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UNIVERSITY OF LOUISVILLE

A PLASTIC PROTECTIVE FILM COATING
FOR METALS

A Thesis
Submitted to the Faculty
of the Graduate School
of the University of Louisville
in Partial Fulfillment
of the Requirements
for the Degree of

MASTER OF CHEMICAL ENGINEERING

Department of Chemical Engineering

Arthur S. Widser

December 1946

**A PLASTIC PROTECTIVE FILM COATING
FOR METALS**

Arthur S. Widser

Approved by the Examining Committee.

Director

R. C. Ernst

G. C. Williams

W. R. Barnes

December, 1946

The author wishes to acknowledge
the kind assistance and helpful guidance
of Dr. R. C. Ernst
who directed this research.

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ABSTRACT

A copolymer was made to produce a protective film of the desired properties. The two monomers were (1) styrene, because of its low cost, high gloss, and chemical inertness, and (2) butyl methacrylate, because of its good adhesion to metal and its close vapor pressure at 76°C to styrene which insured a smooth surface free of bubbles.

Butyl methacrylate and styrene were copolymerized; active centers of butyl methacrylate were first formed, then the styrene was added. The polymerization was not carried to completion, but to the desired degree, which was determined by viscosity measurements.

The partially polymerized copolymer was applied as a film on the metal surface to be protected. The film was then completely polymerized either by infra-red heating for approximately five minutes, one hour in an oven at 110°C, or one and one-half hours in sunlight.

The copolymer film produced in this way had a 4H hardness, excellent adhesion and flexibility, smooth surface, and high gloss. It was chemically inert to hot and cold acids and caustic.

INTRODUCTION

A number of protective film coatings contain drying oils. The gradual polymerization of the drying oil in paint films (due to the action of oxygen in the air and sunlight) causes the paint film to become hard and brittle and to lose adhesion. This degradation results in the cracking and peeling of the film leaving the metal surface unprotected.

A film polymerized upon application would eliminate this difficulty and produce a longer lasting protective film. The chemical inertness inherent in many plastics would be an additional advantage. This could be accomplished by the utilization of an all plastic film.

A further advantage is that a long chain polymer could be formed thus helping adhesion. In lacquers, short chain polymers are necessarily formed so that the resin will be more soluble (in its solvent). The short chain polymers decrease the adhesion and possible film thickness per each lacquer coat.

The problem becomes one of finding the proper monomer or monomers to produce plastic which would have the desired properties for a protective film on metal, such as adhesion, hardness, flexibility, gloss and chemical inertness, and weathering characteristics after polymerization in place.

HISTORICAL

The development of synthetic polymers began with the polymerization of styrene by E. Simon (9) in 1859. However, large scale development of synthetic polymers was not undertaken until the close of the first world war.

In forming a polymer it is sometimes found advantageous to polymerize a mixture of two or more monomers to form a mixed polymer. Such polymers are known as copolymers. This process was discovered by Klatte (1914) (10) who observed the polymerization of a mixture of vinyl esters. Later Voss and Dickhäuser (1930) (11) observed the incorporation of maleic acid into polymerizing styrene. The nature of the process was recognized by Wagner-Jauregg (1930) (12) who described it as a hetero-polymerization (copolymerization). During the past few years copolymerization has been studied extensively by many industrial organizations. The year 1942 was principally concerned with the rapid increase of synthetic rubber production by the copolymerization of butadiene and styrene to form Buna S. Vinyl polymers have been studied particularly by C. S. Marvel and his co-workers (13).

THEORETICAL

The two monomers used for the copolymerization in this study are styrene and butyl methacrylate. The reaction is as follows:

Styrene + Butyl Methacrylate $\longrightarrow$ Copolymer

The mechanism of simple polymerization of one monomer must be understood before the theory of kinetics of copolymerization is undertaken. Polymerization is a chain reaction and is thought to be initiated by radicals. Many reactions proceed in chains, but in the polymerization reaction the chain results in a large molecule, which is the result of the ability of the double bond to form new bonds while the original one remains. This reaction is different from condensation polymerization where a by-product - often water, ammonia, hydrogen chloride, or sodium chloride - is formed in addition to the polymer.

The reactions occurring in polymerization are (1) chain initiation, (2) chain growth, (3) chain transfer, (4) branching, and (5) chain ending. The reactions (1), (2) and (3) are thought to occur consecutively.

