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VINYLITE

TRADE-MARK

RESINS

VINYL BUTYRAL RESINS

FOR COATINGS

APPLICATIONS TECH BULL.

MAY 1952

BAKELITE COMPANY
A Division of Union Carbide and Carbon Corporation
UCC
30 East 42nd Street, New York 17, N. Y.

"VINYLITE" VINYL BUTYRAL RESINS

Introduction

Vinyl butyral resins were originally manufactured by divisions of Union Carbide and Carbon Corporation in 1936 to meet the specific requirements of safety glass manufacturers who required a resin which combined extremely strong tenacious bonding to glass with excellent impact resistance. Unlike previous materials, these safety glass laminates retained their crystal-clear transparency and toughness despite excessive heat, cold, and moisture. In addition to the widely used vinyl butyral safety glass laminants, solution grades of vinyl butyral resins are now available in granular form for use in coatings and adhesives. Recently the use of vinyl butyral resins in coatings has received great impetus through the development of the "wash primer" type of metal conditioner and the wood knot sealer.

These vinyl butyral resins possess excellent specific adhesion to non-porous surfaces such as glass, metal, and molded phenolic resins. They bind wood plies in a strong, shockproof construction, and, in cases where high temperature resistance is required, can be cured or reacted with thermosetting resins.

GENERAL PROPERTIES

The resins are supplied as white granules. At the present time the two grades marketed by Bakelite Company under the trade-mark **VINYLITE** are designated XYSG and XYHL, and are of high and low molecular weight, respectively. The basic properties of these resins are given in Table I.

TABLE I

VINYLITE BRAND RESINS

	XYHL	XYSG
Form	White powder	White powder
Intrinsic Viscosity	0.81	1.16
Specific Gravity	1.12	1.12
Composition:		
Vinyl	Approx. 54.4	Approx. 54.4
Butyraldehyde	Approx. 38.3	Approx. 38.3
Acetate	Approx. 0.3	Approx. 0.3
Hydroxyl	Approx. 7.0	Approx. 7.0

Vinyl butyral resin coatings and adhesives are characterized by:

1. Adhesion to glass, wood, metal, leather, and most plastics
2. Good shock resistance
3. Retention of color on exposure to light and heat
4. Toughness and flexibility

Vinyl butyral resins are compatible with urea formaldehyde and melamines and with many other film-forming materials. They may also be modified with plasticizers to give almost any degree of flexibility desired. They are soluble in alcohols, glycol-ethers and some esters and ketones.

One of the greatest advantages of vinyl butyral resin coatings is that they lend themselves to curing or cross linking. The resulting surface is solvent-resistant, hard, higher softening, and more resistant to blocking than the unmodified resin. In addition, the resistance of the coating to moisture absorption is increased, and its tendency to cold flow lessened. The degree of hardness obtained can be controlled by the selection of curing agents and the quantity used. Both resinous materials and chemical agents can be used; the former is typified by BAKELITE phenolic resins BV-9700-S, BV-1112, and BR-17620, and the latter by formaldehyde and glyoxal. The reaction with glyoxal proceeds in air dried films, and since the reaction is reversible in the presence of water, there is no tendency to gel in solution (when water is present). For the same reason, however, continued water immersion of the reacted film is not recommended.

A unique property of resins XYHL and XYSG is that they absorb moisture and swell when immersed in water. This proceeds to a maximum value beyond which absorption or swelling does not take place. They maintain better film integrity than many other materials which may have higher initial impermeability, but which tend to disintegrate on continual immersion.

Resin coatings of vinyl butyral resin on steel maintain electrical resistance when immersed in water as illustrated in Figure I. The pigmentation in each case was zinc tetroxy chromate, 25 per cent pigment volume. These determinations were obtained by use of a Protectometer (Bacon, Smith and Rugg: "Electrolytic Resistance As a Means of Evaluating Protective Merit of Coatings on Metals." Industrial and Engineering Chemistry, January 1948). From Figure I it is obvious that the physical condition of a film saturated with water is more important than its initial moisture absorption. This property of vinyl butyral resin in maintaining electrical resistance was instrumental in developing the successful wash primers described on Pages 11-22.

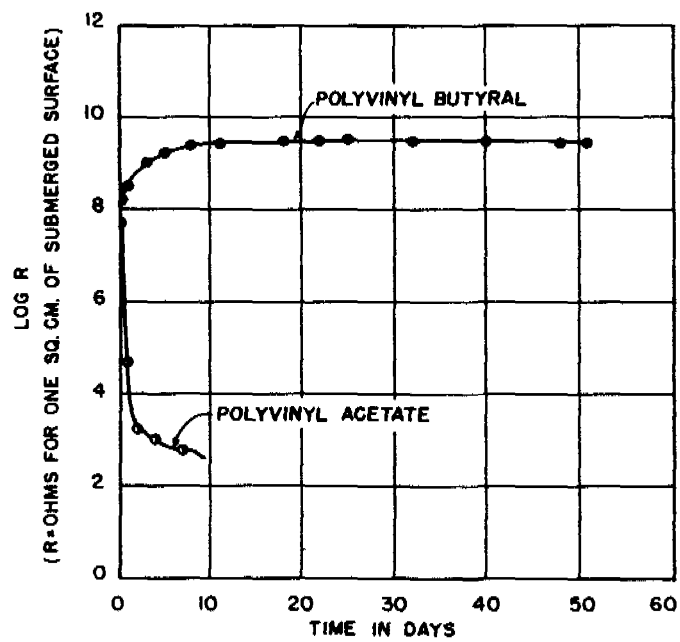

FIGURE I. EFFECT OF VARIATIONS IN BINDER COMPOSITION ON PROTECTION

Vinyl butyral resins permit unusually high pigment volume loadings without undue loss of film strength. They can also withstand blending with large amounts of low molecular weight resins such as rosin and ester gum without excessive loss of strength.

