride organosols approach our best solution fluoropolymer finishes in properties, while being potentially lower in cost. Experimental fluoropolymer finishes made by the Thiokol Corp. and Wisconsin Protective Coating Corp. have also been reported.

If VF_2/TFE copolymers lend themselves to thin film extrusion coating, then they could be used competitively with fluoropolymer finish stripcoating processes. Higher operating speeds, and the absence of a solvent may make extrusion coating economically advantageous to the user.

In view of the Company's expiring patent advantage, and with increasing competitive know-how in fluoropolymer chemistry, there is reason to believe that Du Pont could not long maintain an exclusive position in the fluoropolymer finishes market.

DISCUSSION:

A. BACKGROUND

I. PROPERTIES OF FLUOROPOLYMER FINISHES

One of the main reasons for carrying out this venture analysis is to determine how the company can most profitably exploit the excellent properties fluoropolymers. The following outstanding favorable attributes have been uncovered in the limited fluoropolymer finish research carried out so far:

1. Outdoor durability - Preliminary indications are that finishes based on VF_2/TFE/BCEVP polymer are superior in color and gloss retention to any system known. They seem to be in the same general durability area as "Tedlar" film, which means they are at least two to three times as durable as currently available finishes. They are also superior in cracking, resistance to chalking and dirt pick-up.

2. Post formability - Fluoropolymer finishes are superior in post-formability to the best finishes known.

3. Pressure mottling - Excellent.

On the other hand, there are also some unfavorable aspects:

1. Generally poor solubility of fluoropolymers in common volatile solvents - This has prevented the development of air-drying (by solvent evaporation) finish systems. However, the VF_2/TFE polymers are more soluble in higher boiling butyrolactone which makes them a satisfactory constituent of baked stripcoating finishes.

2. High cost - Fluoropolymers are high in cost because of high cost raw materials and processes.

3. Softness and abrasion resistance - Finishes prepared so far are inferior in this property. Changes in formulation may overcome this.

4. Water permeability - Fluoropolymers are quite moisture permeable, which places their corrosion protection in doubt over substrates such as steel. This problem can probably be solved by the use of a suitable primer or substrate treatment.

The following properties of fluoropolymer finishes are acceptable but not outstanding:

1. Solvent resistance - The finish is attacked somewhat by ketones, but not affected by hydrocarbons.

2. Thermal stability - Discoloration on baking can be avoided by the addition of the proper stabilizing agents.

3. Stripcoating application properties.

4. Impact resistance.

A major unknown factor in fluoropolymer finishes is resistance to chemical attack. Since fluoropolymers generally excel in this property, there is a good possibility it will be transmitted to the finish. However, the more soluble polymers needed for air-drying finishes may no longer be as resistant to chemical degradation.

II. PREPARATION OF VF_2/TFE/BCEVP COPOLYMER

The polymer of current major interest 80/20/1/ - VF_2/TFE/BCEVP is being prepared on a semi-works scale at the Jackson Laboratory (Orchem). The more advanced of the two processes under investigation employs homogeneous polymerization using tetrafluoropropyl acetate as solvent in continuous reactor operating at 90°C and 800 psi. Lauroyl peroxide is the catalyst. The product obtained as a 15% solids solution, precipitates out on cooling, is centrifuged to remove the solvent, washed with methanol and subsequently dried in an oven.

The potentially less expensive aqueous process is still in the exploratory stage of production. The reaction is carried out at 70 to 90°C at 800 psi and the product emulsion which is 10 to 20% solids is then coagulated with an electrolyte, centrifuged, washed and dried. The initiator system for the aqueous process has not been selected at this writing.

Some of the research and cost aspects of these two polymer processes will be discussed later in this report.

B. RESEARCH STATUS

I. F & F DEPARTMENT FLUOROPOLYMER RESEARCH ACTIVITIES

At present the F & F Department has five full time men assigned to research on fluoropolymer finishes and associated activities. In addition, one man spends a small portion of his time in this area. The work may be broken down as follows:

Polymer research - one man

Polymer evaluation - one man

Formable fluoropolymer finish development - one man

Fluoropolymer process research - one man on loan to the Organic Chemicals Department

Fluoropolymer clears for wood - less than one quarter of a man

Venture Analysis - one man

a. Polymerization of Fluoroolefins

This work being carried out at the Experimental Station has been primarily concerned, until recently, with the development of techniques of aqueous polymerization of 80/20 VF_2/TFE copolymers, using a potassium persulfate/sodium metabisulfite redox system. The program, which has paralleled similar research at Orchem, has proven that VF_2/TFE copolymers can be produced in an aqueous system using 400 ml. shaker tubes or a two gallon autoclave. The resulting polymer, which was solvent soluble, remained stable in solution at room temperature. Some difficulty was encountered with excessive molecular weight spread, and attempts to introduce the adhesion promoting termonomer were not successful prior to completion of this phase of the program. (However, work on this problem is continuing in Orchem research). Attempts to prepare acceptable VF_2/isobutylene, VF/VCl, and VF_2/VCl copolymers in water also have not been successful so far.

Emphasis of this research has now been shifted toward the preparation of fluoropolymers for lower cost vehicle candidates, and having generally better property/cost balances than those having been studied in the past.

b. Fluoropolymer Screening and Preliminary Evaluation in End-Uses

Cooperative programs for fluoropolymer screening and evaluation are under way between F & F, Orchem and CRD. Promising polymer candidates are being characterized, and tested in end-uses suggested by their properties. Out of 40 fluoropolymers examined, the group below has properties suitable for baking products:

1. VF_2/TFE/hook
2. TFE/isobutylene/5 methylene norbornene
3. VF/HFA
4. VF/VCl

The following polymers are considered potentially attractive in air-drying* finishes:

1. VF_2/TFE plus small amounts of other monomers

2. TFE/isobutylene plus small amounts of other monomers

3. VF/HFA

4. VF/VCl

5. TFE/ethyl vinyl ether/vinyl glycidyl ether

The major emphasis will be on the development of the necessary data required to allow early selection of one or two polymers for extensive product development.

c. Formable Finishes for Exterior Use Based on Fluoropolymers

The primary goal of the fluoropolymer stripcoating program has been to develop a formable finish having the excellent properties attributable to fluorinated polymers and at the same time, a cost acceptable to the coating industry. The desired product properties are: 100% gloss retention for 5 years, 50% gloss retention after eight years exposure, no film failure and good adhesion for 20 years.

A two-pronged approach to formable finishes has been taken. The first has consisted of using the solvent-soluble 80/20/1-VF_2/TFE/BCEVP polymer available from Orchem. This polymer was chosen because of its excellent weathering characteristics and the relative ease with which it could be processed into a finish. The second approach is the development of an organosol stripcoating finish based on polyvinyl fluoride, or polyvinylidene fluoride. These relatively insoluble polymers, though more difficult to process into a finish, have potentially much lower cost than the VF_2/TFE based polymers and probably similar attractive weathering properties. Current research on fluoropolymer stripcoating finishes is emphasizing formulations with PVF and PVF_2 since work with VF_2/TFE finishes is considered essentially completed.

An apparently acceptable finish based on VF_2/TFE/BCEVP polymer (made by the solution process) has been developed by Heiberger (Ref -24). It has been formulated in a full range of glosses, and a wide variety of colors. The resulting enamel has good application, appearance and initial film properties, and has

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*for most polymer candidates, "air-drying" refers to drying by solvent evaporation.

been successfully tested twice on commercial stripcoating lines using aluminum substrates. It also has an outstanding balance of formability, pressure mottling resistance and thermal stability. Durability is excellent, based on accelerated weathering (3000 hours in AWC-II to surface chalking, but no film failure). These finishes can be applied with conventional stripcoating equipment using normal application speeds and baking temperatures.

Primary concern relative to VF_2/TFE/hook finishes is high coverage costs. The current formulation is relatively low in solids, and hence has low coverage (only 310 $ft.^2$/gal./mil). Further, the finishes are formulated with a rather expensive solvent, butyolactone, whose cost is a significant portion of finish cost as the polymer becomes less expensive.* Therefore, reformulation of the finish is indicated, with different solvents and, if possible higher solids. Some technical problems also still exist with water spotting and poor salt spray resistance on galvanized steel (VF_2/TFE copolymers are relatively water permeable). The latter problem may be corrected by using a low cost, low permeability primer prior to the fluorinated topcoat, which in turn may lower finish costs if thinner films can be used.

The work on polyvinyl fluoride-based stripcoating finishes is still in its initial stages. Using lower molecular weight versions of "Tedlar" grade polyvinyl fluoride, finishes were formulated in medium and low glosses and a variety of colors. The polymer was prepared into a film-forming organosol by ball milling. The resulting films have excellent mechanical properties. However, major difficulties were encountered in laboratory stripcoating application because of poor flow and incomplete coalescing of the film. A longer bake cycle also seems needed, which would mean a slower line speed. Less difficulty with flow, bake and coalescing problems was encountered in preliminary work with polyvinylidene fluoride-based finishes.

At the moment, the finishes based on VF_2/TFE/hook seem to have a better chance of technical success because of the greater inherent versatility of the solvent-soluble polymer. However, if the polyvinyl fluoride or polyvinylidene fluoride finish approach the flow and bake properties, durability, and appearance of the VF_2/TFE/hook finish, then it is quite possible that their lower cost may outweigh any remaining disadvantages.

d. <u>Factory Applied Pigmented Exterior Finishes for Wood</u>

The goal of this brief program was to develop a finish for factory application on wood siding materials. A durability of possibly 10 years to refinishing was sought on normal unstabilized

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*Details of finish costs are discussed in section C of this report.

siding substrates. The initial formulations tested were essentially free of chalking, but failed by cracking after 1500 hours of accelerated weathering. This work has now been discontinued, because chances of technical success are considered quite poor.

e. Exterior Clear Finishes for Wood

The goal of this program, a small part of which has been devoted to fluorine copolymer finishes, is to develop an exterior clear finish as durable as house paint and which will require a minimum of surface preparation prior to refinishing. The work is being directed toward factory applied finishes, as well as air-drying finishes suitable for trade sales.

Unavailability of suitable fluoropolymers has somewhat limited research on long durability baking clears for wood, and the air-drying polymers tested (VF_2/TFE/VBU/BCEVP) have shown loss of adhesion due to moisture penetration at scored areas of panels after only 3 months of Florida exposure. However, film integrity has remained excellent on accelerated weathering exposure, indicating the need for further research on the adhesion problem.

Recently, the addition of non-light scattering extenders to clear finishes (none containing fluoropolymers, so far) has provided an excellent lead toward erosion deterioration of the film. This would minimize the surface preparation needed prior to recoating.

The future direction of the wood clears program has not been decided at this writing. The question of whether to emphasize more conventional clears which fail by erosion, or whether to develop long durability clears is being considered.

f. Polymer Process Development Work

This work being carried out by R. G. Lindsey at the Jackson Laboratory is integrated into the Organic Chemicals Department program. It is discussed under the activities of departments outside of F & F.

g. Venture Analysis

This report is a summary of the venture analysis being carried out by the writer.

h. Summary of F & F Activities

At this writing, F & F fluoropolymer research emphasis is concentrated in two areas - synthesis, screening and development of new polymers for finishes, and the development of an outdoor formable finish of long durability using available fluorine polymers. Research on other types of fluoropolymer finishes has so far been only an incidental part of other programs. F & F research expenditures in the general fluoropolymer finish area are summarized below:

Synthesis and Evaluation of Fluoromonomer Polymers (P-1523, P. F. Sanders & R. G. Lindsey)	$85,762
Fluoroolefin Copolymers (E-1504, H. F. Reinhardt)	24,157
Formable Finishes (P-1215, P. Heiberger and about 6 mos. one-half time by J. C. Fang)	60,000
Durable Clears for Wood (P-1544, R. W. La Berge)	negligible
Factory Applied Pigmented Finishes for Wood* (P-1222, D. F. Strehlau, work now suspended)	3,500
Venture Analysis (F. G. Klein)	13,500
Cumulative Total at the end of 1963	$186,919

The current rate of research expenditure on fluoropolymer finishes in F & F is estimated to be $18,000 per month.

II. FLUOROPOLYMER RESEARCH OUTSIDE THE F & F DEPARTMENT

Five company departments, in addition to F & F, are in one way or another, doing research on fluorinated monomers and polymers of direct interest for use in finishes. The breakdown of personnel and activities is summarized on the chart on the next page:

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*An estimate based on the portion of time expended on fluoropolymer activities.

BREAK-DOWN OF PERSONNEL ASSIGNED TO FLUOROPOLYMER RESEARCH

(exclusive of work on "Tedlar" and "Teflon")

	Fabrics and Finishes	Organic Chemicals (Note-2)	Central Research	Electro-chemicals	Plastics (Note-3)	Elastomers
New Monomer & Polymer Research	1	3	8	1	12	1
Polymer Process Research	1	4		1		
Finishes Research	2+	2				
Miscellaneous (Note -1)	1	1				

Note-1 One F & F man on venture analysis. One Orchem man on economic studies.

Note-2 The F & F man on loan to Orchem listed under F & F dept.

Note-3 Personnel at Experimental Station only. Does not include "Teflon" research.

Some of these assignments relate to F & F interests and work only in a very limited way. Further, there are constant personnel reassignments taking place so that this chart soon may be out of date.