The formation of radicals which start the reaction is accomplished by heat, light, or catalyst but the type of radical formed by heat or light has not been established. In polymerizations initiated by peroxides, the radical is considered to be derived by decomposition of the peroxide, which combines with the monomer to form the radical as benzoyl peroxide decomposes to give a phenyl radical (15).

Benzoyl Peroxide + Vinyl Monomer $\longrightarrow$ Radical

Benzoyl peroxide combines with the monomer to form a radical. The apparent energy of activation in the case of styrene is given as 25,000 - 26,000 cal. per mol. This apparent energy of activation is diminished in the presence of catalysts such as peroxides.

Polymerization proceeds by the successive addition of monomer units to the radicals to form radicals of increasingly larger size. In this process molecules which do not polymerize by themselves may unite with the radical (activated molecule). Copolymerisation results when a radical displays little choice in the selection of a molecule with which to react. The heat of activation of this growth-reaction is small; it is estimated at about 8000 cal. per mol., in the case of styrene.

According to Flory (14), it is possible for a radical to lose its energy quantum to a monomeric molecule, thereby becoming deactivated, while the monomer now acts as a new radical. The course of polymerization differs according to the various factors in operation: the presence of many active centers (radicals) may lead to the formation of short chains, few active centers, and no impurities to long chains.

Branching may occur by the combination of a growing chain and a polymer. The chain of the polymer combines to form a branch in the main chain.

The deactivation of the chain occurs as a result of various factors such as the combination of two growing chains to form a single polymer by colliding with the wall of the vessel or with a molecule of another

species. Certain molecules are particularly effective in absorbing the energy of a growing chain. These are called inhibitors.

The theory of kinetics of copolymerization has been the subject of a number of recent papers (1), (2). The authors of which have recognized four chain-propagating rate constants, governing the addition of monomer molecules X and Y to growing chains ending in X and Y units.

Wall (3), (4) has advanced a simple theory and later an improved theory based on free radical mechanism.

Simple theory of Wall.

If X and Y represent concentrations of two monomers, each monomer disappears in accordance with the first order - kinetics.

$$dX/dt = -kX \quad (1)$$

$$dY/dt = -kY \quad (2)$$

From the quotient of equations (1) and (2) there was obtained

$$\frac{dX}{dY} = \frac{kX}{kY} = \frac{\alpha X}{Y} \quad (3)$$

where α is the ratio of the specific reaction ratio constants. Equation (3) is identical with the differential equation describing the boiling of a mixture of liquids which obey Raoult's Law. Hence equation (3) may be considered the copolymerization counterpart of Raoult's Law of vapor pressures.

Improved theory of Wall.

Assuming a free radical mechanism of chain growth, Norrish and Brookman (2) recognized that four different growth reactions are possible during copolymerization. These reactions are as follows:

where X and represent the two different monomers and R_x and R_y represent the two kinds of free radicals which can be characterized by the last added monomer units. Assigning specific reaction rate constants k_1, k_2, k_3, k_4 to the reactions and letting the symbols also represent amounts of material (in moles) then the following rate equations can be written:

$$dx/dt = -k_1R_xX - k_2R_yX \quad (8)$$

$$dy/dt = -k_3R_xY - k_4R_yY \quad (9)$$

Wall explored the theoretical possibilities attendant upon many kinds of variation in the relative values of the constants k_1, k_2, k_3, k_4 and has provided graphical representations of a number of cases, showing the dependence of the rate of polymerization and of polymer composition upon the composition of the mixture of monomers. Quoting Wall (4), "Copolymerization of styrene and methyl methacrylate by a free radical mechanism indicates that the monomer reaction ratio is independent (within experimental error) of the composition of the monomer mixture, the extent, and rate of conversion (proportions of benzoyl peroxide hasten the reaction)."

Jenkel (2) made an experimental study of the products of polymerization of four monomer mixtures by fractionation and recognized that three of them represent true copolymers, while the fourth - the product of reaction of styrene and vinyl acetate - more closely resembles a mixture of separate polymers. Mayo and Lewis (6) devised a method for

the evaluation of the ratios k_1/k_2 and k_3/k_4 from the quantitative determinations of the composition of the copolymers relative to that of the initial monomer mixtures, and found that for the copolymerization of styrene and methyl methacrylate at 60°C under a variety of conditions both these ratios were near 0.50.

The chain mechanism reaction is initiated by a catalyst or other source of energy as light or heat. In general both heat and catalyst are used. The catalysts most commonly used are peroxides.