Roll milling or intensive grinding of vinyl butyral resin tends to increase solubility but raises the softening point of the resin to such an extent that only a short period of such milling is feasible, beyond which the resin becomes too stiff to handle. Alcohol may be added to the roll mill grind to control this effect on softening temperature. Pigments may be dispersed in vinyl butyral resins by means of milling provided that non reactive types are selected and the above precautions are followed.

Plasticizers may be added to vinyl butyral resin coatings to increase their flexibility for some applications and to reduce viscosity of hot melts. Vinyl butyral resins are compatible with FLEXOL plasticizers 3GH, 8N8, and TOF, dibutyl sebacate, and with other chemical-type plasticizers. Raw castor oil is compatible, but tends to soften the film without developing elasticity. It may be used advantageously, however, when mixed with solvent-type plasticizers.

Compatibility of Vinyl Butyral Resins

Addition of other resins and gums to vinyl butyral resins is often desirable in order to modify their properties for specific applications. Resins with which the vinyl butyral resins are compatible include phenolic and urea-formaldehyde types. Compatibility with nitrocellulose is borderline, differing with the grade of pyroxylin used and the solvents selected. Table II (see pages 12 and 13) lists typical materials with which VINYLITE resin XYSG is compatible, slightly incompatible, or incompatible. In general, these data, are also applicable to VINYLITE resin XYHL. In some applications such as