The work proceeding in departments other than F & F, is summarized in the sections following:

a. Organic Chemicals Department

The Organic Chemicals Department (Orchem) has an extensive background in fluorine chemistry and has a proprietary position in a number of fluoromonomers. In contrast to the Plastics Department, which is doing research on perfluorinated polymers only, Orchem feels that there is a future in fluoropolymers, which are not necessarily fully fluorinated.

Currently, major emphasis is being placed on the synthesis, process development, and application of solvent soluble polymers based on 20 parts tetrafluoroethylene and 80 parts of vinylidene fluoride, with small amounts of adhesion promoting agents such as bis (β-chloroethyl) vinyl phosphonate. This class of polymers which is generally referred to as VF_2/TFE/"hook," seems to show the greatest promise in finishes because of good solubility in reasonably common solvents and because of their excellent outdoor durability. However, finishes from this polymer generally require baking to achieve a satisfactory film.

Two approaches to the synthesis of VF_2/TEF/BCEVP polymers are being extensively studied at Jackson Laboratory. The first and older approach which involves polymerization in a solvent system (tetrafluoropropyl acetate), is currently in operation in the semi-works in a two gallon continuous reactor. Recent attempts to scale up to a 37 gallon system have resulted in a raw material conversion decrease from 37 to 20%, an unacceptably low level. The major defect of the homogeneous polymerization approach seems to be losses of the expensive solvent during polymer isolation. This contributes 10% additional raw material cost to the polymer at a level of 97% solvent recovery.

The second approach to VF_2/TFE polymerization employs an aqueous heterogeneous system. Development in this area is less advanced than the solvent system. Nevertheless, it has been possible to make a polymer containing a small amount of the hook material. Product reproducibility is a problem, with difficulties being encountered with variations in molecular weight (microgels) and solubility. Heat stability and adhesion are also still unreliable. However, there is considerable optimism that production of VF_2/TFE polymers in aqueous systems will be practical. The economics definitely favor the aqueous system because high conversions of monomer are obtained (over 90% versus less than 40% for the solvent process), which means much smaller polymerization and monomer recycle equipment. Further, the absence of the solvent lowers the resin raw material costs and eliminates the need for a polymerization solvent plant.

Much of the fluoropolymer research at the Jackson Laboratory is directed specifically at finishes applications. The VF_2/TFE polymers are being modified with other monomers to achieve specific end properties required in air-drying (solvent evaporation) maintenance finishes, wood finishes, etc. Organosols containing VF, VF_2, TFE and other constituents are being studied, together with "hookless" polymers made in aqueous systems. Orchem is also expressing considerable interest in the potentials of melt extrusion application of VF_2/TFE/"hook" or TFE/isobutylene polymers directly on metallic, cellulosic and fabric substrates. Work is also in progress aimed at developing fluorinated coatings for the paper industry.

New equipment currently is being designed for semi-works production of VF_2/TFE polymers by the aqueous process, and for the production of TFE/isobutylene copolymers.

A total of ten technical men, plus a man on loan from F & F, are currently (December, 1963) assigned to VF_2/TFE, and other fluorinated polymer developments at the Jackson Laboratory. The break-down of these assignments follows:

Polymer scouting -- 3 men

Applications -- 3 men (one man on cellulosics including paper, and melt extrusion; one man on steel and aluminum; and one man studying various aspects of economics).

Process -- 5 men (one man on a study of the technical aspects of the polymerization and chemical variables; one man on solvent polymerization; one man on loan from F & F on aqueous polymerization of VF_2/TFE/hook and TFE/isobutylene; one man on the engineering aspects of polymerization, feed, recovery, and recycle systems; one man on polymer characterization and correlation of physical properties).

There is a possibility that as many as four more men will be added in the near future (one on polymer applications, one to augment the polymerization process studies, and two more for process work in the plant).

The Organic Chemical Department's cumulative research expenditures on fluorinated copolymers were $500 M as of January 1, 1963, possibly 1.0 MM at the end of 1963, and the current rate of spending is about $55 M per month.

b. Central Research Department

Probably no more than three chemists in Central Research (CRD) are involved in fluorinated copolymer work for applications of direct interest to the F & F department (out of a total of eight chemists assigned to work in this general area).

The major goal of current fluoropolymer research in CRD seems to be the development of novel polymers based on at least 50% tetrafluoroethylene. Work of direct interest to the F & F department in fluoropolymer coatings deals primarily with copolymers based on tetrafluoroethylene and isobutylene. These polymers, which are soluble up to 20% in trichloroethylene or tetrahydrofuran, are generally similar to VF_2/TFE in initial film properties, but poorer in solubility and more difficult to apply. However, TFE/isobutylene polymers seem to have some advantage because of lower water permeability, lower density, and lower cost. So far, improved solubility has been achieved only at the expense of other desirable properties. There seems to be considerable interest at CRD in using TFE/isobutylene polymers for high molecular weight plastics, films, and, together with Orchem, for the melt extension coating of metals and other materials.

Other work being carried out at Central Research of possible use to F & F, deals with polymers of vinyl fluoride and hexafluoroacetone, which could be potentially suitable for baking enamels.

c. Electrochemicals Department

The goal of the Electrochemicals Department (Elchem) fluorine polymers research is to find new materials of outstanding outdoor durability for binders and coatings, with the obvious goal of sales to the coatings industry. At present, there are two chemists at the Experimental Station concerned with this work. One is evaluating polymers from Orchem and Elastomers Dept. for coatings purposes. A second man is installing semi-works scale polymerization equipment to prepare fluoro and other polymers. In addition, there is one Elchem man on loan to the Plastics Department to acquire curing technology in connection with the development of completely fluorinated polymers with adhesives potential. One chemist at CRD is also representing Elchem interests in the field of copolymers with hexafluoroacetone.

So far Elchem's research in VF_2/TFE polymers seems to have been quite limited. Preliminary findings are that VF_2/TFE finishes are "very good" on aluminum. Work with pigmented finishes on wood has not been encouraging. Limited work on high zinc maintenance finishes with VF_2/TFE binders showed considerable promise, but was discontinued when cheaper zinc-ethyl silicate system was developed. It is expected that the major area of future Elchem interest will be copolymers of vinyl acetate and TFE, and similar materials where the Electrochemicals Department has a proprietary interest in one of the monomers.

Two economic studies have been made in Elchem by J. R. Harrison and F. J. deVries (Ref-3 & 4) to determine the opportunity existing for more expensive finishes in long life maintenance of structural steel. These studies were carried out using modern discounted cash flow, calculation techniques. Although there is some question about the basic assumptions made, it is felt that the results obtained are of considerable interest to the F & F Department.

In both studies, the premium finish was compared to a "conventional" finish system costing 5¢/ft.^{2} for materials. In actual practice, an alkyd maintenance finish system of two coats each of primer and metal protective topcoat costs about 3.3¢/ft.^{2} (Ref.-8) and even this is considered high for bridges. On the other hand, a catalyzed epoxy finish system currently used for severe chemical exposure costs about 6.2¢/ft.^{2} (Ref-8). Therefore, the assumed "conventional" finish system at 5¢/ft.^{2} used by Harrison and deVries is high for ordinary maintenance uses and low for comparison under severe corrosion conditions.

In the first study (Ref-3), a premium finish costing 10¢/ft.^{2} (probably an optimistic assumption for a fluorinated polymer maintenance finish), applied over sandblasted steel and about 3 times as durable, was compared to the conventional finish at 5¢/ft.^{2}, applied over a brushed steel. The general conclusions reached by Harrison and deVries, and summarized on Table I indicate that the longer durability premium maintenance finish can be justified under almost all circumstances in "severe environment" chemical plants, but not under average environment situations. A premium finish can be more easily justified on highway bridges because of lower interest rates required, and because there are no taxes to pay on the savings obtained.

In a more detailed study (Ref-4) the same authors confirmed their initial findings. In addition they found that:

1. Any finish twice as durable as conventional maintenance finishes can be sold for considerably more than the 10¢/ft.^{2} assumed in reference 3, even if the current interest rate is considered to be 10%. For chemical plants, under severe environment conditions, a finish having twice the durability of conventional finishes over blasted steel could be sold at 21¢ per square foot, assuming a 5% discount rate, or 17¢ per square foot with a 10% discount rate, provided the premium and conventional finish are compared when applied over shop blasted steel. If the comparison is made by assuming that neither finish requires sandblasting prior to painting and thereafter, then the premium finish justification improves.

2. In chemical plants having an average environment, it is much more difficult to justify premium maintenance finishes. Nevertheless, a finish four times as durable as conventional ones could be sold at 17¢/ft.^{2} (10% discount rate), if it could be applied over unblasted metal. If the economic comparison is made over blasted steel, it is barely justifiable at a 5% discount rate (11¢/ft.^{2}) and the justification is highly questionable at a 10% rate.

3. In the case of major highway bridges, justification of premium maintenance finishes is highly attractive independent of surface treatment, even if the durability increase is only two-fold. In the case of a four-fold durability increase, the paint could be sold for 4 times the cost of conventional finishes. Similar justification exists for minor highway bridges.

The main reason for the easier justification of premium finishes on highway bridges is that a 5% discount rate can be assumed and no taxes are paid on the savings.

TABLE I

SUMMARY OF ECONOMIC STUDY TO DETERMINE JUSTIFICATION OF A 10¢/FT^2 LONG-LIFE VS. A 5¢/FT^2 CONVENTIONAL MAINTENANCE FINISH (REF-3)

Justification Rating	Surface Preparation for Premium Finish			
	No Blasting	Shop Blasting	Site Blasting	Blasting After Erection
Chemical Plant Severe Environment	1	1	1	3
Chemical Plant Average Environment	1	4	4	4
Major Highway Bridges	1	2	3	4
Minor Highway Bridges	1	2	2	4

Definition of Justification Rating

1 - Easily justified at highest interest rate listed
2 - Can be justified at highest interest rate listed
3 - Questionable justification at either interest rate listed
4 - Cannot be justified

Comparison made with the standard finish using no surface preparation and premium finish lasts three times as long if applied over a blasted surface, twice as long if applied over an unblasted surface.

Assumed life of structure -

Chemical plants - 15 years
Highway bridges - 50 years

Interest rate used -

8 & 15% for chemical plants
5% for major highway bridges (No taxes)
10% for minor highway bridges (No taxes)

Refinish cycle -

Varied according to structure, type of finish, and surface preparation (See Ref-3 for details)

d. Elastomers Department

The Elastomers Department has one chemist assigned to copolymerization of vinylidene fluoride and tetrafluoroethylene with perfluoromethylvinyl ether. This work is mostly aimed at elastomers, but may result in some polymers of interest to the F & F Department.

e. Plastics Department

Work in this department is primarily aimed at extending tetrafluoroethylene technology, and the development of plastics having perfluorinated structures. Of greatest interest to the F & F Department are copolymers of TFE with NAVE*, the later constituent contributing to make the first known water soluble** fluoropolymer which would make a self-supporting film. This film has been found to have water repellent properties upon drying, and could possibly be used in water soluble paints. The Plastics Department is working on a large variety of other fluorinated polymers which do not seem to have any immediately obvious applications to the F & F Department. It is not possible to determine personnel allocation directly associated with work of interest to F & F. There are currently twelve chemists working on fluoroolefin copolymers and intermediates at the Experimental Station.

C. COST CALCULATIONS

To permit a detailed analysis of the factors entering into the cost of the VF_2/TFE/BCEVP solution polymer and the resulting fluoropolymer stripcoating finish, all economic calculations were made on a "Company cost plus return" basis. That is, cost and investment summations were kept separate throughout, starting from raw material information and ending with the finish.

It must be recognized that all the cost data used and discussed in this report are strictly preliminary, and have not been cleared through the Control Divisions of the various departments involved. The sources of cost information used are listed in Appendix A.

----

*NAVE is $CF_2{=}CF{-}O{-}CF_2{-}\overset{\overset{CF_2}{|}}{C}F{-}O{-}CF_2{-}CF_2{-}SO_3Na$

**It is not known whether true solubility exists, more likely a very fine dispersion.

I. COST OF VF_2/TFE/BCEVP COPOLYMER

An Orchem "research guidance" cost estimate for the manufacture of 80/20/1 VF_2/TFE/BCEVP copolymer using tetrafluoropropyl acetate as polymerization solvent has formed the basis for all polymer cost calculations in this report (Ref-5). Because of the preliminary nature of this estimate, projected cost and return data for VF_2 and TFE were used, and some technology, which has not been fully developed, had to be assumed. Naturally, deviations from the projected raw material costs, and failure to meet technological assumptions could significantly affect resin cost. The results obtained are summarized on Table II.

Two different plant sizes were assumed for this estimate:

1. Up to 140 M pounds of resin per year an existing pilot plant would be put into operation with little new investment required.

2. For larger scales of production a plant having a capacity of 5 MM pounds of polymer will have to be built, together with necessary facilities to produce the tetrafluoropropyl acetate solvent and additional vinylidene fluoride.

The assumption of these two plants' sizes leaves a gap in the cost estimate between the 140 M and about 1 MM pound annual production scales, where the pilot plant would be too small, and the full scale plant probably too large for economical production. Since this capacity gap may occur during an important product development period, which may last for some time, additional interim production facilities may have to be considered.