Robinson (16) has shown that the decomposition of acetyl peroxides into free radicals follows generally the reaction

The free radical catalyzes the reaction, and it was demonstrated that the peroxide residues formed part of the chain. It has been shown that two-thirds of the molecules after polymerization contain $\bar{R}$ radicals and one-third contained $RCOO$ radicals.

On the basis of the energy of activation of the decomposition reaction a number of peroxides have been classified in the order of their effectiveness as catalysts for styrene. A partial list in the order of increasing activity is as follows:

1. Stearyl	5. Lauroyl	9. Crotonyl
2. Caproyl	6. Capryl	10. O-Cl benzoyl
3. Anisoyl	7. O-toluyyl	11. Cinnamoyl
4. α Butyryl	8. 2-5 dichloro-
benzoyl	12. α Propionyl
		13. Napthoyl

Conversely in order to stop or slow down the polymerisation reaction rate, chemical inhibitors are used. The inhibiting action on styrene has

been studied by Goldfinger, Skeist, and Mark (7). They believe that each active center formed while there is still an appreciable concentration of inhibitor has no chance to grow out to a chain but is deactivated by collision with a molecule of the inhibitor.

Thus the amount of inhibitor has an influence both on the length of the induction period and the final molecular weight of the polymer formed.

Specifically, Foord (8) studied the effects of many groups as styrene inhibitors. He classified them according to their inhibiting power (total prevention of polymerization) and retarding power (decreased polymerization rate and lower molecular weight). He found the most effective groups to be

1. Nitro - good retarder, weak inhibitor.
2. Phenolic hydroxide - fair retarder, weak inhibitor. (Improve with
the addition of hydroxy groups)
3. Quinonoid - weak retarder, strong inhibitor.
4. Nitroso - weak retarder, strong inhibitor.
5. Amine - weak retarder, fair inhibitor.

Of necessity oxygen is present while the film is being completely polymerized. The oxygen present during polymerization is thought to incorporate in the polymer chains form C-O-O-C- linkage. When heated the chain is broken preferentially at the $[-O-O-]$ linkage because of the lower bond energy as compared to -C-C-. A catalytic free radical of the C-O form may result which may accelerate thermal decomposition. Oxygen present in ultra-violet polymerization of styrene reduced the reaction rate and lowered the molecular weight of the product. This is not detrimental as the length of the molecule can be controlled, and a slow polymerization cycle is desired.

EXPERIMENTAL

The experimental apparatus used in this investigation consisted of a washing unit, a polymerization reactor, and an auxiliary equipment.

The washing unit which consisted of a 500 c.c. separatory funnel and two 500 c.c. beakers was used for the removal of the hydroquinone inhibitor from the monomers.

The polymerization reactor consisted of a 125 c.c. erlenmeyer flask which was heated in a water bath kept at 76°C. Because of the low vapor pressure and slow polymerization rate the erlenmeyer was merely capped with a cork in which was inserted a glass tube. On the other end of the glass tube a valved "T" and an aspirator bulb were attached for the removing of samples in order to determine the viscosity of the solution so that the degree of polymerization could be followed. The viscosity was measured by means of Gardner Viscosity Tubes.

An infra-red lamp ($\lambda = 10,000$ and $20,000 \text{ \AA}$ units) was used as a source of heat for completely polymerizing the film on the metal.

The metal panels were steel plates 3" x 5", 18 gauge and were prepared for the film by washing with a solvent to remove grease and oil.

The film hardness was determined by the pencil hardness technique ("H" through "8H").

The monomers as shipped contained a trace of inhibitor (.0006% hydroquinone) which was removed before polymerization.

The inhibitor was removed by a treatment of the monomer with an equal volume of 2% sodium hydroxide solution in a separatory funnel. The solution of alkali, containing the inhibitor, was drained from the bottom of the funnel, and the washing was repeated until a fresh portion of solution of alkali was not discolored by contact with the monomer.

Then the monomer was washed twice with an equal volume of distilled water. The small amount of water remaining in the monomer then was removed by allowing it to stand overnight in a refrigerator in contact with anhydrous sodium sulfate or calcium chloride. The desiccant was removed by filtration.

Inhibitor free monomer was stored in a refrigerator at about 40°F.

Because the styrene molecule polymerized more readily than the butyl methacrylate molecule, the butyl methacrylate was placed in the reactor with the catalyst to form active centers for the copolymerisation. If this is not done a considerable amount of styrene will polymerize with itself producing small insoluble particles of polystyrene which produces a cloudy film. The styrene was added and the two monomers partially copolymerized to the desired degree, as measured by viscosity change.