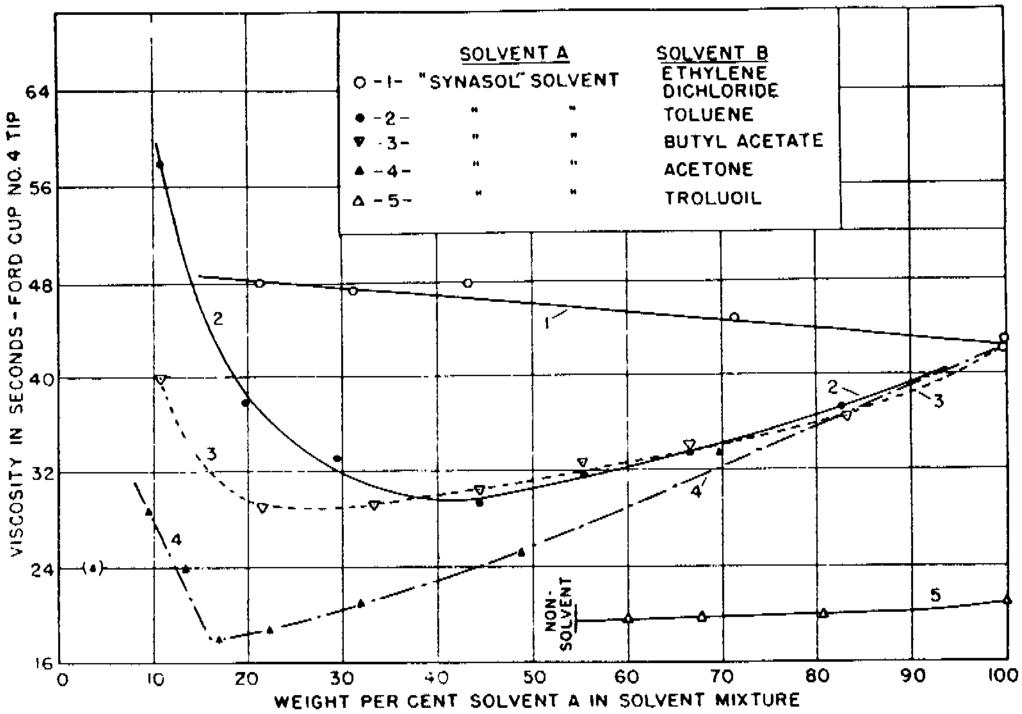

FIGURE 2. VISCOSITY OF SOLUTIONS OF VINYL BUTYRAL RESIN XYHL IN MIXED SOLVENTS

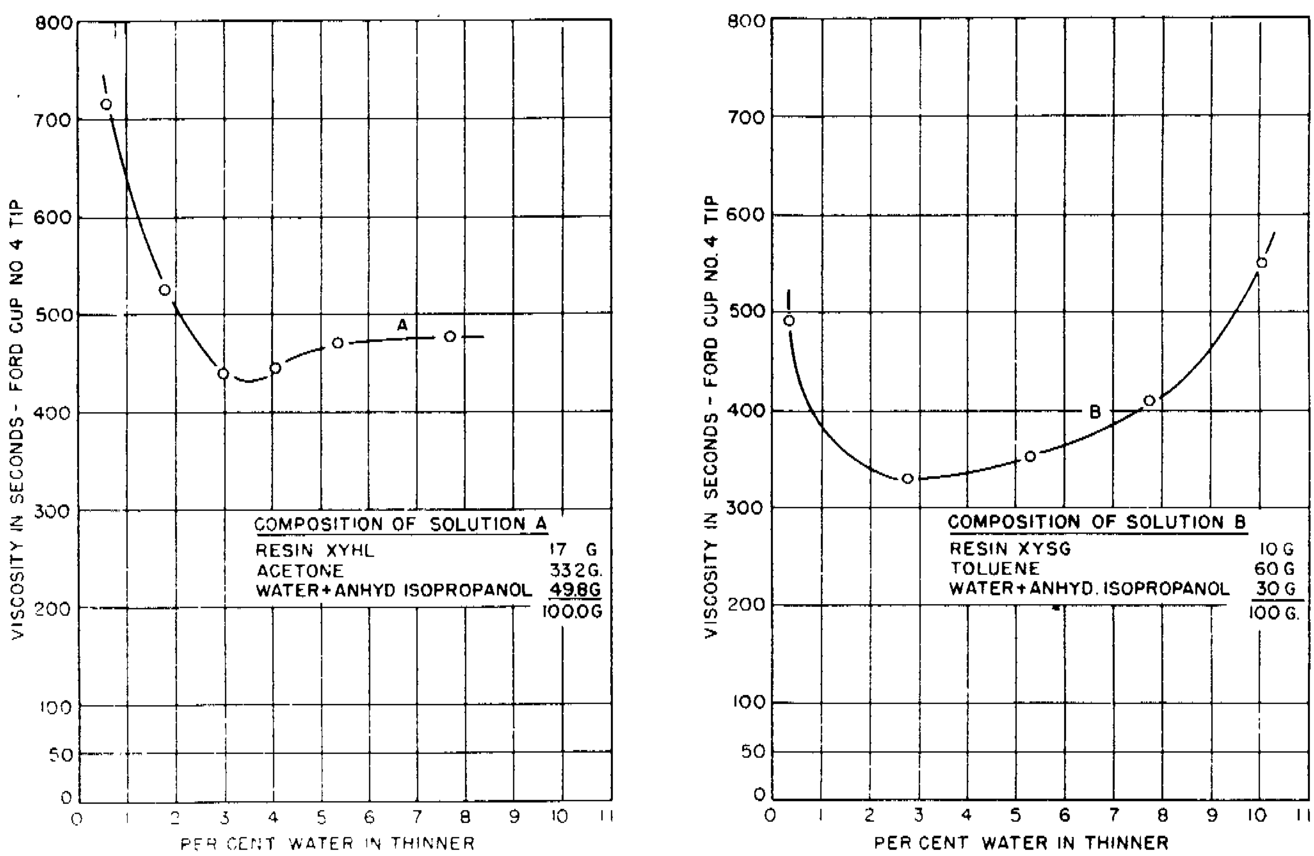

FIGURE 3 EFFECT OF WATER ON VINYL BUTYRAL RESIN SOLUTION

adhesives, complete compatibility between the components may not always be essential, hence many modifiers can be added to reduce viscosity or introduce other properties.

Solubility of Vinyl Butyral Resins

VINYLITE resins XYHL and XYSG are soluble in alcohols, CELLOSOLVE solvents, and esters. The solubility characteristics of these resins are illustrated in Figure 2. Although the resins are soluble in commercial alcohols, they are insoluble or form gels in anhydrous alcohols. This behavior is illustrated in Figure 3, which indicates that from three to eight per cent water should be present in the thinner; five per cent is usually recommended. While ethanol and methanol are the most active solvents, mixed thinners containing about 40 per cent alcohol and 60 per cent ester, ketone, or aromatic hydrocarbon produce solutions of lower viscosity than the pure alcohol. Isopropanol also exhibits a similar coupling effect with acetone and toluene and from Figure 4, solutions of optimum viscosity can be formulated.

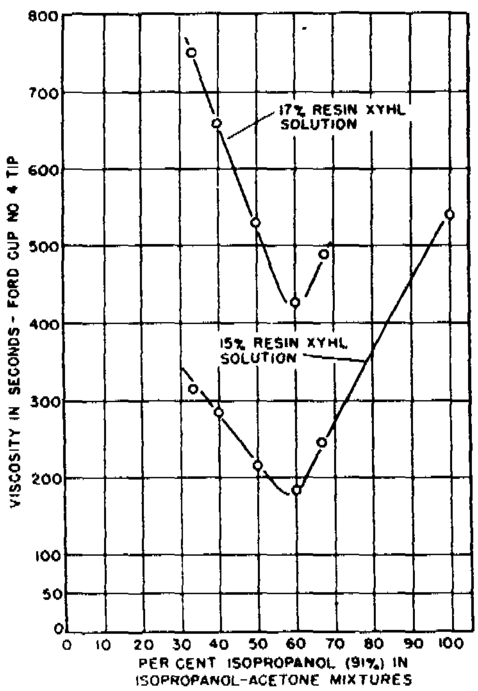

FIGURE 4 VISCOSITY MEASUREMENTS OF RESIN XYHL IN ISOPROPANOL-ACETONE MIXTURES

APPLICATIONS OF VINYL BUTYRAL RESINS

Adhesives

The excellent adhesive qualities of vinyl butyral resin evidenced in its early and extensive use as a safety glass interlayer have been instrumental in encouraging evaluation of these resins in strictly adhesive applications.

Vinyl butyral-phenolic adhesives may be used for bonding rubber, cork, asbestos board, wood, glass or ceramic parts, cloth, paper, or metals to plastics of the thermosetting type. After the bond has been cured, it will be stable to at least 100 deg. C. and will not be softened readily by the action of water or solvents.

In order to bond two metal pieces together, the surfaces, which should be grease-free, are coated and dried to remove solvent. Drying may be accomplished at room temperature or at a low bake not above a temperature of 250 deg. F. for about 5 minutes. Temperatures higher than 250 deg. F. cause excessive hardening of the adhesive and make subsequent bonding difficult.

After the solvent has been completely removed, the surfaces are pressed together and heated. The time and temperature required will depend on the materials being bonded; from 15 minutes at 275 deg. F. to a few seconds at 400 deg. F. will suffice.

In bonding wood to metal, vinyl butyral-phenolic adhesives should be air-dried rather than dried at the elevated temperatures used for metal-to-metal adhesives for heat is likely to decrease the adhesion to cellulosic materials.

Adhesives based on vinyl butyral-phenolic resins are also used in the lamination of plywood. The vinyl butyral resin acts as a "plasticizer" or fortifier for the phenolic resins, serves to increase the shock resistance, and improves the adhesion of the phenolic to wood, especially under conditions of high humidity.

While the ratio of vinyl butyral resin to phenolic resin will vary for different applications depending on the materials being bonded and the nature of the application, increasing the ratio of butyral resin will have the following general effects:

1. Increase the tensile strength.
2. Increase the impact strength.
3. Decrease creep resistance.
4. Decrease boiling water resistance.