An examination of the cost and return data summarized on Table II, reveals a number of important factors:

1. At a production level of 1 MM pounds of resin per year, both the VF_2 plant and the resin plant are assumed to be operating at a small fraction of their ultimate capacity. Therefore, an unusually large per pound raw material and resin investment is carried through the calculations. The resulting resin transfer price is over two and a half times the resin replacement cost, because of the very high operative earnings required to achieve a 20% return on investment. At 5 MM pounds of annual resin production, the investment burden is reduced and the transfer price, as a consequence is much lower.

TABLE II
SUMMARY OF PRELIMINARY COST
ESTIMATES FOR VF_2/TFE/BCEVP
COPOLYMER BY SOLUTION PROCESS (REF. 5)

Resin Production Volume Assumed (lb./yr.)	140 M	1 MM		3 MM		5 MM	
	Cost only	Cost	Invest.	Cost	Invest.	Cost	Invest.
Raw Material Costs and Investment Used in Calculations ($/lb. raw material)							
VF_2 (.89 lb./lb. resin)	1.80*	0.83	2.55	0.47	0.88	0.42	0.71
TFE (.222 lb./lb. resin)	2.55	1.07	0.87	0.91	1.00	0.69	0.67
BCEVP (.01 lb./lb. resin)	3.00	3.00	---	3.00	---	3.00	---
C_3fluoroacetate (.12 lb./lb. resin)	9.80*	1.41	0.68**	1.08	0.77**	0.83	0.55**
Lauroyl Peroxide (.0025 lb./lb. resin)	3.25	3.25	---	3.25	---	3.25	---
Carbon Tetrachloride (.15 lb./lb. resin)	0.087	0.087	---	0.087	---	0.087	---
Calculated Resin Costs and Investment							
Total raw material cost ($/lb. resin)	4.21	1.20	---	0.88	---	0.67	---
Resin cost exclusive ($/lb. resin)	2.30	0.37	---	0.25	---	0.20	---
Resin mill cost ($/lb. resin)	6.51	1.57	---	1.03	---	0.87	---
Research & Development expense ($/lb. resin)	---	0.10	---	0.04	---	0.03	---
Company replacement cost ($/lb. resin)	---	1.67	---	1.07	---	0.90	---
Allocated raw material investment exclusive of C_3fluoroacetate ($/lb. resin)	---	---	2.54	---	1.10	---	0.85
New direct resin and C_3fluoroacetate plant investment required ($/lb. resin)	---	---	1.80	---	0.60	---	0.36
Total new investment required for resin and C_3fluoroacetate plant ($/lb. resin)	---	---	3.34	---	1.26	---	0.81
Total "company investment" for resin and raw materials ($/lb. resin)	---	---	5.88	---	2.36	---	1.66
Gross increment for 20% return ($/lb. resin)	---	---	2.69	---	1.09	---	0.76
Increment for 20% net return ($/lb. resin)	---	---	1.18	---	0.47	---	0.33
Transfer Price of Resin -- cost plus 20% return ($/lb. resin)	---	4.36	---	2.16	---	1.66	---

*Development Price
**Includes only allocated raw material investment for C_3fluoroacetate. New investment for C_3fluoroacetate included with resin investment.

The relationship of cost and return on investment to transfer price is illustrated graphically on Figure 1. It is obvious that the rate of VF_2 utilization for other end-uses sharply affects the resin cost plus return picture. For the purpose of these calculations it was assumed that half the VF_2 produced would be used in VF_2/TFE resin manufacture.

2. The polymerization solvent, tetrafluoropropyl acetate (C_3fluoroacetate) is another important factor affecting VF_2/TFE/BCEVP resin cost. The pie charts of Figure 2 indicate it contributes between 10.1 and 11.1% to the resin replacement cost, even though 97% recovery of the solvent is assumed (which has not been demonstrated in the laboratory). In addition, the solvent contributes $300 M out of $1,800 M of new plant investment required for resin manufacture.

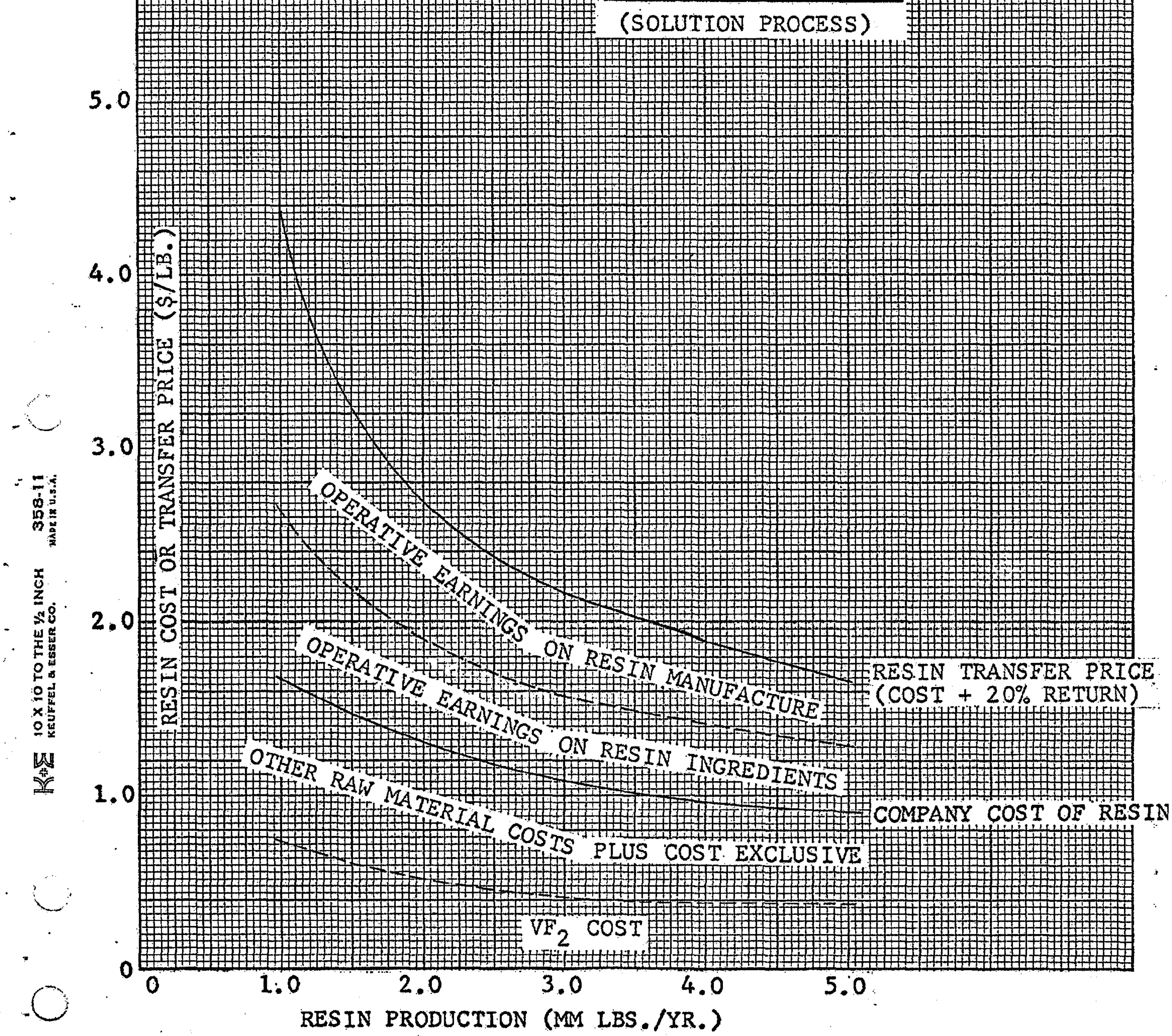
The development of an aqueous polymerization process under investigation at Orchem, would eliminate the use of the solvent, thus reducing the replacement cost of the resin by about 12¢ per pound (5 MM pound production level). In addition, the lower investment required would reduce the increment needed for a 20% return, giving by 8¢ per pound, giving an estimated cost plus return of about $1.46 per pound of resin by the aqueous process, at the 5 MM pound annual production level. This would being the VF_2/TFE/BCEVP resin into the range of $1.50 per pound anticipated for PVF polymer (Ref-6), although the former retains a disadvantage by having much higher specific gravity (1.75 vs. 1.37).

3. TFE, having a generally higher cost plus return than that anticipated for VF_2, also tends to raise the price of the resin. Therefore, with captive production of VF_2, a resin like Pennsalt's "Kynar" would be cheaper than the VF_2/TFE/BCEVP resin.

The effect of resin cost variables on the finish cost will be discussed separately in section C-III-a of this report.

II. FORMABLE FINISH COSTS

The costs of stripcoating finishes made with 80/20/1 VF_2/TFE/BCEVP solution process polymer were based on a formula developed by P. Heiberger in the middle of October, 1963 (See Appendix A). The results listed on Table III used the polymer cost data of Table II and were calculated according to procedures specified by R. S. Wright. Various finish cost and investment factors which were suggested by R. S. Wright and G. H. Sutton are explained and summarized in Appendix A.

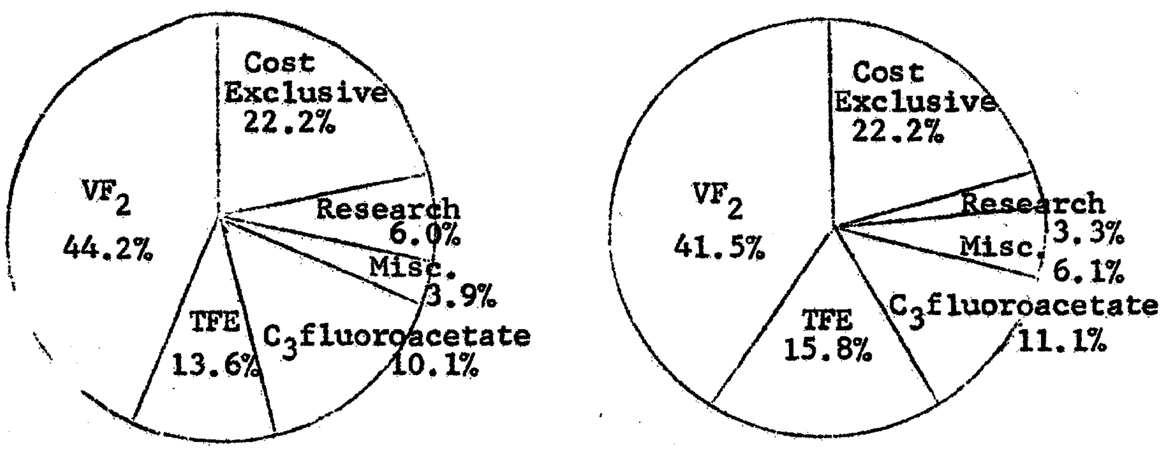


(SOLUTION PROCESS)
RESIN COST OR TRANSFER PRICE ($/LB.)
5.0
4.0
3.0
2.0
1.0
0
OPERATIVE EARNINGS ON RESIN MANUFACTURE
RESIN TRANSFER PRICE
(COST + 20% RETURN)
OPERATIVE EARNINGS ON RESIN INGREDIENTS
COMPANY COST OF RESIN
OTHER RAW MATERIAL COSTS PLUS COST EXCLUSIVE
VF2 COST
0
1.0
2.0
3.0
4.0
5.0
RESIN PRODUCTION (MM LBS./YR.)
10 X 10 TO THE ½ INCH 358-11
KEUFFEL & ESSER CO. MADE IN U.S.A.

FIGURE 2

BREAKDOWN OF VF_2/TFE/BCEVP RESIN COST
(COMPANY COST BASIS)

1 MM lbs. annual resin production 5 MM lbs. annual resin production



Company replacement cost of resin

$1.67/lb. $0.90/lb.

Estimated transfer price of resin
(Company cost plus increment for 20% net return)

$4.35/lb. $1.66/lb.

TABLE III

VF_2/TFE/BCEVP FORMABLE FINISH COSTS

Case Number	1	2	3	4	
Assumptions					
Annual finish production (gals)*	30 M	220 M	650 M	1100 M	
Annual polymer production (lbs)	140 M	1 MM	3 MM	5 MM	
Capacity of polymer plant (lbs/yr)	140 M	5 MM	5 MM	5 MM	
Polymer company replacement cost ($/lb)	6.50	1.67	1.07	0.90	
Rolled-up polymer investment ($/lb)	---	5.88	2.36	1.66	
Calculated Finish Cost Plus Return					
Cost of resin in finish ($/gal)	14.60	3.84	2.46	2.07	
Total raw material cost ($/gal)	18.75	7.14 90	5.76 80	5.37	19 63
Company replacement mill cost ($/gal)	19.69	8.04	6.56	6.14	.77/gal
Selling & adm. expense ($/gal)	---	0.80	0.80	0.80	
Packaging & freight ($/gal)	---	0.17	0.17	0.17	
Cost of sales ($/gal)	---	9.01	7.52	7.11	
Operative Earnings on resin raw matl. & resin investment ($/gal)	---	6.18	2.48	1.75	
Operative Earnings on finish investment ($/gal)	---	3.27	2.30	2.08	
Total Operative Earnings on finish for 20% net return ($/gal)	---	9.45	4.78	3.83	
Finish sales price - cost plus 20% return on investment ($/gal)	---	18.46	12.30	10.94	
Cost of Finish Coverage (Sales Price Basis)					
at 310 ft^2/gal at 1 mil thick (¢/ft^2)	---	6.0	4.0	3.5	

Notes:

1. Preliminary finish formula supplied by P. Heiberger (Appendix B)
2. Polymer costs based on Orchem estimate (Ref 5)
3. Sources and basis for cost and investment factors, see Appendix A)

*Assumed half of resin plant production used for finish.