The partially polymerized copolymer was then applied by dip, brush, or spray to a clean metal surface and further polymerized by heat, infrared waves, or daylight.

The procedure was as follows:

Twenty-one grams of butyl methacrylate and 0.3 grams of benzoyl peroxide were placed in the reactor and held at 76°C until the viscosity of the solution reached "B" in the Gardner Viscosity Tube (about four hours). Then nine grams of styrene and 0.3 grams benzoyl peroxide were added. The reaction was continued at 76°C until the viscosity became "D" on the Gardner Viscosity Tube (about five additional hours). To the resulting partial copolymer an inhibitor was added (.006 grams of tertiary butyl catechol) which permitted storage (away from sunlight) without continued polymerization.

A steel plate (3" x 5") was then washed thoroughly with any good

grease solvent or hot caustic. The partial copolymer was spread (as a film) over the steel plate. The film on the plate then was polymerized by one of three methods:

1. Five minutes under an infra-red lamp.
2. One hour in an oven at 100°C.
3. One and one-half hours in the sunlight.

The film was tested by the usual procedures for adhesion, hardness, corrosion resistance, and flexibility (as described in "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors" by H. A. Gardner).

Butyl methacrylate and styrene were chosen to form the copolymer. Styrene was chosen because of its low cost, gloss, hardness, and low vapor pressure. An acrylate was chosen because of its good adhesion to metals.

Thirty-nine tests in all (see appendix, preliminary data) were run before any good results were obtained. On the initial test runs styrene and methylacrylate were copolymerized, producing a good adhesive film but poor surface because of the formation of bubbles in the polymerized coating. The difference in the vapor pressure of styrene methylacrylate at 76°C caused the poor surface. Butyl methacrylate was then chosen as its boiling point (164°C) was close to styrene's (146°C), and it was assumed that its vapor pressure would be close to styrene's at 76°C and thereby obtain a smooth film.

The copolymer was formulated to produce the desired film hardness, adhesion, flexibility, gloss, and chemical inertness. This was done by choosing the correct monomers as explained above, and by the control of the molecular weight and number of active centers of butyl methacrylate and the total polymerization cycle time.

Film hardness (4H pencil hardness) was obtained by controlling the number and molecular weight of active centers of butyl methacrylate. This was done by reacting the butyl methacrylate first to the desired viscosity. This is indicated by experimental results of tests 40, 41, 42, and 43. The initial polymerization time of butyl methacrylate in these tests was varied from two hours to five hours all other factors being held constant. The resulting hardness varied from H pencil hardness to 5H pencil hardness.

Table No. 1

EFFECT OF INITIAL BUTYL METHACRYLATE POLYMER ON FILM HARDNESS											
No.	Composition		1st Poly		Results	Composition		2nd Poly		Results	
	Bu Me- acrylate grs.	BzO ₂ grs.	θ	t°C	η	Styrene grs.	BzO ₂ grs.	θ	t°C	η	H Adh.
40	21	.3	2	76	7 A	9	.3	4	76	A	H E
41	21	.3	3	76	7 A	9	.3	4	76	B	3H G
42	21	.3	4	76	B	9	.3	4	76	D	4H E
43	21	.3	5	76	E	9	.3	4	76	G	5H E

Where:

Bu Meacrylate Butyl Methacrylate
 BzO₂ Benzoyl Peroxide
 θ Time in hours unless
 otherwise specified.
 t°C Temperature °C
 η Viscosity, Gardner Tubes
 H Pencil Hardness

Adh Adhesion
 E Excellent
 G Good
 Grs Grams
 Poly Polymerization

The polymerized film showed excellent adhesion. This property was obtained by adjusting the temperature and catalyst to give a long polymerization cycle, thereby growing long chain molecules which produce good adhesion. Short polymerization cycles produced short chain molecules. This is shown by the experimental results of tests 44, 45, 46, and 47. The film becomes harder with increased adhesion by the lengthening of the total polymerization time from six hours to nine hours, with but a small increase of viscosity.