Vinyl butyral resins can be used in hot melt form if mixed with compatible plasticizers and resins. Hydroabietyl alcohol and resin XYHL in equal parts will make a melt that is pourable at 350 deg. F., yet remains tough and shock-resistant at room temperature. Hot melts based on vinyl butyral resins are used commercially for high-speed bookbinding.

Wood Finishes

Although the use of clear wood coatings based on vinyl butyral resins alone is not recommended because of rather high moisture absorption and tendency to check, it has been found that when these resins are mixed with other resins and film formers, excellent coatings are obtained. An outstanding example is a 50-50 mixture with shellac which results in a coating that sands and polishes well, is more moisture-resistant than either resin alone and permits the use of higher solids content than is the case with the butyral resin alone. Other combinations with natural gums and resins are possible since many are compatible with vinyl butyral resins.

Vinyl butyral resin can also be used with phenolic resins to produce durable wood finishes, either clear or pigmented. These coatings have been used for wooden gasoline tanks and for other chemical-resistant finishes. Vinyl butyral-phenolic resin coatings make excellent primers for house paints and enamels. Better adhesion is obtained especially under humid conditions. One of the most interesting applications at the present time is a knot sealer for pine lumber. Where knot sealing is not a factor and a primer for damp conditions is desired, vinyl butyral resin alone is effective, even in extremely light coatings.

The development of this knot sealer for the lumber and housing industry makes it possible to use "economy" lumber for exterior use without sacrifice in appearance or durability as compared to better grade, knot-free wood. Knots, even though they do not loosen, often exude pitch and volatile materials that destroy the adhesion of paint films covering them long before the clear portion of the wood needs repainting.

The Western Pine Association, after conducting extensive research to solve this problem and evaluating over 600 formulations, developed a knot sealer based on BAKELITE resin BV-9700-S and VINYLITE resin XYHL. The sealer is brushed over the unprimed knots and the surrounding area. Regular outdoor house paint can then be applied in the usual manner. Several years exposure has shown this treatment to have outstanding merit.

The formulation for Knot Sealer WP-578 is as follows:

WP-578	Parts by Weight	(Approx.) % by Wt.
BAKELITE Resin Varnish BV-9700-S, 60% solids	5.0	33.3%
VINYLITE Resin XYHL	0.5	3.3
95% Alcohol (denatured)	9.5	63.4
	15.0 parts	100.0%

Resin XYHL should be dissolved by adding it to the alcohol under agitation, after which the BV-9700-S solution should be added with thorough mixing.

Another use of this sealer is its application over asphaltic materials to prevent bleeding of enamel topcoats.

Cloth Coatings

Extremely tough, resistant coatings for cloth have been based on vinyl butyral resins, which contain heat-reactive ingredients or vulcanizing agents. They can be applied with standard spreading equipment. The coatings have better adhesion to most fabrics than other plastics; in fact, the adhesive strength in some cases will exceed the fabric strength. Coatings of this type are resistant to water, alcohol, acetone, and dry cleaning fluids. They have been used as waterproof cloth coatings to replace rubberized fabrics for the armed services. Typical uses include raincoats, food bags, and ponchos. The coatings have unusual resistance to heat and do not block at temperatures up to 180 deg. F. or crack when flexed sharply at 0 deg. F.

Protective coatings based on vinyl butyral resins can be used for many applications requiring contact with solvents such as ketones and esters. Typical formulations involve VINYLITE resins XYSG and XYHL modified with BAKELITE resin varnish BV-9700-S and glyoxal. This insolubilization not only renders the coating solvent resistant but facilitates the application of subsequent coats. These coatings have been used for gasoline tank linings and laboratory equipment which is exposed to a wide range of solvents, such as ketones, esters, and hydrocarbons.

A typical air-drying finish for steel based on vinyl butyral and phenolic resins is:

VINYLITE resin XYSG	10.2
Zinc tetroxy chromate	15.3
BAKELITE resin varnish BV-9700-S	20.3
Glyoxal	1.0
FLEXOL plasticizer 3GH	1.0
Water	2.3
SYNASOL solvent (denatured alcohol)	3.6
Butanol	6.3
Isopropanol	20.0
"Solvesso" #1	20.0
	100.0 parts by weight

The brittleness and lack of extensibility of many phenolic coatings have limited their use in many metal coating applications. Vinyl butyral resins can be used in fortifying or "plasticizing" phenolic coatings, thereby widening their use. A minimum of 20 per cent VINYLITE resin XYHL with resins such as BAKELITE phenolic resin BR-17620 is suggested to improve the flexibility of can linings and closure coatings. Approximately 1/2 to 1 per cent vinyl butyral resin XYHL used with other phenolic resins of more limited compatibility improves their coating properties by eliminating a tendency to "eye" or crater when applied over surfaces not properly cleaned.

Wash Primers

An outstanding achievement in the field of metal coatings is the development of a wash primer based on an entirely new and original concept in the field of coatings.

This material serves a twofold function as a metal pretreatment or conditioner acting as an excellent adhesive bond for subsequent paint films and, in addition, provides an anti-corrosive film. As it is applied in an extremely thin film of approximately 0.1 - 0.3 mils, it supplements, but does not entirely replace, the anti-corrosive primers or intermediate coats for use under severe corrosive conditions and is most aptly described as a metal conditioner.

Before the development of the wash primer, the standard metal preparation for many applications, such as painting ship bottom, consisted of wet sandblasting followed by an aqueous phosphoric acid wash treatment. The aqueous phosphoric was objectionable because of freezing at low temperatures and bad adherence of paint film due to uneven concentration of the phosphoric acid. The phosphate-treated surface was unable to withstand exposure to high humidity or rain between the time of surface preparation and application of an anti-corrosion primer.