It will be noted that no specific levels of finish production were associated with the cost figures of Table III because maximum batch sizes could be used throughout. Selling expense and permanent investment per gallon of finish were assumed to be constant, independent of scale of finish production (See Appendix B). Therefore, in essence the table is a compilation of finish cost plus return as it is affected by VF_2/TFE/BCEVP resin cost. Figure 3 illustrates the same information graphically.

Summarizing the results of Table III, it can be said that:

1. The fluoropolymer stripcoating finish Company replacement cost ranges from \$6.14 to \$8.04 per gallon, depending on scale of resin production.

2. Taking a full 20% net return on all investment involved, the finish could be sold between \$10.94 and \$18.46 per gallon, depending on scale of resin production.

3. The minimum finish coverage cost achievable using VF_2/TFE/BCEVP produced at a rate of 5 MM pounds per year (materials only, no application cost) and taking a full 20% return throughout is about 3.5¢/$ft.^2$ at 1 mil.

The major factors entering into formable finish cost will be discussed in the following sections of this report.

III. VARIABLES AFFECTING FLUOROPOLYMER FORMABLE FINISH COSTS

a. Resin and Solvent Price

The finish ingredient replacement cost has been broken down at two levels of resin production. The charts of Figure 4 indicate that the solvent and the resin contribute the major portion of finish ingredient costs. At a level of 1 MM pounds of annual resin production, the resin contributes about 53% to ingredient cost and the solvent (butyrolactone) 38.1%. At the 5 MM pound resin production level, the roles are reversed with the solvent contributing about 51% and the resin 38%.

Butyrolactone was chosen as the sole solvent because it contributes a unique combination of properties needed for the fluoropolymer stripcoating finish:

1. A high boiling point for blister-free baking.

2. Acceptable flow properties for film uniformity.

3. High enough resin solubility to achieve a practical finish solids level.

4. Relatively low toxicity.

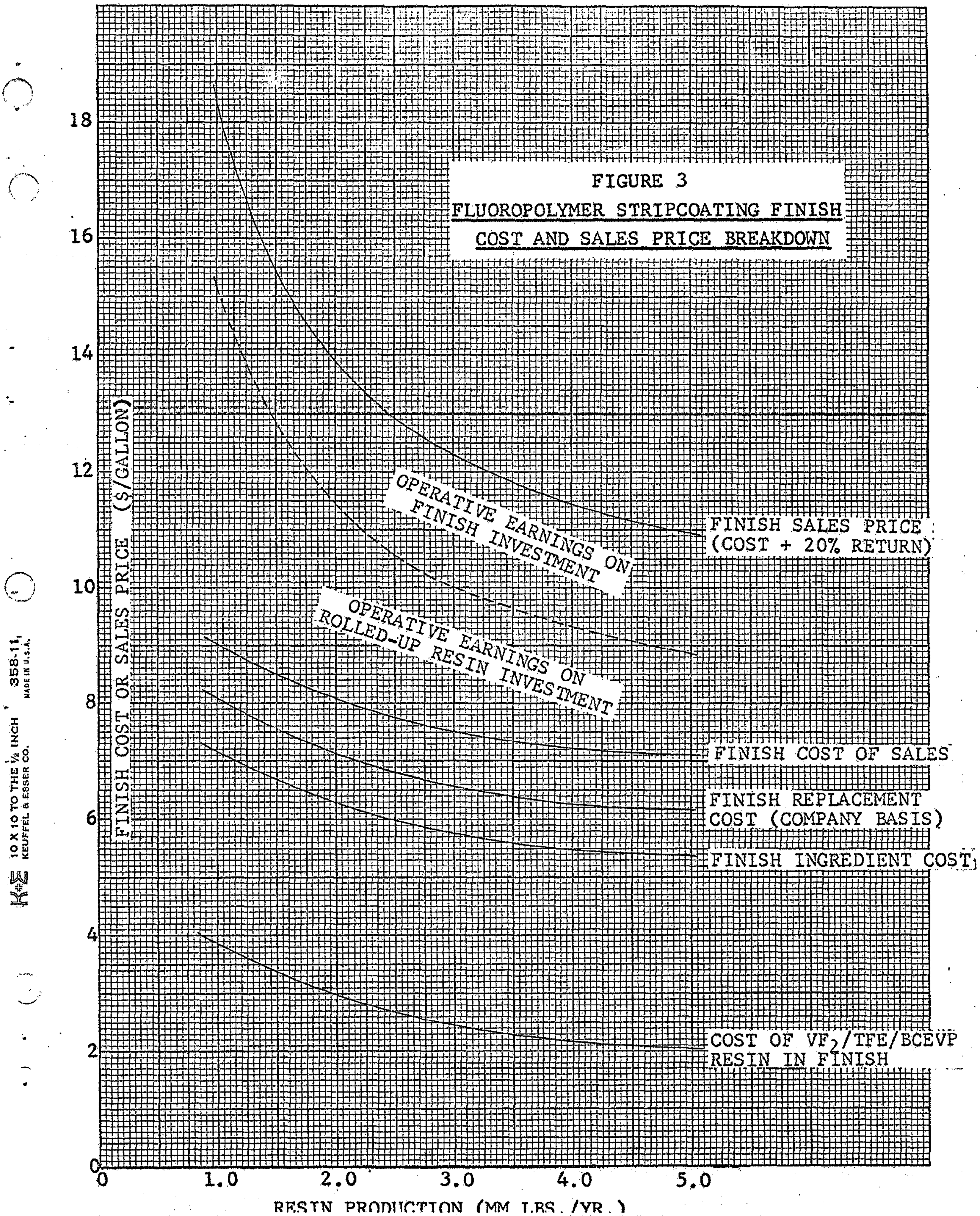
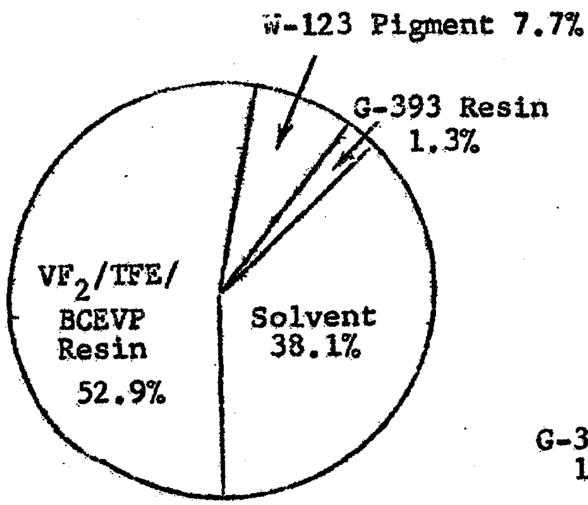


FIGURE 3
FLUOROPOLYMER STRIPCOATING FINISH
COST AND SALES PRICE BREAKDOWN
FINISH COST OR SALES PRICE ($/GALLON)
RESIN PRODUCTION (MM LBS./YR.)
OPERATIVE EARNINGS ON FINISH INVESTMENT
OPERATIVE EARNINGS ON ROLLED-UP RESIN INVESTMENT
FINISH SALES PRICE (COST + 20% RETURN)
FINISH COST OF SALES
FINISH REPLACEMENT COST (COMPANY BASIS)
FINISH INGREDIENT COST
COST OF VF2/TFE/BCEVP RESIN IN FINISH
0
2
4
6
8
10
12
14
16
18
1.0
2.0
3.0
4.0
5.0
10 X 10 TO THE 1/2 INCH 358-11
KEUFFEL & ESSER CO. MADE IN U.S.A.

FIGURE 4

BREAKDOWN OF VF_2/TFE/BCEVP FORMABLE FINISH INGREDIENT COST
(COMPANY REPLACEMENT COST BASIS)

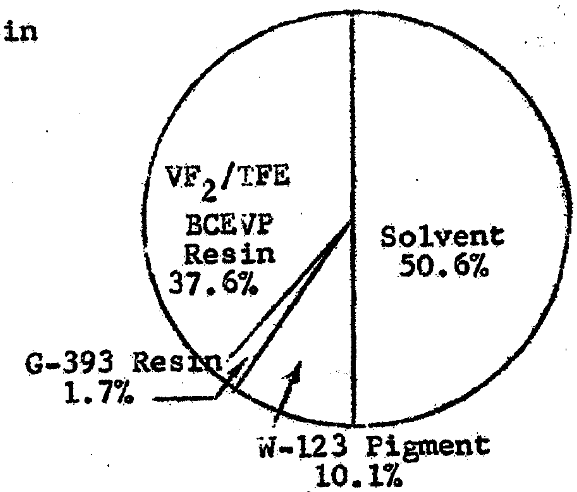
Reference Case 2, Table III
Resin Production 1 MM lbs./yr.
Finish Production 220 M gal./yr.



Finish Ingredient Replacement Cost - $7.14/gal.

Estimated Finish Sales Price* $18.46/gal.

Reference Case 4, Table III
Resin Production 5 MM lbs./yr.
Finish Production 1.1 MM gal./yr.



Finish Ingredient Replacement Cost $5.37/gal.

Estimated Finish Sales Price* $10.94/gal.

*Cost plus 20% return for ingredients and finish.

It has a projected price of 35¢/lb. as purchased in tank cars from General Aniline and Film Corp. (Ref-21) and its high specific gravity of 1.13 further enhances its high cost.

There are two possible approaches to lower solvent cost: a cheaper solvent system, or solvent recovery by the stripcoater. For purposes of comparison, it was assumed that the formable fluoropolymer finish could be made with a solvent costing 20¢ per pound. This could be achieved by either finding a new solvent system for the finish, or by the stripcoater recovering 85% of the solvent and selling it back to Du Pont at half price, or 17.5¢ per pound. The data on Table IV illustrates the substantial savings which could be achieved with the lower solvent cost.

A graphical comparison of the relative importance of independent changes of resin and solvent cost on finish replacement cost (Figure 5) shows that the solvent is by far the more critical of the two. Even if the resin cost were to carry a full 20% return on investment with it, which it does not in Figure 5, the effect of any price change would still be less than a similar change for the solvent.

b. Finish Solids

The cost to the user of any finish is best expressed by the surface area coverage that he gets out of it. The formable finish formula used in the computations for this report (See Appendix B) contains 19.5 volume percent solids and has a coverage of only 310 $ft.^2$/gallon at one mil of film thickness. Hence, it has a relatively high cost to the user, not only because of its expensive ingredients, but also because of its relatively low coverage.

There are two possible approaches to a lower cost VF_2/TFE/BCEVP finish to the user: reformulation, and the application of thinner films. The chances of successful reformulation to higher solids are not known, at this time. However, Table IV illustrates the effect on finish and coverage cost, if 415 $ft.^2$/gal./mil could be achieved by raising the paint solids while lowering the solvent content. For purposes of illustration, the composition of the solids was not changed, only their ratio to the solvent altered. The use of this hypothetical expedient to increase the coverage one-third, reduces finish cost per unit area by 16%. If such an approach could be put into practice, substantial savings would result. By combing a 20¢/pound solvent with a 415 $ft.^2$/gal./mil coverage, a 23% saving compared to the current stripcoating finish formula could be obtained. This is also illustrated on Table IV.