Table No. II

EFFECT OF COPOLYMERIZATION TIME ON HARDNESS AND ADHESION											
No.	Composition		1st Poly		Results	Composition		2nd Poly		Results	
	Bu Me-acrylate grs.	BzO ₂ grs.	θ	t°C		Styrene grs.	BzO ₂ grs.	θ	t°C	H	Adh.
44	21	.3	4	76	B	9	.5	2	76	A	2H G
45	21	.3	4	76	B	9	.5	2½	76	A	2H G
46	21	.3	4	76	B	9	.3	5	76	D	4H E
47	21	.3	4	76	B	9	.3	5½	76	D	4H E

For test numbers 48, 49, 50, and 51 approximately the same number and molecular weight of active centers were produced by controlling the viscosity of the initial reactant (butyl methacrylate). The total

polymerization time was held constant, and only the concentration of styrene was varied. The adhesion and hardness of the final product in each case was the same. The viscosity of the final solution was the only change noted. This verifies Wall's (4) statement (see page 9). The excess styrene served as a solvent. Thus the viscosity of the final solution can be controlled, as noted in Table III. The styrene was varied from 3 grams to 17 grams, all else kept constant. The only variation was the viscosity of the final solution.

Table No. III

EFFECT OF STYRENE CONCENTRATION ON COPOLYMER PROPERTIES												
No.	Composition		1st Poly		Results	Composition		2nd Poly		Results		
	Bu Me-acrylate grs.	BzO ₂ grs.	g	t°C	A	Styrene grs.	BzO ₂ grs.	g	t°C	A	H	Adh.
48	21	.3	4	76	B	3	.3	5	76	O	4H	G
49	21	.3	4	76	B	6	.3	5	76	E	3H	G
50	21	.3	4	76	B	12	.3	5	76	A	3H	G
51	21	.3	4	76	B	17	.3	5	76	7A	3H	G

Good flexibility was obtained by the internal plasticization of the copolymer (thus no additional plasticizer was necessary). This was obtained by using the correct monomers. "In acrylate copolymers good flow characteristics are obtained with a large compact molecule in the side chain so that the spatial compactness is in close proximity to the main chain", says Dr. Staudinger. This can be shown by the formula of the polymerized chain.

High gloss was also obtained by choosing the correct monomers which would produce a high gloss on polymerization.

The cure time (complete polymerization) is satisfactory. It requires approximately five minutes for complete polymerization under infra-red waves, one hour in oven at 110°C, one hour under ultra-violet rays, and one and one-half hours in sunlight. However, the monomer loss (during the complete polymerization) is high (80%). This percentage can be reduced by adding the catalyst to the copolymer before applying it to the metal surface. However the smoothness of the film would be endangered by the formation of bubbles caused by the heat of reaction by extremely fast polymerization. The film at present is very smooth with good flowing characteristics. Experimental runs 52, 53, 54 and 55 show the cure time of the film.

Table No. IV

EFFECT OF CURING PROCEDURE ON MONOMER LOSS												
No.	Ultra-Violet			Infra-Red			Oven			Sunlight		
	% Loss	°	H	% Loss	°	H	% Loss	°	H	% Loss	°	H
52	95	1 hr.	2H	66	5 min.	4H	70	1 hr.	4H	80	1½ hrs.	2H
53	55	1 "	2H	65	5 "	3H	70	1 "	3H	60	1½ hrs.	4H
54	25	1 "	2H	66	5 "	4H	65	1 "	3H	60	1½ hrs.	3H
55	50	1 "	2H	56	5 "	4H	60	1 "	2H	61	1½ hrs.	5H
Adhesion good on all samples.												

The storage ability of the partially copolymerized solution is very good. Two samples of solution - one inhibited with hydroquinone and one inhibited with tertiary butyl catechol - were stored for three months and no apparent viscosity change has been noted.

Test runs were made on the plastic film to determine the inertness of the film. These test runs were made by soaking the film with the test solution for twenty-four hours, and they showed that the film was impervious to sulphuric acid (concentrated and diluted), hydrochloric acid (concentrated and diluted), caustic (50%) both hot and cold, ethanol, and water, and will not discolor under ultra-violet radiation. The film is soluble in most petroleum solvents.

The greatest difficulty during the experimentation was obtaining sufficient hardness. Butyl Methacrylate itself is a soft polymer (about H pencil hardness). It tends to make the copolymer soft and tacky. Styrene on the other hand (which is a hard polymer) will react readily with itself causing a cloudy film and very poor adhesion. Thus care had to be taken to control the degree of copolymerization of butyl methacrylate and styrene.