TABLE II

COMPATIBILITY OF VINYL

Resin XYSG with Commercial Resins

Resin	Solvents	Ratio of Resin XYSG to test substance 9/1	4/1	1/1	1/4	1/9	Remarks
"Acryloid" B-7, Solution in Ethylene Dichloride (1)	Isopropanol	SI	SI	SI	SI	SI	Poor adhesion; soft.
"Acryloid" B-72, Solution in Toluene (1)	Isopropanol	SI	SI	SI	SI	SI	
"Acryloid" C-10, Solution in Ethyl Acetate (1)	Isopropanol				I	SI	Short; adhesion fair.
"Acryloid" F-10, Solution in Mineral Spirits (1)	Isopropanol	I	I				
Amberol No. 226 (1)	Butanol	C	C	C	C	C	
BAKELITE phenolic resin BR-3360 (2)	Isopropanol-Toluene	I	I	C	C	C	1/1 to 1/9 soft.
BAKELITE phenolic resin BR-9432 (2)	Isopropanol-Toluene	C	C	C	C	C	Films cheesy.
BAKELITE phenolic resin BR-3180 (2)	Isopropanol-Toluene	I	I	I	I	I	
BAKELITE phenolic resin BV-9700 (2)			C	C	C		
BAKELITE phenolic resin BV-1112 (2)			C	C	C		
"Beckacite" 1001 (3)	Isopropanol-Toluene	C	C	SI	SI	SI	1/1 to 1/9 very hard, good adhesion 9/1 to 4/1 hard & brittle.
"Beckacite" 1003 (3)	Isopropanol-Toluene	C	C	C	SI	SI	9/1 to 1/1 slightly tacky
"Beckacite" 1110 (3)	Isopropanol-Toluene-Hexone	SI	SI	SI	C	C	
"Beckacite" 1111 (3)	Isopropanol-Toluene	I	I	SI	C	C	
"Beckacite" 1115 (3)	Isopropanol-Toluene-Hexone	I	SI	SI	C	SI	
"Beckosol" 5 (3)	Isopropanol-Toluene-Hexone	I	I	I	I	I	
"Beckosol" 1320 (3)	Isopropanol-Xylene	I	I	I	I	I	
"Beckosol" 1324 (3)	Isopropanol-Toluene	C	C	C	C	C	Adhesion poor, tacky with higher resin content.
Cellulose Acetate	Esters, Ketones-Alcohols	I	I	I	I	I	
Cellulose Aceto-propionate	Isopropanol-Acetone-Ethyl Dichloride.	I	I	I	I	SI	
Cellulose Aceto-butyrate	Isopropanol-Acetone-Ethyl Dichloride	I	I	I	I	I	
Chlorinated Rubber (4)		I	I	I	I	I	
Cumar P-25 (5)	Isopropanol-Toluene	I	I	I	I	I	
Cumar VLC (5)	Isopropanol-Toluene	I	I	I	I	I	
Cumar W 1/2 (5)	Isopropanol-Toluene	I	I	I	I	I	

Resin XYSG with Commerci

Resin	Solvents	Ratio of Resin to test subst. 9/1	4/1	1/1	1/
"Duraplex" C-45 LV (1)	Butanol	I	I	I	I
"Durez" No. 550 (6)	Butanol	C	C	C	C
Ester Gum (Synthe Copal) (3)	Isopropanol-Toluene	SI	I	I	I
Kopal No. 501 (3)	CELLOSOLVE	I	I	I	I
"Nevillac", Hard (7)	Isopropanol-Toluene	C	C	C	C
"Nevillite" No. 465 (7)	Isopropanol-Toluene	SI	I	I	I
"Nevillite" R-17 (7)	Isopropanol-Toluene	I	I	I	I
"Nevindine" R-1 (7)	Isopropanol-Toluene	I	I	I	I
"Petropon" 2138 (8)	Butanol	C	C	I	I
"Plaskon" 3402 (9)	CELLOSOLVE	I	I	I	I
"Poly N-Butyl Methacrylate (10)	CELLOSOLVE	I	I	I	I
"Rezyl" No. 330-5 (11)	Isopropanol-Toluene-Xylene	I	I	I	I
"Rezyl" No. 227-8 Solution in Xylene (11)		SI	I	I	I
"Santolite" MS (12)	Isopropanol-Toluene	C	C	C	S.
"Santolite" K (12)	Isopropanol-Toluene	C	C	I	I
"Teglac" No. 15 (11)	Isopropanol-Toluene	SI	SI	SI	I
"Teglac" Z-152 (11)	Isopropanol-Toluene	I	I	I	I
"Teglac" No. 161 (11)	CELLOSOLVE	I	I	I	I
"Uformite" F-220 (1) (Resinous Products & Chemical Co.)	Butanol	I	I	I	I
"Varcum" No. 250 (13)	Butanol	C	C	C	C

Resin XYSG with Nat

Accroides	Isopropanol	SI	SI	C	C
Batavia Damar	Isopropanol-Toluene	I	I	I	I
Beea Bold	Isopropanol-Toluene	C	C	C	C
Congo Hard	Isopropanol-Hexone	C	C	C	C

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C - Compatible I - Incompatible SI - Slightly Incompati

3LE II

VINYL BUTYRAL RESINS

mmercial Resins (cont.)

of Resin XSG est substance /1	1/1	1/4	1/9	Remarks
I	I	I	I	
C	C	C	C	
I	I	I	I	
I	I	I	I	
C	C	C	C	Little film strength, softness increased by resin, good adhesion.
I	I	I	I	9/1 Soft, short.
I	I	I	I	
I	I	I	I	
C	I	I	I	
I	I	I	I	
I	I	I	I	
I	I	I	I	
I	I	I	I	
C	C	S	I	9/1 to 1/1 hard, adherent. 1/4 soft.
C	I	I	I	
I	SI	I	I	Hard, brittle
I	I	I	I	
I	I	I	I	
I	I	I	I	
C	C	C	C	

with Natural Gums

SI	C	C	C	9/1 to 4/1 adhesion fair. 1/1 to 1/1 to 1/9 hard, brittle.
I	I	I	I	
C	C	C	C	9/1 to 1/1 hard, short. Good adhesion. 1/4 to 1/9 soft.
C	C	C	C	9/1 to 4/1 hard, adhesion poor. 1/1 fair adhesion. 1/4 to 1/9 short.