TABLE IV

COST EFFECT OF CHEAPER SOLVENT AND HIGHER COVERAGE

Basis: 5 MM lbs./yr. resin production

	Sales Price of Fluoropolymer Finish ($/gal)	Coverage Cost (¢/ft.^{2}) at 1 mil
Current formula finish: 35¢/lb. solvent & 310 ft^2/gal/mil coverage	$10.94	3.5
Current formula finish with 20¢/lb. solvent & 310 ft^2/gal/mil coverage	9.41	3.0
One third higher coverage finish 35¢/lb. solvent & 415 ft^2/gal/mil coverage	12.38	3.0
Combination 415 ft^2/gal/mil coverage and 20¢/lb. solvent	11.07	2.7
Use of thinner topcoat film using tandem coat of 1/2 mil primer (0.7¢/ft^2/mil) and 1/2 mil fluoro-polymer finish	10.94	2.1

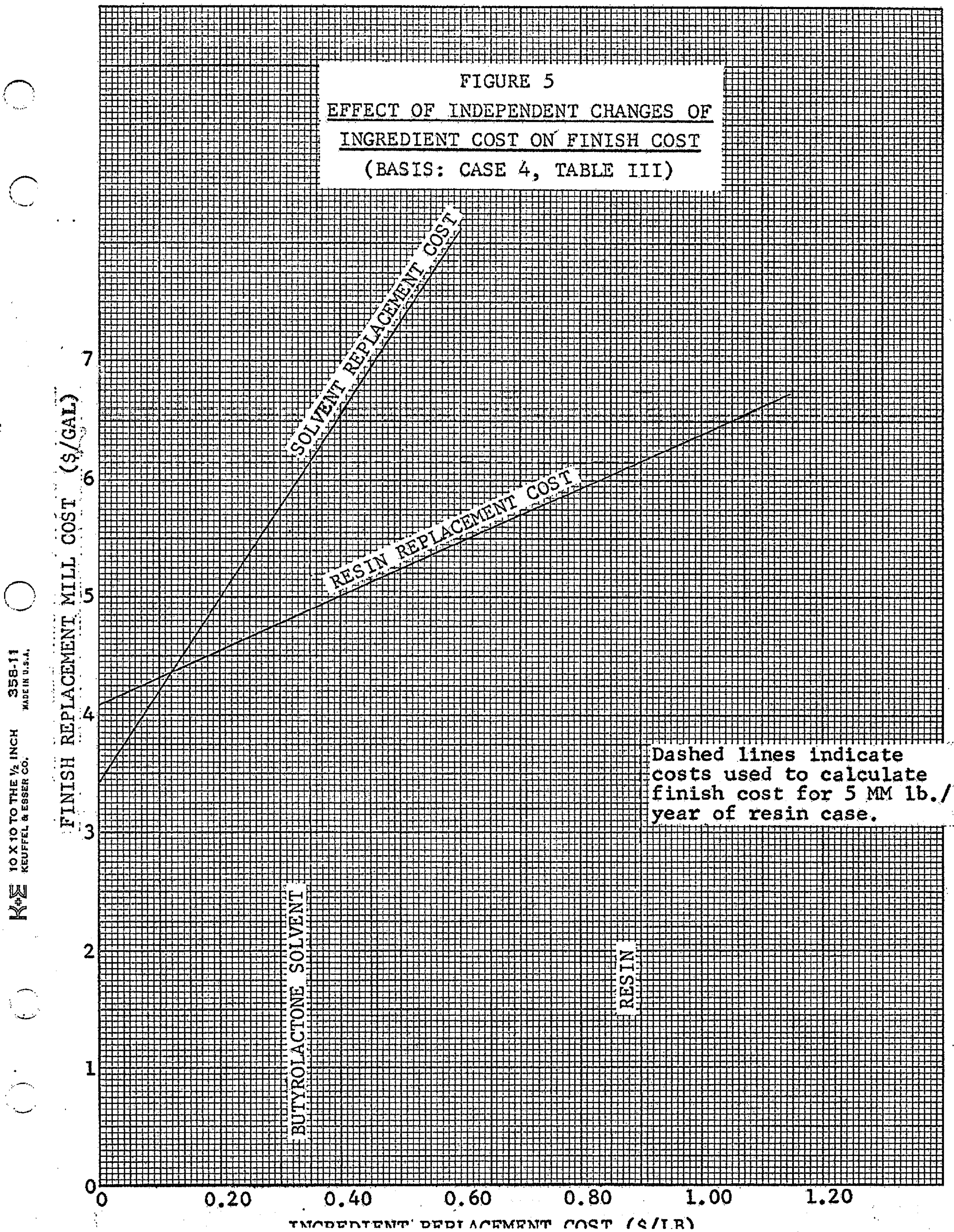


FIGURE 5
EFFECT OF INDEPENDENT CHANGES OF
INGREDIENT COST ON FINISH COST
(BASIS: CASE 4, TABLE III)
SOLVENT REPLACEMENT COST
RESIN REPLACEMENT COST
Dashed lines indicate costs used to calculate finish cost for 5 MM lb./year of resin case.
BUTYROLACTONE SOLVENT
RESIN
FINISH REPLACEMENT MILL COST ($/GAL)
INGREDIENT REPLACEMENT COST ($/LB)
0
1
2
3
4
5
6
7
0.20
0.40
0.60
0.80
1.00
1.20
10 X 10 TO THE ½ INCH
KEUFFEL & ESSER CO.
358-11
MADE IN U.S.A.

c. Thinner Films by Use of Primer

At present, the use of thinner films of fluoropolymer finish also seem a possible approach to lower coverage cost. The use of a thin coat of primer would aid in retaining the hiding power of the finish system, while possibly reducing the moisture permeability associated with the VF_2/TFE polymers. For instance, if the fluorinated topcoat were reduced from 1 mil to 1/2 mil thick, in conjunction with the use of a 1/2 mil thick coat of primer, then a cost savings of 40% could result. Table IV illustrates this effect.

Although such a scheme has not been experimentally proven so far, any commercial tandem stripcoating line should be able to apply the two thin coats of finish, without marked increase in application cost over a single coat.

IV. COST OF OTHER FLUOROPOLYMERS

Detailed cost calculations for polymers other than VF_2/TFE/BCEVP (solution process) were beyond the scope of this work. However, for purposes of comparison the estimated raw material costs of various fluoropolymers of interest are listed below:

	Company Cost Basis ($/lb. resin)	Transfer Price Basis ($/lb. resin)
Polyvinyl fluoride	0.34	0.59
Polyvinylidene fluoride	0.42	0.76
VF_2/TFE/BCEVP aqueous process	0.52	0.85
VF_2/TFE/BCEVP solvent process	0.61	0.96

The above raw material costs are approximations based on 100% resin yield and sources listed in Appendix A.

It can be seen from the data, that among the fluoropolymers of interest here, polyvinyl fluoride holds a substantial cost advantage. This advantage is further accentuated on an area coverage basis when one takes into account the low specific gravity of the PVF (1.37 versus about 1.7 for vinylidene fluoride based polymers).

D. MARKET INFORMATION

Detailed market information was sought only for those finishes whose formulations and final properties were known with some degree of confidence. It was felt that it would be wasteful and misleading to make formal market surveys for products where the necessary fluoropolymer had not been developed and where the chances of technical success were unknown. Hence, detailed market opportunity data were obtained only for the post-formable fluoropolymer stripcoating finish (Ref.-2).

However, it was felt necessary to also seek some perspective on the market possibilities for fluoropolymer finish products which have not been developed so far. This was done by combing information from Company and outside literature and through personal interviews with Company personnel.

I. MARKET SURVEY FOR FACTORY-APPLIED POST-FORMABLE FLUOROPOLYMER FINISH

The Market Research Section of the F & F Department has carried out a market survey to determine the potential of a fluoropolymer stripcoating finish in exterior applications. The results of the survey are summarized in detail in Table V (Ref-2).

The analysis of the market was based on a list of questions prepared by H. C. Place (See Appendix C). A table of fluoropolymer film properties submitted was prepared in cooperation with Research personnel. It was emphasized that the fluoropolymer finish would have excellent formability in conjunction with substantially superior durability. However, no absolute numbers were placed on finish life characteristics. Instead it was pointed out to the potential user that the fluoropolymer material would be superior by a factor of two or three times in characteristics like color stability, chalking, etc.

Thirteen companies, producing an estimated 50% of the stripcoated area, responded to the interviews. Their replies brought out the following important points:

1. Stripcoating market growth -- Continued rapid growth (about 10% per year) can be expected for the next five years in the formable finishes market.

2. Fluoropolymer stripcoating finish market potential -- The data presented in Table V summarize the market potential based on the interviews, assuming the absence of competition from a similar product. The possible penetration by fluoropolymer finishes appears highest, percentage-wise, in industrial panels. On a sales dollar basis, the biggest market opportunity exists in residential siding. Stripcoater interest in high durability finishes is less marked in mobile homes, and non-existent for awnings and patios.

TABLE V

SUMMARY OF THE MARKET OPPORTUNITY FOR A POST-FORMABLE
FLUOROPOLYMER STRIPCOATING FINISH AT SELECTED PRICE LEVELS* (REF-2)

	Market Potential (MM Sq. Ft.)	Market Opportunity					
		Percent Penetration		$MM Sales		Gallons of Finish	
		at 2¢/ft.^{2}	at 4¢/ft.^{2}	at 2¢/ft.^{2}	at 4¢/ft.^{2}	at 2¢/ft.^{2}	at 4¢/ft.^{2}
Industrial and Commercial Panels							
1963	195	57	36	2.2	2.8	350 M	230 M
1968	315	57	36	3.6	4.5	580 M	360 M
Residential Siding							
1963	630	28	20	3.5	5.0	560 M	400 M
1968	990	28	20	5.5	7.9	890 M	640 M
Mobile Homes							
1963	132	18	2	0.5	0.1	80 M	8 M
1968	213	18	2	0.8	0.1	130 M	8 M
Awnings, Car Ports, Patios							
1963	113	0	0	0	0	0	0
1968	163	0	0	0	0	0	0
TOTALS							
1963	1070	-	-	6.2	7.9	990 M	638 M
1968	1681	-	-	9.9	12.5	1600 M	1008 M

*Finish cost to the user expressed in ¢/ft.^{2}/mil.

The estimates of potential sales revenues from the fluoropolymer stripcoating finish in 1963 and 1968 are higher at the 4¢/ft.^{2} level than at 2¢/ft.^{2}, indicating that demand is relatively inelastic at this price range, i.e. a price reduction does not necessarily result in increased sales revenue.

3. Substrates -- Aluminum is the predominating substrate in the two largest areas of the market, since it is used in almost all residential siding production. However, galvanized steel which is used in 90% of the industrial and commercial panels is also important, so that fluoropolymer finish systems will have to be developed for both substrates to capture a maximum of the market potential. A recent article has mentioned that U.S. Steel Corp. is seeking to enter the residential siding field with galvanized steel, which is potentially cheaper than aluminum, and less subject to be noisy due to thermal expansion and contraction (Ref.-20). A concerted campaign for steel use in residential siding, may cause aluminum to lose its preeminence, further emphasizing the need for fluoropolymer stripcoating finishes for both important substrates.

4. Customer Satisfaction with Existing Finishes -- Stripcoaters are generally satisfied with application and cure properties of existing finishes. However, they express dissatisfaction with short-term and long-term durability of the product.

There is a strong differentiation between long-term and short-term durability. The latter deals primarily with extension of the original finish apppearance (color, gloss, dirt pick-up, mildew) from the present three years to ten years. This is of greatest interest to producers of residential siding and mobile homes, since average residence occupancy is only 7 to 8 years. Long term durability, on the other hand, deals with substrate protection and film integrity. Stripcoaters would like to see this extended from the existing 15 year level to 25 years to reduce maintenance costs. A combination of long-term and short term durability is considered most important for commercial and industrial panels.

5. Competition from Other Products -- Strong interest was expressed by stripcoaters in potential fluoropolymer liquid finishes that have properties comparable to "Tedlar" film, in order that they may obtain the excellent durability without making the equipment alterations required for lamination.

Among potentially competitive coating materials mentioned by the industrial contacts are Hypalon®, a vinyl residential siding sheet by Monsanto, and experimental fluorocarbon finishes produced by three other companies (Pennsalt, Thiokol, and an unknown company). Competitive materials will be discussed in more detail in section F, of this report.

a. Conclusions based on Fluoropolymer Stripcoating Finish Market Survey

The following conclusions on fluoropolymer finish opportunities can be drawn from the Market Research Section report (Ref.-2):

1. A substantial market potential exists for fluoropolymer finishes in formable finishes for exterior use.

2. If Du Pont captures a fraction, say 25%, of the indicated potential, this, by itself, will not be enough to justify construction of a fluoropolymer plant. The current finish contains 2.3 lbs. of fluoropolymer per gallon, and if the Company captures 25% of the most optimistic situation on Table V, this would require only 920,000 pounds of resin per year. At that rate of polymer production it would be hard to produce a finish costing 4¢/ft.^{2}/mil, not to speak of 2¢/ft.^{2}/mil with a full 20% return on investment: Therefore, additional outlets will have to be found for the same, or related resins, to justify construction of a commercial plant.

3. The fluoropolymer finish will have to be developed to be usable for use on both aluminum and galvanized steel substrates.

4. When introduced into the trade, the fluoropolymer finish may be faced with competition from similar finishes, as well as durable films.

II. INDUSTRIAL MAINTENANCE FINISHES

A substantial market opportunity may exist for an air-drying* fluoropolymer industrial maintenance finish provided the following important favorable finish attributes are obtained:

1. Outstanding corrosion protection and resistance to weathering either by itself, or in combination with a suitable primer.

2. Unusual resistance to chemical attack.

3. Application properties similar to existing maintenance finishes.

It must be recognized that none of the above attributes, with the exception of weathering resistance, have been demonstrated in the existing VF_2/TFE/BCEVP formable finish. Since no acceptable air-drying fluoropolymer system has been developed so far,

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*Air-drying in this case refers to drying by solvent evaporation.

no formal market survey has been carried out and no attempt will be made here to forecast the size of the market for fluoropolymer maintenance finishes. Instead, we will try to point to areas of market potential which would benefit from the expected long repainting cycles and which could possibly absorb the high cost of the finish. Much of the data discussed here originate from the report on potential markets for V54 by Merchant and Tallman (Ref. 7). The opinion of Company authorities in industrial maintenance have been used to shape some of the conclusions (Ref. 8).

a. Major and Minor Bridges

Estimated size of finish market in 1965 (Ref-7):

Primer:	
New Construction	2.4 MM gallons/year
Maintenance	1.5 MM " "
Total Primer	3.9 MM " "
Topcoat:	
New Construction	2.9 MM gallons/year
Maintenance	3.4 MM " "
Total Topcoat	6.3 MM " "
Total finish	10.2 MM gallons/year (60 vol. % solids)

Potential market for fluoropolymer maintenance finish, assuming an acceptable air-drying system is developed -- probably most of the above.

Estimated size of the market, fluoropolymer finish cost considered -- unknown.

Rate of expected market penetration if a product is developed -- slow.