If the monomers of styrene and butyl methacrylate are mixed together and then polymerized, the results are not reproducible, since there is no control over the molecular weight or number of active centers formed. The final solution is a mixture of styrene and copolymer.

A redox (oxidation - reduction) type of catalyst was tried but failed. This type of catalyst had been used to reduce the time of vinyl polymerizations in water emulsions from 18 hours to 15 minutes. This

would be beneficial for reduction of the monomer loss during complete polymerisation providing the heat generated during the fast polymerisation reaction did not ruin the film surface by the formation of bubbles.

COMMERCIAL FEASIBILITY

The all-plastic film is a commercially feasible product. If desired it can be manufactured in jacketed reactors of 1000 gallons or larger. The process will lend itself easily to a continuous polymerization reaction since the necessary agitation is low and there is no build-up on the reactor walls to interfere with the heat transfer. A steam jacketed tube of desired length with two proportioning pumps and two temperature controllers are all that are necessary. The equipment may be built of standard steel pipe since the vapor pressures of both monomers are low, and at the slow rate of polymerization the vapor pressure is not great enough to pop a cork out of a stoppered erlenmeyer flask used as a reactor during the polymerization tests.

The raw material cost for the manufacture of one gallon of solution is \$4.94. The steam cost is negligible as the reaction is exothermic. "Heat-up" steam plus a small amount of make up, because of conduction and convection loss, is necessary. It takes one pound of steam at 150 p.s.i. to heat four gallons of solution (see cost calculations in the appendix).

SUMMARY AND CONCLUSIONS

The polymerization of liquid monomers to form an all plastic protective film on metal was successfully accomplished. The desirable film characteristics (hardness, adhesion, flexibility, gloss, and chemical inertness) were obtained by the copolymerization of styrene and butyl methacrylate. The butyl methacrylate was first partially polymerized to the desired degree as indicated by viscosity measurements. The styrene was added and the solution was again partially polymerized to the desired degree. The partially polymerized copolymer was spread on the metal panel which had been washed with a solvent to remove any oil or grease. The panel was then polymerized either by infra-red heating for five minutes, one hour in the oven at 110°C, one hour under ultra-violet light, or one and one-half hours in sunlight.

The rate of polymerization was necessarily slow for two reasons: (1) to control the desired degree of polymerization and (2) to form long chain molecules. It has been proved by a number of observers that the longer the polymerization cycle the longer the molecular chain. This is desirable for adhesion purposes.

The additional plasticizers were of no benefit as the copolymer had good internal plasticization characteristics. The film was flexible to the degree of withstanding a blow by a hammer and a bend of 360 degrees.

The elimination of drying oils (which cause the detrimental polymerization of aging paint) lengthens the life expectancy of the polymerized film. Thus, the all plastic film is a superior product to that of paint films.

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APPENDIX

NOMENCLATURE

Bu Meacrylate	Butyl Methacrylate
BzO ₂	Benzoyl Peroxide
t°C	Temperature °C
θ	Time in hours unless otherwise specified
μ	Viscosity, Gardner Tubes
H	Pencil Hardness
adh	Adhesion
%	Percent monomer loss of film under infra-red while undergoing complete polymerization unless otherwise specified.
Meacrylate	Methylacrylate
D.O.P.	Di Octyl Pthalate
T.C.P.	Tri cresyl Phosphate
p.s.i.	Pounds per square inch
H.Q.	Hydroquinone
T.B.C.	Tertiary Butyl Catechol
G	Good
E	Excellent
Poly.	Polymerization
Grs	Grams

RAW MATERIALS

Butyl Methacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_2\text{C} = \text{C} - \text{C} - \text{O} - \text{OC}_4\text{H}_9 \end{array}$
Molecular Weight.	142.09
Specific Gravity.	.895
Boiling Point	163 - 164°C
Cost	75¢ per lb. in 55 gallon drums (4000 lbs. or over)
Manufacturer.	Rohm and Hass, Philadelphia, Pa.
Styrene	$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$
Molecular Weight.	104.14
Specific Gravity.	.903
Boiling Point	145 - 146°C
Cost	14½¢ per lb. in 55 gallon drums (carload lots)
Manufacturer.	Dow Chemical Co., Midland, Mich.
Benzoyl Peroxide	$(\text{C}_6\text{H}_5\text{CO})_2\text{O}_2$
Molecular Weight.	242.22
Melting Point	108°C
Cost	\$4.50 per lb.
Manufacturer.	Lucidol Co., Buffalo, N. Y.
P-Tertiary Butyl Catechol.	$\text{C}_3\text{H}_5(\text{OH})_2 \text{C}_4\text{H}_9$
Cost	\$1.40 per lb.
Manufacturer.	Dow Chemical Co., Midland, Mich.