Incompatible - faint haze in film

Resin XYSG with Natural Gums (cont.)

	Solvents	Ratio of Resin XYSG to test substance 9/1	4/1	1/1	1/4	1/9	Remarks
Damar (dewaxes)	Ethanol-Isopropanol-Toluene	C	C	C	C	C	9/1 to 4/1 good film strength. 1/1 to 1/9 brittle.
Damar (Singapore)	Isopropanol-Toluene	SI	SI	SI	SI	SI	9/1 to 1/1 hard, adhesion fair. 1/4 to 1/9 soft.
Damar (P.E.I. Macassar)	Isopropanol-Toluene	I	I	I	I	I	
Elemi	Isopropanol-Toluene	C	C	C	C	C	9/1 strong film, poor adhesion. 4/1 to 1/9 short.
Manila	Isopropanol-CELLOSOLVE	C	C	C	C	C	Hard, brittle, adhesion fair.
Manila Loba	Isopropanol-CELLOSOLVE	C	C	C	C	C	Hard, brittle, adhesion fair.
Mastic	Isopropanol-Toluene	C	C	C	C	C	1/1 to 1/9 short, good adhesion. 9/1 to 4/1 strong, hard, poor adhesion.
Pontianak	Isopropanol-Hexone	C	C	C	C	C	9/1 to 4/1 hard, poor adhesion. 1/1 to 1/9 short.
Sandarac	Isopropanol	C	C	C	C	C	9/1 to 1/4 hard, good adhesion. 1/9 very short.

Resin XYSG with Waxes and Oils

HALOWAX 1012 (14)	Isopropanol-Toluene	SI	I	I	I	I	
HALOWAX 1013 (14)	Isopropanol-Toluene	SI	I	I	I	I	
HALOWAX 1014 (14)	Isopropanol-Toluene	SI	I	I	I	I	
No. 100 Linseed Oil (15)	Isopropanol-Toluene	C	C	I			
OKO-M-7 Linseed Oil (15)	Isopropanol-Toluene	I	I	I	I	I	
Pale Blown Castor Oil	Isopropanol-Toluene	C	C	C	C	C	Audition of oil causes softness.
Raw Castor Oil AA	Isopropanol-Toluene	C	C	C	C	C	Oil causes softness.
Refined Perilla Oil	Isopropanol-Toluene	I	I	I	I	I	
Tung Oil	Isopropanol-Toluene-Hexone	I	I	I	I	I	
White Heavy Bodied Oil (15)	Isopropanol-Toluene-Hexone	SI	C	SI	I	C	1/9 soft, greasy.

SUPPLIERS

(1) Resinous Products Division, Rohm & Haas Co.
(2) Bakelite Company
(3) Reichold Chemicals Co.
(4) Hercules Powder Co.
(5) Barrett Co.
(6) Durez Plastics & Chemicals Co., Inc.
(7) Neville Co.
(8) American Mineral Spirits Co.
(9) Libby-Owens-Ford Glass Co.
(10) E.I. duPont de Nemours, Inc.
(11) American Cyanamid Co.
(12) Monsanto Chemical Co.
(13) Varcum Chemical Co.
(14) Halowax Products Division, Union Carbide & Carbon Corp.
(15) Archer-Daniels-Midland Co.

Using the wash primer, it is now possible to apply a coating in the field that is at least equivalent to shop-applied pretreatments on metal. A complex resin-chromate-phosphate is formed by the chrome pigment-vinyl butyral resin-phosphoric acid solution which meets the objections to the aqueous wash treatment. The complex has excellent adhesion to clean metal surfaces; the alcohol solvent permits its application over a wide temperature range and under high humidity; a uniform film is applied which air-dries rapidly; temporary protection against corrosion is obtained; and most paints or coatings readily adhere to the wash primer. The wash primer, as originally developed, consists of a two-container system composed of a base grind and an acid diluent. The base grind contains VINYLITE resin XYHL, an insoluble type chrome pigment and some of the solvent. The acid diluent is composed of phosphoric acid, water, and the remaining solvent.

Four wash primer formulations in current use are prepared by pebble mill grinding the base and adding the acid diluent to the base grind, using the following formulations:

Base Grind	WP-1 (MIL-P-15328) Parts by Weight	XE-5220 Parts by Weight	XE-5298 Parts by Weight	XE-5300 Parts by Weight
VINYLITE Resin XYHL	7.2	9.0	9.0	9.0
Chromic Phosphate	--	--	9.0	4.5
Basic Zinc Chromate Pigment	6.9	--	--	4.5
Lead Chromate (low in soluble salts)	--	8.6	--	--
Talc (Asbestine 3X)	1.1	1.4	1.4	1.4
Ethanol (or equivalent anhydrous "Synasol")	--	--	54.5	54.5
Lampblack	Trace	--	--	--
Isopropanol, 99% or Ethyl Alcohol	48.7	53.0	--	--
Butyl Alcohol	16.1	--	--	--
Methyl Isobutyl Ketone	--	13.0	16.1	16.1
	80.0	85.0	90.0	90.0
Acid Diluent				
Phosphoric Acid, 85%	3.6	2.9	1.8	1.8
Water	3.2	2.9	1.8	1.8
Isopropanol, 99% or Ethyl Alcohol	13.2	9.2	--	--
Ethanol (or equivalent anhydrous "Synasol")	--	--	6.4	6.4
	20.0	15.0	10.0	10.0
	100.0	100.0	100.0	100.0