Status of research on product -- not started.

Discussion -- Harrison and de Vries have shown that the economics of premium maintenance finishes are quite attractive on both major and minor highway bridges (Ref-4), because such structures generally are publicly financed at low rates of interest and because no taxes have to be paid on the savings resulting from improved maintenance efficiency. However, the extent to which a fluoropolymer maintenance finish would penetrate the bridge maintenance field would, in part, depend on the following technical and economic factors:

For new construction:

1. The improved durability of the finish and the savings resulting from longer repaint cycles.

2. The possibility of using thinner finish films because of the better resistance to weathering and the savings resulting from the use of smaller quantities of paint.

3. The political implications involved in reducing labor requirements and buying an expensive product to achieve this.

4. The purchase of maintenance finishes for public structures by open bidding. This would work against the introduction of a high cost premium finish.

For maintenance:

1. Whether the fluoropolymer finish is compatible with conventional finish systems would determine the maintenance use at early stages.

2. At later stages the growth of fluoropolymer maintenance finishes on bridges would be determined by their acceptance in new construction.

3. All the factors mentioned under "new construction" also hold.

In view of the conditions mentioned above, it is felt that a lengthy educational and testing program will be required, before any broad acceptance of fluoropolymer finishes on highway bridges can be expected. The acceptance of a premium finish on railroad bridges is considered unlikely (Ref-3).

b. <u>Chemical Plants</u>

<u>Estimated size of maintenance finish market</u> --

	Gallons of Paint Per Year (Ref-7)	
	Primer	Topcoat
New Construction	1,250 M	1,750 M
Maintenance	500 M	2,000 M
Total	1,750 M	3,750 M

(at 50 vol. % solids)

Sales of maintenance finishes to chemical plants amounted to $13 MM for the year 1962 (Ref-8).

Potential market for an air-drying fluoropolymer finish -- probably most of the above.

Estimated size of the market fluoropolymer finish cost considered -- thought to be economical for use in corrosive atmospheres only, which are estimated to amount to only 10% of the painted area of chemical plants. Therefore, the market potential, cost considered, may be around 500 M gallons per year, taking into account longer repainting cycles.

Rate of expected market penetration once product is developed -- dependent on the rate at which maintenance engineers can be convinced of the utility of a fluoropolymer finish. Penetration may be fairly rapid for severe environment because proof of product superiority can be achieved in less time.

Status of research on product -- not started.

Discussion -- There is a trend toward improved coating systems and longer service life in the chemical industry (Ref-7). Finishes are needed to withstand some highly corrosive situations, but it has been estimated by Industrial Maintenance Sales Management that these amount to only about 10% of the surface area of chemical plants (Ref-8). It is in these specific areas where fluoropolymer finishes would find the most use. Harrison and de Vries have shown mathematically that a premium maintenance system can be economically justified only in severe environment areas of chemical plants. (Ref-4).

c. Petroleum Refineries

Estimated size of finish market --

	Gallons of Paint per Year (Ref-7)	
	Primer	Topcoat
New Construction	550 M	850 M
Maintenance	300 M	2,900 M
Total (50 vol. % solids)	850 M	3,750 M

Sales of maintenance finishes for petroleum refineries amounted to $10 MM for the year 1962 (Ref-8).

Potential market for fluoropolymer maintenance finishes -- probably most of the above.

Estimated size of market, fluoropolymer finish cost considered -- the same comments hold as for chemical plants. Thought to be economical only on areas subject to severe corrosion (Ref-4), about 10% of the total area (Ref-8) or about 450 M gallons per year, taking into account longer painting cycles.

Rate of expected market penetration once product is developed -- same as for chemical plants.

Status of research on product -- not started.

Discussion -- In this area too there is a trend to improved finish systems with longer life (Ref-7). Penetration will depend on our ability to convince maintenance engineers of the superior economics of our product.

d. Pipelines, Exterior Protection

Estimated size of finish market -- 750,000 gallon/year potential at 2 mils thick, 50 vol. % solids, new construction only. (Ref-7).

Potential market for fluoropolymer maintenance finish- if moisture permeability problems of fluoropolymers are solved, most of the market.

Estimated size of the market fluoropolymer finish cost considered -- unknown.

Rate of expected market penetration once product is developed -- unknown.

Status of research on product -- none started.

Discussion -- Pipelines present unusually severe acid or alkaline corrosion problems because they are buried in damp soil. Since it is uneconomical to unearth pipelines for repainting, elaborate precautions are being taken to protect them from corrosion. These include combinations of primers, bituminous coatings, anodic protection and an external wrap. A recent development uses a continuously extruded polyethylene covering over a mastic prime coat (Ref-9). A dependable finish which could simplify this protection at lower cost could undoubtedly capture a substantial market.

e. Pipeline Interiors

Estimated size of finish market -- unknown, but could be substantial.

Potential market for fluoropolymer finish -- entire market, provided necessary balance of durability, smoothness and corrosion resistance is achieved.

Estimated size of market, fluoropolymer finish cost considered -- unknown.

Rate of market penetration once product is developed-- unknown.

Status or research on product -- none.

Discussion -- Considerable savings to pipeline operators can be achieved by presenting a smooth surface to the flow inside pipelines, thereby lowering pumping costs. This property in combination with good corrosion resistance,could provide a substantial market for a suitable finish.

f. Other Petroleum Industry Applications

It is doubtful that there is any large market for high cost, high durability fluoropolymer finishes in other areas of the petroleum industry, such as drilling and producing. Drilling equipment generally has a relatively short life, making a high cost finish impractical. Producing and storage equipment falls into the same category as "average environment" chemical plants and therefore is also an unlikely market for fluoropolymer finishes. Offshore drilling equipment requiring protection from severe salt water corrosion may be a market of unknown size for fluoropolymer maintenance finishes.

g. Shipbuilding and Ship Maintenance

Even though this is a large market for paints of various kinds (6.3 MM gallons/yr. for commercial vessels at 60% solids - Ref.-7), it does not seem to be suited for a high durability, high cost finish, except for limited applications. For instance, most ships suffer enough damage to the hull between annual drydockings,that it is necessary to do so much repainting that a premium high durability finish would not be economically worthwhile. Most accessible parts of the ship are painted periodically by the crew while at sea, so that a reduction of labor costs is not an important factor. The only area of potential for fluoropolymer finishes would be the less accessible parts of the superstructure, and hull interiors subject to severe corrosion amounting to possibly one-tenth of the ship for a potential market of about 600 M gallons per year (or about $1.5 MM in sales according to Ref-8).

However, an interesting possible application for high durability fluoropolymer finishes would be the holds of oil tankers. Severe corrosion problems exist, due to the transportation of sour crudes, or fillings with salt water for ballast, etc. In addition, recent trends have been to ship a variety of cargoes in tanker holds. Currently, coatings of "Saran" dissolved in methyl ethyl ketone are being used with an expected life of ten years. However, they are very hazardous to apply, requiring 58 days for a 16,000 ton tanker, during which no other work can be done (Ref-7).

Using a fluoropolymer finish, ten mils thick for this application, at 50 vol. % solids, it is estimated that a market of 160 M gallons per year exists (Ref-7). However, an outstanding finish of this sort could probably be exported widely for the larger foreign fleets, thus increasing the size of the potential market.

h. <u>Electrical Transmission Tower Paint</u>

<u>Estimated size of finish market</u> -- 1.5 MM gallons/ year (Ref-10).

<u>Potential market for fluoropolymer finish assuming an acceptable air-drying system is developed</u> -- a sizeable portion of the above, especially for use in industrial, high humidity, and salt spray atmospheres.

<u>Estimated size of market, fluoropolymer finish cost considered</u> -- unknown.

<u>Rate of expected market penetration if a product is developed</u> -- probably slow.

<u>Status of research on product</u> -- none started.

<u>Discussion</u> -- There seems to be a substantial market for an outstanding maintenance paint for electrical transmission towers. New towers are generally built of galvanized steel, which will require repainting 8 to 35 years after installation, depending on atmosphere. The finish desired should protect weathered galvanized steel surfaces for 8 - 10 years in industrial or seashore atmospheres and for at least 15 years in rural areas (Ref.10). In addition to normal atmospheric deterioriation, the flexing of towers and electrolysis are constant problems.

The ideal finish for transmission towers should have high build, easy application, overnight dry, and should not crack or check on aging. Ordinary galvanized metal primers containing metallic zinc, generally are unsatisfactory because they require frequent mixing, an aspect difficult to control among most painters (Ref.10). The suggested mill cost for a new finish is $4.50 per gallon (Ref.10), but a more expensive product may be acceptable, provided it has the necessary favorable attributes.

i. Miscellaneous Industrial Maintenance Applications

Other applications have been suggested for a fluoropolymer maintenance finish. These are primarily dependent on chemical and abrasion resistance. For instance, a good liner for railroad hopper cars is needed to prevent product contamination or car corrosion. Possibly 50,000 such cars could use 15 gallons of finish each (Ref-8) for a total of 750,000 gallons. It is not known how frequently this business would be repeated.

Currently "Kynar," Pennsalt's polyvinylidene fluoride, is being advertised as a protective interior pipe coating material. A highly resistant VF_2/TFE polymer film could be suitable for the same use, possibly eliminating corrosion resistant alloys in some process piping applications.

Corrosion and abrasion resistant coatings are needed for the interior of floating roof storage tanks handling sour crudes and other petroleum products.

An improved finish having superior color and gloss retention is needed for locomotives. This,however, is felt to be a small market.

Overall, it is doubtful that the above mentioned miscellaneous areas would contribute much to the development of a market for fluoropolymer maintenance finishes.

j. Summary

The limited knowledge of potential markets for an air-drying fluoropolymer maintenance finish is summarized on Table VI. The size of the total market was generally based on Company information (Ref. 7 and 8). The potential fluoropolymer maintenance finish markets assumed that an air-drying finish could be developed having excellent weathering resistance, superior resistance to chemical attack, good corrosion protection, and standard application properties for the market segment being considered.

Although, having the above properties, a fluoropolymer finish could be suitable for much of the industrial maintenance market, the cost considered sales potential seems less promising. It is felt that such a premium finish would be commercially accepted only for the following reasons (Ref. 3 and 4):

1. If no other product can now provide the necessary protection.

2. If cost to the user can be substantially reduced by providing superior corrosion protection, lengthening repainting cycles, and decreasing down-time.

TABLE VI

SUMMARY OF MARKET POSSIBILITIES FOR A FLUOROPOLYMER MAINTENANCE FINISH

	Size of Total Market (Gals./Yr.)	Possible Fluoropolymer Finish Market* (Gals./Yr.)	Potential Fluoropolymer Finish Market Cost Considered (Gals./Yr.)
Major and Minor Bridges	10.2 MM	ca. 10 MM	
Chemical Plants	5.5 MM	ca. 5.5 MM	0.5 MM (?)
Petroleum Refineries	4.6 MM	ca. 4.6 MM	0.45 MM (?)
Pipeline Exteriors	0.75 MM	ca. 0.75 MM	
Pipeline Interiors	?		
Marine, Exterior	6.3 MM	ca. 6.3 MM	0.6 MM (?)
Marine, Holds	0.16 MM	ca. 0.16 MM	
Electrical Transmission Towers	1.5 MM	ca. 1.5 MM	
Miscellaneous:			
Locomotives	0.3 MM		
Hopper Car Linings	0.75 MM		
Floating Roof Tanks	?		

*Assumes properties of Section D-II are attained.

III. INDUSTRIAL FINISHES

As in the case of industrial maintenance finishes, it was not possible to define market potentials for industrial finishes because suitable fluoropolymer products have not been developed. The only exceptions are post-formable finishes applied on aluminum and steel sheet by stripcoating, which are discussed in detail in Section D-I this report. Since one cannot generalize the property requirements of a fluoropolymer industrial finish, they will be listed individually for each end-use discussed. However, in every area, excellent weathering resistance manifested in long finish life, and outstanding color and gloss retention, are prime criteria for successful sale of the high priced fluoropolymer finish.

a. Pigmented Factory-Applied Finishes for Wood and Other Cellulosic Substrates

Estimated size of the market -- thought to be 400 MM ft^2 for a finish costing between 5 and 8-1/2¢/ft^2 (Ref.-11). Converting this to a $12 per gallon finish having 400 ft^2/gal./mil coverage andusing a 2 mil film, the market amounts to 2.0 MM gallons or $24 MM annually.

However, it is felt, that the wood industry would prefer not to spend more than 5¢/ft^2, including application costs.

Potential market for a fluoropolymer finish -- unknown.

Estimated size of the market, fluoropolymer finish cost considered -- unknown.

Status of research on product -- only preliminary work carried out. Finish failed by cracking after 1500 hours of accelerated weathering, but was essentially free of chalking. The work has been discontinued due to reassignment of personnel.

Discussion -- The size of the wood siding market has been shrinking steadily as it is being replaced by aluminum in this end-use. This trend could possibly be reversed with the development of a suitable durable prefinishing material for wood. The product desired not only would have to be highly durable (gloss and color retention), it should dry with only a brief bake at relatively low temperatures, and it should resist the deformation of the relatively unstable wood substrate as it is exposed to the weather.

Evidence of the lumber industry's interest in a durable prefinish material may be seen in a recent advertisement by the Weyerhauser Co., introducing a completely prefinished wood siding "guaranteed not to require repainting for at least seven years" (Ref. 12). This four mil thick finish consists of a blister resistant alkyd primer with a baked acrylic topcoat.