COST CALCULATIONS

Specific heat of styrene	.32 B.T.U. per lb.
Specific heat of butyl methacrylate.	.45 B.T.U. per lb.
Specific gravity of copolymer.	.9
Weight of copolymer	7.5 lbs. per gallon

Raw material cost

21 lbs. butyl methyl methacrylate @ \$0.75 per lb. \$15.75

9 lbs. styrene @ \$0.14 $\frac{1}{4}$ per lb. 1.29

.6 lb. BzO_2 @ \$4.50 per lb. 2.70

.006 lb. T.B.C. @ \$1.42 per lb. 0.01

Total \$19.75

30 lbs. copolymer / 7.5 4 gallons

1 gallon costs \$19.75 / 4 \$ 4.94

Steam cost

$$Q = (\text{lbs.}) (\text{Temp. Diff.}) (\text{Sp. Ht.})$$

For styrene

$$(9) (169 - 75) (.32) = 271 \text{ B.T.U.}$$

For butyl methacrylate

$$(21) (169 - 75) (.45) = \underline{890} \text{ B.T.U.}$$

Total 1161 B.T.U. (to heat batch from 75°F to 169°F)

1 lb. steam at 150 p.s.i. = 1193.4 B.T.U.

Thus it requires 1 pound of steam at 150 p.s.i. to heat 4 gallons of copolymer to reaction temperature. If steam costs 5¢ per pound it would cost 1 $\frac{1}{4}$ ¢ per pound to heat one gallon to reaction temperature.

PRELIMINARY DATA

Table No. V
Preliminary Data

INVESTIGATION OF STYRENE AND METHYLACRYLATE COPOLYMER						
No.	Composition				Infra-Red Waves @ min.	Remarks
	Styrene grs.	Me-acrylate grs.	BzO ₂ grs.	T.C.P. grs.		
1	10		.2		10	Film too brittle, no adhesion.
2		10	.2		10	Soft mass.
3	8.5	2.5	.02			Solution immisicible.
4	1.8	8.5	.02		10	Solution cloudy, poor surface (bubbles), brittle film.
5	1.7	8.6	.02			On addition of 3.4 grs. D.O.P. solution became cloudy.
6	1.7	8.5	.03	3.4	10	
7	1.5	8.5	.03	.05	10	Too much plasticizer.
8	3	17.9	.03	.2	10	.2 to .5 gram T.C.P. correct amount of plasticizer. Poor surface (bubbles).
9	3	17.0	.03	.5	10	
10	3	17.0	.03	.5	10	H pencil hardness.

Table No. VI
Preliminary Data

INVESTIGATION OF METHYLACRYLATE AND STYRENE COPOLYMER							
No.	Composition				Poly		Remarks
	Styrene grs.	Me- acrylate grs.	BzO ₂ grs.	T.C.P. grs.	t°C	θ	
11	6	58.6	.1	.4	76	1	Poor film (bubbles).
12	6	56	.1	.4	76	2	Poor film (bubbles).
13	6	56	.1	.4	76	5	Became solid over night.
14	6	56	.1	.4	76	5	Became solid over night.
15	6	56	0	.3	76	12	No polymerization.
16	6	56	0	.3	76	12	No polymerization.
17	6	56.5	.1	.2	76	3	.01 H.Q. inhibitor added.
18	6	57.6	.1	.3	76	3	.01 H.Q. inhibitor added.

Remarks:

It is evident that the difference in boiling point of methacrylate (80°C) and styrene (146°C) caused the bubbles in the surface during total polymerization. Therefore butyl methacrylate boiling point (164°C) was ordered.

Tests No. 17 and 18 were tests on inhibitors for determining if the solution can be stored. The viscosity of the two samples remained the same over a three month period.