These formulations are representative of the systems based on basic zinc chromate and lead chromate pigments. It is important to use grades of these pigments containing a minimum amount of water-soluble materials. It is also important that the essential ratio of resin-pigment-phosphoric acid be kept constant, although more solvent may be added to the acid diluent to reduce the viscosity and change the ratio of diluent to base. Variation can also be made in the selection of solvents. Denatured alcohol and butanol may be used, and dilution with ketones or aromatic hydrocarbons will reduce the viscosity of WP-1 formulation as indicated in Figure 2. Aromatic hydrocarbons should be used with caution because of their adverse effect on storage stability. Under conditions of high humidity or for applications to damp surfaces, it is suggested that the thinner contain approximately 25 per cent butanol. As indicated in Figure 3, the water content of vinyl butyral resin solutions is quite critical, and this is especially true of wash primer formulations. Approximately 5 per cent water should be present in the complete mixture introduced either from the alcohol or separately. Talc or "Asbestine" 3X is present as an extender to prevent settling and lampblack can be added to increase the hiding power.

These base grinds are best prepared by grinding in a pebble mill using flint pebbles. Steel lined mills and steel balls should be avoided, since iron contamination may interfere with the performance of the finished product. Base solutions should be stored in terne-plate or similar non-reactive containers, and the acid diluent in glass or polyethylene containers or containers having a baked phenolic or vinyl chloride-acetate resin coating.

Application of wash primer type of metal conditioners can be made by conventional methods such as brushing, spraying, dipping, or roller coating. Since these coatings are formulated with low solids, they penetrate into the cavitation or corrosion pits instead of bridging them. (This prevents the pinholes which lead to premature failure from under-film corrosion which often occurs when using other treatments.) Adequate surface preparation such as sandblasting or vapor degreasing is to be recommended, although the wash primers usually exhibit better adhesion to poorly prepared surfaces than most paints. They will not, however, give best results over loose mill scale and corrosion products, acetic acid, salts or grease.

TYPES OF WASH PRIMERS

Each of the wash primer formulations has its specific advantages, as well as its limitations. WP-1 is recommended for adhesion to a wide variety of metal surfaces including steel, zinc, cadmium, tin, aluminum, and galvanized iron. It is recommended particularly for application to steel, such as ship hulls where exposure to salt water will be encountered. WP-1 has an effective life of eight hours after the acid diluent is added to the base. There is a gradual decline in the adhesion of the films applied after this period. It is believed that the complex reaction between vinyl butyral resin, zinc chromate, and metal which occurs after application to the metal surface gradually takes place in the mixture alone, and it loses its ability to adhere. It should be noted that this is not accompanied by any immediate visible change in the solution so that precautions must be taken to insure that it is used within this period. Eventually the mixed material may gel, but its usefulness is spent long before this occurs.

In the WP-1 formulation, one part of diluent is added to four parts of the base to prepare the wash primer for application. As the specific gravities of the base and acid diluent are approximately equal, parts by weight or volume can be used, and one gallon of diluent can be added to four gallons of base. Agitation is needed during the mixing operation to prevent local gelatin.

Wash primer XE-5220, as described above, has greatly increased stability over its counterpart, WP-1, which makes it possible to use this material as a one-package system. The stability of XE-5220, using the recommended solvents, is at least a year after mixing the two components, but this may vary with the particular pigment used in the primer. This formulation is recommended only for use on steel, and it takes somewhat longer for it to develop adhesion than WP-1. Once developed, however, the adhesion of the two wash primers is comparable. Both wash primers can be overcoated with coatings based on VINYLITE resin VAGH after an air-dry of about 15 minutes, or a force dry of 1 to 2 minutes at 200 deg. F. Coatings based on VINYLITE resin VAGH develop better adhesion to XE-5220 if they contain no basic lead pigments such as red lead, chrome orange, etc. Comparison of XE-5220 with WP-1 indicates that on steel XE-5220 gives comparable performance in atmospheric exposures. In fresh water service XE-5220 is suggested. The lower soluble salt content of available lead chromate pigments seems to have an important bearing on the superior performance of XE-5220 in fresh water exposure.

A recent development in wash primers involves the use of chromic phosphate as a rust inhibitive pigment to prepare stable one-package primers. While these have not been tested as extensively as the WP-1 and XE-5220 types, they have given excellent performance in all accelerated tests. The formulation XE-5298 is suggested for use on steel while the XE-5300 is preferred for aluminum, or galvanized surfaces. Both formulations may be stored with the acid diluent without any apparent loss of ability to adhere.

These chromic phosphate primers show less tendency to develop osmotic blisters than the WP-1 formulation. For this reason, they should be preferred for use in installations involving high humidity or fresh water immersion.

A clear metal conditioner for application to all types of metal, but having better storage stability than WP-1 is made by modifying butyral resin solutions with chromic and phosphoric acids. A typical metal treatment made by this process is XL-5367 solution which is prepared as follows:

Solution A

	Parts by Weight
Chromium Trioxide (CrO_3)	4.65
Water	9.30
	13.95

CAUTION! Chromium trioxide must first be added directly to the water. If added directly to some organic thinners, chromium trioxide results in spontaneous combustion.

Solution B

	Parts by Weight
85% Ortho Phosphoric Acid	10.95
Acetone	98.60
	109.55

Solution C

VINYLITE resin XYHL	109.5
Denatured Alcohol (1)	622.0
	731.5

(1) 90% of 190 proof ethanol and 10% methanol.

Solution A is prepared by adding 4.65 grams of chromium trioxide to 9.30 grams of water in a glass container with constant stirring until all of the chromium trioxide is dissolved.

Solution B is prepared in a second glass container by slowly adding the phosphoric acid to the acetone with constant stirring.

Solution C is prepared by dissolving the VINYLITE resin XHYL in alcohol.