The Film Dept. is also seeking to enter this field with "Tedlar" PVF film.

b. Clear Finishes for Wood

Estimated size of market -- 2.2 MM gallons/year (a figure thought to be highly optimistic, Ref. 13).

Potential market for a fluoropolymer finish -- unknown.

Estimated size of the market, fluoropolymer cost considered - unknown.

Status of research on product -- in early stages. Difficulties are being encountered with poor adhesion to the wood.

Discussion -- Currently use of clear finishes on wood for exterior use is limited because of short life and difficulties associated wiih refinishing. If a finish were developed, which would protect the substrate for several years without discoloration or cracking, then a new market could open up as acceptance is gained by builders and architects. Clear baking finishes would have to be developed for factory application, as well as a trade sales item usable for repair and repainting.

c. Clear and Pigmented Factory Applied Finishes for Aluminum (Other Than Stripcoating)

Little or no market is visualized in protective fluoropolymer finishes for aluminum in areas of current use, such as storm doors, windows, and extruded shapes because of the high anticipated price. There is a possibility, however, that a fluoropolymer finish, clear or pigmented, may be acceptable for protective and decorative outdoor use in applications such as garden and beach furniture. Orchem is also considering the use of a protective coating for aluminum conduits buried in concrete, which currently are subject to severe alkaline deterioration. Indications are that this latter market would amount to only 40 M gallons per year at 1 mil (Ref. 14). Altogether, the aluminum protective and decorative market, outside of formable finishes, does not seem very lucrative for a fluoropolymer based finish.

d. Can and Drum Coatings

Sanders and Gebhard (Ref. 13) have calculated a value in use for TFE of greater than $1.24 per pound in an interior topcoat for beer and beverage cans, provided it replaces the tin and the interior topcoat with no loss in functionality. On the same basis, one may be able to justify a coating based on VF_2/TFE polymer, especially in view of the lower projected VF_2 cost compared to TFE.

Since no research with fluoropolymers has been carried out in this area there is no possibility in determining the market potential, property and cost considered. A finish with the properties generally attributed to fluoropolymers may also be a suitable replacement for stainless steel or specially lined drums.

e. Coatings for Process Pipe Interiors and Exteriors

Pennsalt is currently seeking to penetrate this market with its "Kynar" polyvinylidene fluoride resins. There is no reason to believe that the same results could not be achieved with other fluoropolymers which can be applied in liquid form or by extrusion. The size of this market is unknown. However, a fluoropolymer coating free of imperfections can conceivably be used in applications currently requiring alloy piping to prevent corrosion or to maintain product purity standards.

IV. AUTOMOTIVE FINISHES

In view of the cost consciousness of automobile manufacturers, there is little reason to believe that a fluoropolymer finish of excellent durability could penetrate the new car market, unless it brings with it a saving in finish plus application cost. According to Sanders and Gebhardt (Ref. 13), a fluoropolymer automotive topcoat containing 50% TFE would have a value in use for TFE between 0.00 and $0.40 per pound of TFE. This obviously eliminates most any kind of fluoropolymer finish from the conventional primer plus topcoat system. On the other hand these same authors feel that if a primer-less finish system is developed, the TFE would have a value-in-use between $0.87 and 1.04 per pound. Such a major technical development would make a fluoropolymer finish an important contender for this lucrative market.

In view of the limited durability required in the automotive refinish market, it is unlikely that there will be any interest for fluoropolymer finishes in this area, unless they are introduced at equal or lower cost of materials and labor, as compared to finishes currently in use.

a. Truck Trailer Bodies

There is a need for a clear product to protect aluminum trailer truck bodies from corrosion, erosion, and general deterioration of appearance. The market potential estimated at between 100 and 150 M gallons per year for new equipment. (Ref. 15). There may also be some interest in refinish and touch-up materials. It is felt that a fluoropolymer finish could fill this need.

b. Automotive Chrome Protection

There has been a long-standing need for a protective finish to improve the appearance and life of chrome plated automobile parts. In addition to resisting corrosion, the finish would require excellent adhesion, clarity, abrasion resistance and long life. In combination with reduction of chrome thickness requirements, it might be economically attractive to automobile manufacturers.

Assuming a chrome area of eight square feet per car, and a film thickness of one mil, there may be a market potential of over 100 M gallons per year.

V. TRADE SALES FINISHES

There is little likelihood that fluoropolymer finishes will have much appeal in the trade sales finish area. The improved durability generally cannot be justified by the increased cost of the finish except in a few special areas listed below:

a. Clear Wood Finish

This area of market potential has already been partially discussed under industrial finishes. It is not known whether a trade sales clear finish will receive wide acceptance. It should be noted that our current product entry into this market, "Ultra V" spar varnish, has only a very limited sales. Undoubtedly, a fluoropolymer finish will be very similar in price, although possibly superior in properties.

b. Swimming pools

A product is badly needed in this rapidly growing field to give several years of protection to the surfaces of concrete, steel or aluminum swimming pools. It has been estimated that in 1970 with 1.4 MM paintable pools there will be a 1.2 MM gallon annual market for a fluoropolymer finish which lasts for five years (Ref. 13). It is not known at this time, whether an air-drying finish can be developed to satisfactorily fulfill this requirement.

E. PATENT SITUATION

Du Pont currently has a proprietary position in VF_2 polymer and copolymers with TFE, but the pertinent patent (U.S. 2,468,664) will expire April 26, 1966. At present, Pennsalt is licensed under U.S. 2,435,537 (expiration Feb. 3, 1965) to make, use, and sell vinylidene fluoride homopolymers, while Minnesota Mining is licensed to produce copolymers containing 5 to 95 mol percent each of trifluorochloroethylene and vinylidene fluoride under U.S. 2,435,537 and 2,468,054. There are no significant basic patents relating to VF_2 issued to competition, but some more specific ones have been issued to Minnesota Mining, Kellogg, Pennsalt, Monsanto, and U.S. Rubber. The patent situation on copolymers containing VF_2 is described in more detail in two letters from C. E. Bartsch to C. W. Theobald, January 18, 1963, and February 1, 1963. (Ref. 16)

Coverage is being sought for the hook type VF_2/TFE copolymers in OR-3694 (Serial No. 286470 filed June 10, 1963) which deals with compositions of the type: more than 60% VF_2, 0.5 to 39.9% TFE, and 0.1 to 10% "hook."

The special pigmentation procedures used to stabilize fluorocarbon polymers containing inorganic pigments are covered in FFD-1194 (Serial No. 291279 filed June 28, 1963). This application covers the use of acrylic resins adsorbed on the pigments. FFD-1184 is a closely related case referring to universal tinting bases.

F. COMPETITIVE MATERIALS AND APPLICATION TECHNIQUES

This discussion will be limited to materials and techniques competitive to the use of a long durability fluoropolymer finish applied to a substrate by stripcoating.

I. "TEDLAR" POLYVINYL FLUORIDE FILM

"Tedlar" PVF film is the only known commercial material that has weathering resistance similar to that anticipated for the formable finishes containing VF_2/TFE/BCEVP polymer. It is a pigmented film made with a polyvinyl fluoride binder, currently sold in 1.7 and 2.0 mil thicknesses, in eight colors. In addition, it is available as a clear film in thicknesses from 0.5 to 2.0 mils. "Tedlar" can be laminated to a wide variety of metallic, cellulosic and plastic substrates by using appropriate adhesives. It can also be used as an unsupported film, where desired. At present, "Tedlar" is in the early stages of production in a commercial plant.

Some cost data on "Tedlar" coverage were prepared by the Film Department (Ref. 6). From the summary presented in Table VII, it will be seen that the material cost to the user for "Tedlar" is generally higher than comparable costs for a formable finish formulated with VF_2/TFE/BCEVP copolymer. The fluid finish costs data presented are conservative in that a full 20% return on investment was assumed for all the departments involved in the manufacture of raw materials, resin and finish. A cost of 0.6¢ per square foot for adhesive was added to the "Tedlar" cost to obtain a total finish material cost, and efficiency factors suggested by the Film Department were used. No comparison of application cost was made, because they are not known for "Tedlar" with any degree of certainty. However, it is felt that the application costs for the PVF film will not be lower than for the fluid formable finish, as the processes are quite similar. The 1.0 mil "Tedlar" film included in this cost comparison, is not commercially available. A high pigment to binder ratio PVF film will have to be developed before the thin film is saleable.

TABLE VII

COMPARATIVE MATERIAL COSTS TO THE USER
VF_2/TFE/BCEVP FORMABLE FINISH AND "TEDLAR" PVF FILM

Material	Thickness (mils)	Sales Price ($/lb. or $/gallon)	Material Cost (¢/ft²) Film (Note 3)	Adhesive	Total
"Tedlar" (1963 Price-Ref. 6)	2.0	4.50	8.8	0.6	9.4
	1.7	4.50	7.0	0.6	7.6
"Tedlar" (at Plant capacity - Ref. 6)	2.0	3.25	6.4	0.6	7.0
	1.7	3.25	5.1	0.6	5.7
	1.0 (Note 1)	2.81	2.9	0.6	3.5
VF_2/TFE/BCEVP formable finish (polymer plant at 20% of capacity) (See Note 2)	1.0	18.46	6.3	---	6.3
VF_2/TFE/BCEVP formable finish (polymer plant at capacity) (See Note 2)	1.0	10.94	3.7	---	3.7

Note - 1 1.0 mil "Tedlar" not available commercially. Film Department "believes that this film could be produced within the next several years." (Ref. 6)

Note - 2 Finish cost based on Company cost plus 20% return on rolled-up investment.

Note - 3 Assumes 85% material efficiency for "Tedlar" and 95% for liquid finish.

Only limited recent market opportunity and sales projection information on "Tedlar" has come to the attention of the writer (Ref. 17). The data listed on Table VIII indicate a very large total market, which in essence is the total area which could be covered with "Tedlar" disregarding price and properties. For instance, in the case of new residential siding this includes the outside area of all new housing construction independent of siding material used (brick, wood, asbestos, stucco, aluminum and other materials). These data for the total residential siding market agree closely with those reported by Place (Ref. 2). The "Tedlar" market potential at 4 to 5¢/ft^2, converted to coverage area for easier translation to finish potential, undoubtedly includes the use of "Tedlar" on wood siding as well as metallic substrates. Therefore this information is not directly comparable to the data obtained by Place for stripcoating fluoropolymer finish on metal. However, adding the "Tedlar" potential market information for industrial siding, residential siding, and panels we obtain an area of 1056 MM ft^2, which is remarkably to the market potential reported by Place (See Table V). The 1967 "Tedlar" sales projections in areas of interest in this report are equivalent to about 0.95 MM gallons of liquid finish calculated on 310 ft^2/gal./mil coverage.

An older market survey for "Tedlar" on exterior siding carried out in 1960 by Alderson, Assoc. (Ref. 22) present a much more conservative outlook. For exterior siding applied on aluminum and steel, they predict the following "maximum sales potentials" for the year 1965: 65.7 MM $ft.^2$ at 4.2¢/$ft.^2$, and 160.5 MM $ft.^2$ at 3.0¢/$ft.^2$ material cost. This in terms of a stripcoating finish would be equivalent to 210 M gallons and 550 M gallons respectively. These market opportunity figures fall considerably below those obtained recently by Place (Ref. 2). No attempt will be made here to rationalize these conflicting forecasts.

II. POLYVINYLIDENE FLUORIDE FINISHES

The Pennsalt Co. has been licensed by Du Pont to make, use, sell and transfer vinylidene fluoride homopolymers (Ref. 16) and is currently seeking to introduce this product to the market under the trade name of "Kynar." These PVF_2 polymers are available in dispersion and solution form, and efforts are being made to use the product in finishes and pipe linings, among others.

Polyvinylidene fluoride polymers have some advantages over VF_2/TFE and PVF polymers:

1. PVF_2 polymers are potentially somewhat cheaper than VF_2/TFE because of the higher projected price of TFE.

2. "Kynar" dispersions have more uniform particle size than PVF "Tedlar" dispersions, and hence may permit higher solids levels and flow properties in organosol finishes.

TABLE VIII

"TEDLAR" MARKET OPPORTUNITY (REF. 17)
(MM SQUARE FEET)

(Assumes average film thickness of 1.8 mils*)

End Use	Total Market	Opportunity at 4-5¢/ft.^{2} to the user**	1967 Sales Projections
Roofing	13,650	113	53
Industrial Siding	2,325	300	75
Residential Siding			
Replacement	450	150	71
New	2,325	638	105
Building Panels	225	68	36
Pipe Insulation	60	15	8
Release Coating	75	38	21
Original Equipment	?	?	21
Miscellaneous	150	113	68
	19,260	1,435	458

*75 ft.^{2}/pound coverage

**cost of "Tedlar" plus adhesive. This column had the caption "Potential at 4-5¢/ft.^{2} to the user" on the chart distributed by the Film Dept.

3. The lower melting point of PVF_2 as compared to PVF may also aid in making coherent films in the baking process.

On the other hand, PVF_2 has some severe disadvantages:

1. Its high specific gravity compared to PVF (1.75 vs. 1.37) accentuates the price disadvantage of PVF_2.

2. PVF_2 is soluble in only few solvents (dimethyl acetamide, dimethyl formamide) which are not suitable for finishes, and hence can be used only where polymer solubility is not needed.