Table No. VII
Preliminary Data

INVESTIGATION OF BUTYL METHACRYLATE AND STYRENE COPOLYMER											
No.	Composition			1st Poly		Results	Composition		2nd Poly		Results
	Monomer	BzO ₂ grs.	T.C.P.	g	t°C	✓	Monomer	BzO ₂ grs.	g	t°C	✓
19	10 grs. Bu Me- acrylate							.3	8	76	
20	3 grs. styrene		.5				21 grs. Bu Me- acrylate	.6	3	76	A
21	3 grs. styrene		.5				21 grs. Bu Me- acrylate	.6	2	76	A
22	3 grs. styrene	.3	.6	$\frac{1}{2}$	76	A	21 grs. Bu Me- acrylate	.3	5	76	A
23	3 grs. styrene	.3	.6	$\frac{1}{2}$	76	A	21 grs. Bu Me- acrylate	.3	5	76	A
24	21 grs. Bu Me- acrylate	.3	.6	$\frac{1}{2}$	76	A	6 grs. styrene	.3	5	76	D
25	21 grs. Bu Me- acrylate	.3	.6	$\frac{1}{2}$	76	A	3 grs. styrene	.3	5	76	C
26	21 grs. Bu Me- acrylate	.3		4	76	Syrup	9 grs. styrene	.3	4	76	C
27	21 grs. Bu Me- acrylate	.3		4	76	Syrup	3 grs. styrene	.3	4	76	C

Remarks:

Test No.

19. This was the butyl methacrylate monomer polymerized by itself. The polymer was softer than H pencil hardness and had good adhesion.
20. Styrene and butyl methacrylate were combined and polymerized. and The film had a hardness of 2H, showed fair adhesion and an 80% monomer loss on complete polymerization under infra-red lamp for five minutes.
21. Styrene was first added and polymerized initially for one-half hour at 76°C; then the butyl methacrylate was added in small droplets for a period of five hours. The solution was cloudy and the resultant film soft and tacky.
22. The butyl methacrylate was first added and polymerized initially and for one-half hour at 76°C; then the styrene was added in small droplets for a period of five hours. The film had H pencil hardness and good adhesion and showed a 60% monomer loss on complete polymerization of the film on the panel.
23. By polymerizing the butyl methacrylate to a syrup constituency and the film became harder. All the styrene was added at one time; no plasticizer was used. The film was flexible enough from internal plasticization of the copolymer. The film would not chip on receiving a sharp blow with a hammer. The hardness of the film was 3H pencil hardness; the adhesion was excellent and showed a 50% monomer loss on complete polymerization.

Using No. 26 copolymer, tests were run to determine whether certain plasticizers were of any value. The results were as follows:

Test No.	Plasticizer	Film
28	Aroclor 1254	Tacky
29	Aroclor 1260	Tacky
30	Aroclor 4465	Brittle
31	Paraplex RG-8	No adhesion
32	Paraplex RG-2	No adhesion
33	Resyl X-315	No adhesion

Rodox catalyst (oxidizing reducing catalyst) is stronger than Benzoyl Peroxide alone as a catalyst; thus Benzoyl Peroxide plus several reducing agents were used to try to find a stronger catalyst to reduce the monomer loss on complete polymerization.

Using No. 27 copolymer and .5 grs. of Benzoyl Peroxide and .2 grs. of reducing agent, the results were the following:

Test No.	Reducing Agent	Results
34	Butyl Aldehyde	No polymerization
35	Furfural	Caused a precipitate
36	Benzidine Hydrochloride	Insoluble
37	Sodium Sulphide	Insoluble
38	Hydroxylamine Hydrochloride	Slightly soluble
39	Benzine Aldehyde	Poor - tacky film

VITA

ARTHUR SHELDON WIDZER

The Author is the son of Lewis Jack Widzer and Sarah Saltuper Widzer. He was born in Elyria, Ohio, on the sixth of February, 1914.

He attended elementary school at Brownell located in Elyria, Ohio, and high school at East Technical in Cleveland, Ohio.

The Author attended four Colleges. At Case School of Applied Science he received his Bachelor of Science degree in Chemical Engineering. His under graduate thesis concerned the aeration of varnishes and was directed by Dr. C. F. Prutton, head of the Chemical Engineering Department. He then attended Cleveland College at nights undertaking a Business Administration course supervised by Mr. D. White. He entered the Graduate School of Cincinnati University studying under Dr. C. Green. He then entered the Graduate School of the University of Louisville, where Dr. R. C. Ernst was his counselor.

He has had industrial experience with J. E. Seagram and Sons, Inc., of Louisville, Kentucky; The American Rolling Mills of Middletown, Ohio; The Ameco Chemical Company of Rochester, New York; The Easterly Sewage Disposal Plant of Cleveland, Ohio; and B. F. Goodrich Chemical Company, Geon Plant, of Louisville, Kentucky.