After all of the resin is dissolved, Solution C is heated to 50 deg. C with agitation. Solution A is slowly added to Solution B with constant stirring. The mixture of Solution A and Solution B is then slowly added to Solution C. Mild agitation should be maintained throughout the mixing and heating cycle. A glass lined, steam jacketed container with reflux condenser is suggested as suitable manufacturing equipment to reduce solvent loss and fire hazards.

When all ingredients are mixed, the charge is held at 45 to 50 deg. C for 25 minutes. The steam is turned off and cooling water circulated through the jacket. When the temperature of the batch has reached approximately 35 deg. C. 145 parts of butanol are added and the product is cooled to room temperature.

Properties of XL-5367:

Color	Green
Drying time	5 minutes
Total solids	12% ± .5%
Specific gravity	0.826
Viscosity	50-54 K.V.
Flash point	45 deg. F.
Wt. per gal.	6.9 lb.
Adhesion	Good on smooth steel, zinc, iron, aluminum and glass
Keeping time	6 months or more

The XL-5367 solution is adherent to the same metallic surfaces as the WP-1 type. It is relatively free from soluble ions, and therefore develops fewer osmotic blisters than WP-1 when immersed in fresh water. As in unpigmented composition XL-5367 has good rust inhibitive properties. When necessary, however, rust inhibitive pigments may be used in the XL-5367.

Almost all types of paints adhere to the wash primers and the performance of phenolic, alkyd and oleoresinous paints is usually improved when applied over the wash primer in preference to clean metal. Acrylic and methacrylic polymers, vinylidene chloride resins and nitrocellulose coatings do not generally adhere to the wash primer surfaces, although pyroxylin lacquers containing modifying resins may adhere.

Of the vinyl resins, VINYLITE resin VAGH develops excellent adhesion to wash primer films, but the other vinyl chloride-acetate resins do not generally adhere.

Although these vinyl butyral resin coatings are not recommended as a single coat system for providing corrosion protection, they nevertheless provide varying degrees of temporary protection to metal depending upon the severity of the exposure conditions. The wash primer films with no topcoat give excellent protection to steel for months where the coated metal is stored indoors, but only a few weeks protection when the metal is exposed to the rain or where moisture can collect on the surface. Heavier than normal thickness of wash primers increase the period of resistance.

These materials are widely used in marine finishing. It was in this field that the original development work was carried out. A forerunner of the present marine system for steel vessels used anti-corrosive and anti-fouling coats based on vinyl butyral resins. Outstanding performance, however, has been demonstrated by an all-vinyl system comprising the wash primer WP-1 and an anti-corrosive primer and an anti-fouling coat, both based on vinyl chloride-acetate resins. On laboratory tests of exposure panels and actual service tests now in the seventh year, the marine system based on VINYLITE resins has outperformed all other systems with which it has been compared.

Because of the valuable characteristics of the VINYLITE resins on which they are based, the coatings used in these systems possess several advantages over ordinary, marine coatings. They have unusual toughness, adhesion, and chemical resistance. Under a wide range of climatic conditions, these coatings dry to a tough film in thirty minutes. In addition, they are not sensitive to normal dry-dock conditions, since the wash primer is not affected by the slight amount of moisture often present on the surface of the hull if the solvent is composed of at least 25 per cent butanol.

The wash primers or metal conditioners prevent the spread of corrosion under the paint film if any mechanically damaged spots occur possibly because of scraping at a pier. The corroded area can be cleaned, touched up with the primer and the anti-corrosive and anti-fouling coats applied.

Another outstanding advantage of wash primer type of metal conditioners is its short drying time. In refinishing large areas, it is necessary to sandblast the area and immediately apply an anti-corrosive coat to prevent rusting. Using conventional paints, there is often an appreciable time lag necessary to permit the coating to dry before sandblasting the next area, otherwise sand particles would adhere to the wet paint film, resulting in weak spots which would lead to premature failure of the coating. Using the wash primer type of metal conditioner, this difficulty is not experienced, as it is possible to sandblast adjacent areas within a few minutes after applying the wash primer, to the preceding section. Reduced "shut down" time for tanks and processing equipment, therefore, results in appreciable savings in maintenance costs.

Similarly, in applications involving drydocking or lighterage service, great economies are obtained as a result of the rapid drying schedules possible using wash primer type of metal conditioner and fast drying anti-corrosive coats based on vinyl chloride-acetate resins.

The outstanding results obtained in the marine field have obviously indicated their uses in other fields, and experience to date is proving their merit in industrial and maintenance fields. For example, they are being extensively used in the petroleum industry as coatings for pipe lines, oil storage tanks, and drilling platforms. Other applications include air conditioning equipment, particularly fans where the corrosion on the edge of fan blades is very severe. The wash primer provides a tight, adherent bonding surface and the vinyl resin topcoating provides wear and abrasion resistance.

The development of wash primers permits the application of house paints to aluminum metal surfaces. Aluminum sheets can now be obtained which have a shop-applied wash primer on the flat sheet. This prime-coated sheet can be utilized for the manufacture of any item where painted or coated finish s are used and where drawing, forming, or stretch forming is required. The XL-5367 type of coating is very effective in improving the adhesion of inks and adhesives to aluminum foil.

Alkyd, melamine, oleoresinous, phenolic, and oil base finishes have also shown improved adhesion and corrosion resistance when applied over these metal conditioners. However, where maximum corrosion and chemical resistance are desired, vinyl chloride-acetate coatings applied over the wash primer type of metal conditioner is recommended.

CONCLUSION

The information in this technical release will enable manufacturers to utilize VINYLITE resins XYHL and XYSG, in the preparation of coatings and adhesives. Bakelite Company maintains laboratories and a staff of technically trained representatives whose services are available to manufacturers interested in using these products.

The information contained in this bulletin has been carefully checked for accuracy and is believed to be reliable. However, it is urged that users check their formulations carefully and evaluate the results on the basis of their own equipment.

BAKELITE COMPANY

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