3. At present, finishes made with "Kynar" are less durable and stable than those made from VF_2/TFE/BCEVP solution polymers. However, additional research may decrease this difference.

The use of "Kynar" in liquid finishes is a potential source of competition from outside the Du Pont Company. In fact, Pennsalt has submitted experimental finishes for industrial evaluation. In addition, it is known that the Thiokol Corp., and an "unknown" company have been testing fluoropolymer finishes (Ref. 2). The "unknown" company may be Wisconsin Protective Coating Corp. which claims to have developed a finish based on vinylidene fluoride (Ref. 23). In view of this, there is ample reason to believe that with know-how in the formulation of vinyl finishes, vinylidene fluoride homopolymers can be used to develop competitive fluoropolymer organosol paints at an early date.

III. EXTRUSION COATING

Extrusion coating on metallic or cellulosic substrates may be competitive with stripcoating for the deposition of post-formable films. Considerable interest is being shown in this type of process by the Plastics and Organic Chemicals Departments. In essence, it consists of extruding a thin film of molten plastic which is subsequently chilled and pressure bonded to the substrate. There is considerable indication that extrusion coating may be potentially cheaper than stripcoating, because it eliminates the need for a solvent in the finish, and because it apparently requires lower investment for equipment. In addition, extrusion coating equipment is anticipated to run at much higher speeds than comparable strip-coaters. Table IX lists some of the comparable information.

The most important characteristics needed in polymers used for extrusion coating are "melt strength," a low enough melting point so that the hot extruded polymer will not degrade, and the desirable end-properties after application. "Melt strength" is the requirement for the molten polymer film to maintain integrity and some degree of uniformity, while it is being drawn away from the extrusion die by the rapidly moving substrate. Recent tests by Orchem personnel have shown VF_2/TFE and TFE/isobutylene copolymers to be promising candidates for this coating application.

TABLE IX

COMPARISON OF STRIPCOATING AND EXTRUSION COATING

	Stripcoating	Extrusion Coating
Operating speeds	80-110 ft./min.	350 ft./min. process with polymer "A" on aluminum. Hope to achieve speeds of 1000 to 2000 ft./min.
Permanent Invest.	$100-125 M for 20" wide	$120 M (Ref. 18) for 300 ft./min.
	$600 M for 60" wide The above for aluminum coating, steel coating equipment costs up to 50% more. (Ref. 25)	$275 M for 1000 ft./min. 30" wide. (Ref. 18)
Coating Material Cost	-----	Less by cost of solvent used in liquid finishes for the same polymer composition.

BIBLIOGRAPHY

(1) Theobald, C. W., Letter to G. T. Vaala, "Finishes from Fluorinated Polymers", File 5305, 8/9/63.

(2) Place, C. H., Marketing Research Section, F. & F. Department Report #3-59, "The Sales Potential for V-T Fluorocarbon Finish in Exterior Applications", January, 1964.

(3) Harrison, J. R., and F. W. DeVries, "The Opportunity for Long-Life Maintenance Finishes for Structural Steel", Elchem Report 10/16/63.

(4) Harrison, J.R., and F. W. De Vries, "The Permissible Cost of Maintenance Finishes as a Function of Durability", Elchem Report 10/28/63.

(5) Quattlebaum, J.M., to W. W. Ranson, Organic Chemicals Dept. Memorandum "Vinylidene Fluoride/Tetrafluoroethylene/Hook Terpolymer Costs" 7/17/63.

(6) T. B. Carvalho to C. E. Dengler, Film Dept. Memorandum "VF_2, PVF, and "Tedlar" Prefinished Metal Strip - Economic Analysis" 9/18/63.

(7) Merchant, E. Jr., and Tallman, J.C., "Potential Market for V54 in Four Selected Industries", F & F Marketing Research Division Report #0-34, February, 1961.

(8) Rode, J.D., Personal Communications, 1963.

(9) "Chemical Engineering", 70, #26, page 34, Dec. 23, 1963.

(10) Bradley, R.O., Letter to J. A. Klacsmann, "Transmission Tower Paint", October 4, 1963.

(11) Strehlau, D. R., F & F Research Report R-62-88, Dec. 7, 1962.

(12) "Chemical Engineering", 70, page 98, Sept. 16, 1963.

(13) Sanders, P.F., and J. C. Gebhard, F. & F. Research Report R-62-40, May 28, 1962.

(14) Woods, W.S., Personal Communication, 10/8/63.

(15) Rowe, E. W., Personal Communication, 10/8/63.

(16) Bartsch, C.E., Letters to C. W. Theobald, "Copolymers Containing Vinylidene Fluoride, Jan. 18, 1963 and Feb. 1, 1963.

(17) Theobald, C.W., "Tedlar" Market Opportunity, information noted during research review at Buffalo week of 10/28/63.

(18) Busche, R.M., Plastics Dept., Communication "Extrusion Coated "Alathon" Polyethylene Can Liners - High Spot Estimate-Investment", 11/15/63.

(19) Heiberger, P., Communication, 9/4/63.

(20) "Wall Street Journal", about October 1, 1963.

(21) Whitehead, L.J., Purchasing Dept., Personal Communication, Sept., 1963.

(22) Alderson Associates, Inc., (Philadelphia), the market for "Teslar" as an Exterior Finish for siding, October, 1960.

(23) "Chemical Week", Sept. 21, 1963, p. 54.

(24) Heiberger, P., F & F Research Report R-63-57, November 6, 1963.

(25) Bryan, J.C., Personal Communication.

APPENDIX A

SOURCES OF DATA FOR COST CALCULATIONS

A. VF_2/TFE/BCEVP AND OTHER FLUOROPOLYMER COSTS AND INVESTMENT

I. VF_2 mill cost and investment information from F. Mader, Organic Chemicals Department, Jackson Laboratory.

Transfer Price ($/#)	Mill Cost ($/#)	Permanent Investment ($/#)	Working Capital ($/#)	Total Investment ($/#)
2.03	0.72	2.35	0.20	2.55
0.90	0.42	0.80	0.08	0.88
0.76	0.38	0.64	0.07	0.71

The above mill costs were converted by the writer into an approximate replacement cost by adding research expense (3% of the total investment per pound), administrative expense of transfer (1.2% of transfer price), and freight ($0.01/ lb.). Thus the following were obtained:

Mill Cost ($/#)	R&D ($/#)	Administrative Expense ($/#)	Freight ($/#)	Replacement Cost ($/#)
0.72	0.08	0.02	0.01	0.83
0.42	0.03	0.01	0.01	0.47
0.38	0.02	0.01	0.01	0.42

II. TFE mill cost and investment information from W. J. Burich, Plastics Dept., Planning Division. The investment figures had to be approximated as they were not readily separable from other portions of "Teflon" investment data.

Transfer Price* ($/#)	Mill Cost ($/#)	Permanent Investment ($/#)	Working Capital ($/#)	Total Investment ($/#)
1.35	1.01	0.66	0.21	0.87
1.25	0.86	0.81	0.19	1.00
1.12	0.60	0.55	0.12	0.67

*In the case of TFE, the transfer price is not near to cost plus 20% net return, because of major changes in investment anticipated as the demand for TFE increases. As a result, the curve for anticipated transfer prices was smoothed out, and is not fully indicative of cost and investment changes.

APPENDIX A (CONT'D)

The above mill costs were converted to an approximate replacement cost using the same factors as for VF_2:

Mill Cost ($/#)	R&D ($/#)	Adm. Expense ($/#)	Freight ($/#)	Replacement Cost ($/#)
1.01	0.03	0.02	0.01	1.07
0.86	0.03	0.01	0.01	0.91
0.60	0.02	0.01	0.01	0.64

III. VF mill cost and transfer price information from L. C. Chin, Organic Chemicals Department, Jackson Laboratory. At capacity (12 MM lbs./yr) operation of existing facilities these are:

Mill Cost: $0.30/#

Transfer Price: $0.59/#

Estimated Replacement Cost: $0.34/#

IV. All other data for polymer cost calculation obtained from J. M. Quattlebaum (Ref. 5).

B. Finish Costs and Investment

I. Finish cost and investment calculations based on factors and procedures specified by R. S. Wright, Jr., except as listed below:

II. Selling expense fixed at $0.80 per gallon, the average value for Industrial Finishes as specified by G. H. Sutton and approved by G. T. Vaala. The reason for this was that it was considered unwise to apply a percentage factor for determination of selling expense. The use of the fixed average selling expense to these calculations avoided the artificially high expense burden which would have been obtained by applying a percentage factor on replacement mill cost.

III. Permanent F & F Investment was fixed at $1.04 per gallon, the investment at the Toledo plant. This information obtained from G. H. Sutton and approved by G. T. Vaala. The reason for using a fixed permanent investment value was again to avoid an abnormal burden which would result from the application of a factor on mill cost. The $1.04/gallon investment, however, does not take into account any new investment required as a result of inadequate plant capacity, or changes in per gallon investment resulting from different production levels.

APPENDIX B

FORMULA FOR FLUOROPOLYMER STRIPCOATING FINISH (REF. 19)

Resin solution:

VF_2/TFE/BCEVP	27.75 parts
G-393 (acrylic resin)	2.25 parts
Butyrolactone	70.0 parts

Mill base:

W-123 (TiO_2 pigment)	55 parts
Resin solution	25 parts
Butyrolactone	20 parts

Let down:

Mill base	145 parts
Resin solution	297 parts
Butyrolactone	58 parts
Gallon weight:	11.8#/gallon
Solids:	36%
Pigment to binder ratio:	80/100

Comments:

1. The resin solution is prepared by agitating at 180°F.
2. Mill base is prepared by "47 Process" grind.
3. All other steps employ standard production techniques.

APPENDIX C

QUESTIONNAIRE

MARKET POTENTIAL FOR A NEW FLUOROCARBON FINISH

1. Can you tell us how much precoated steel and aluminum you produced in 1962 as well as your estimated production and capacity for 1963? If available, this information will be held in strict confidence.

2. The approximate percentage of your precoated metal used for residential siding, commercial panels, industrial panels, roofing (residential, commercial, industrial), mobile homes and trailers, awnings and other major areas.

3. In rough terms what percentage of vinyls, acrylics and alkyds do you use for the various end uses above?

4. What are the critical film properties for each of the six major end uses previously mentioned? Can you weigh these properties on a one (unimportant) to ten (critical) basis. Do you consider the service lives of the current finishes adequate?

5. Can you reveal your costs (cents/ft.^{2}/mil) for currently available alkyds, vinyls, and acrylics broken down into material and application cost? As in question #1, this information would be held in strict confidence.

6. If a new fluorocarbon finish had the property ratings shown in Chart I, what share of the following markets could the finish expect at two times the price of a current vinyl or \$.02/ft.^{2}/mil and at four times or \$.04/ft.^{2}/mil?

Markets	% at Two Times Vinyl	% at Four Times Vinyl
Residential sidings	______	______
Commercial panels	______	______
Industrial panels	______	______
Mobile homes & trailers	______	______
Awnings	______	______
Roofing	______	______
Others	______	______
"	______	______
"	______	______
"	______	______

7. Do you know the specific applications within the six major end use areas represented by the market potential percentages?

8. From which markets are precoated steel and aluminum limited because of finish deficiencies? What are these deficiencies and how are they measured?

9. Can you tell us what your annual growth rates have been in recent years in the above markets? Are these growth rates expected to continue at the same level in the near future?

APPENDIX C (CONT'D)

CHART I

FILM PROPERTY DATE - CURRENT METAL COATING ENAMELS VERSUS A NEW FLUOROCARBON FINISH

Film Type	Fluorocarbon (Thermoplastic)	Alkyd (Thermoset)	Acrylic (Thermoset)	Vinyl Organosol (Thermoplastic)
Film Properties				
Formability	8	4	5	7
Solvent resistance(1)	9	8	6	2
Hardness	5	6	7	8
Pressure Mottling	8	7	7	7
Durability (2)				
Exterior	10	2	3	5
Cost c/sq. ft. at 1 Mil (3)	2.0-4.0	0.55-0.65	0.7-0.8	0.8-1.0

(1) Solvent resistance refers to the property of retaining good film integrity during clean up of joint compounds (caulks, putties). Normally, hydrocarbon-type solvents are used.

(2) Durability (exterior) of a finish is evaluated in terms of resistance to peeling, checking, cracking, chalking, color change, mildew growth, and dirt pickup. The new fluorocarbon finish is expected to have a lifetime of two to three times currently available finishes in any given atmosphere.

(3) The cost figures given refer to white enamels - colors are slightly higher in cost.

APPENDIX D

GLOSSARY OF ABBREVIATIONS

BCEVP	- bis-(β-chloroethyl) vinyl phosphonate
C_3 Fluoroacetate	- Tetrafluoropropyl Acetate
HFA	- Hexafluoroacetone
IB	- Isobutylene
PVF	- Polyvinyl Fluoride
PVF_2	- Polyvinylidene Fluoride
TFE	- Tetrafluoroethylene
VBU	- Vinyl Butyrate
VCl	- Vinyl chloride
VF	- Vinyl fluoride
VF_2	- Vinylidene Fluoride
VF_2/TFE/BCEVP 80/20/1	- Copolymer of VF_2, TFE, and BCEVP in a weight ratio of 80 to 20 to 1.

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