Improving the Receptivity of PVC Articles Toward Water-Based Inks, Coatings or Adhesives

Abstract

Typically, the measure of hydrophobicity in polyvinyl chloride (PVC) films and sheets is a surface energy measurement in dynes/cm in the low-to-mid thirties. More recently, the trend has been to lower the amounts of solvents used in inks, coatings and adhesives that in turn are used to coat or print the flexible PVC article. With the change in the makeup of coating systems, a modification in the surface energy of the flexible PVC film is needed to make an inherently hydrophobic material more hydrophilic.

Hallstar has found that the combination of a polymeric plasticizer and a monomeric plasticizer in conjunction with a metal oxide unexpectedly increases the hydrophilicity of PVC sheets or films by factors of roughly 25–33 percent.

This paper will discuss the use of RX-13705 in conjunction with Calcium Oxide HP to increase surface tension from 33–36 dynes/cm to 40–43 dynes/cm.

Introduction

Typically, flexible PVC is plasticized with one or more polymeric or monomeric plasticizers at 20–100 PPHR. If long-term permanence is required, more polymeric material is needed versus short-term plasticization that uses relatively more monomeric product.

Considering that polymeric and/or monomeric plasticizers are necessary additives for flexible PVC, RX-13705 can be used to improve the hydrophilicity of the compound. Flexible PVC sheets plasticized with such polymeric and/or monomeric plasticizers are used as substrates that can be printed upon such articles as PVC banners, decals, awnings, signs, etc. For many years, materials used to print on the flexible PVC substrates traditionally have been solvent-based compositions. Recently, the trend has been towards eliminating the higher solvent-based or volatile organic compound (VOC) materials and formulating with lower VOC or water-based systems. The "new" inks, coatings and adhesives formulated with these low or no-VOC systems do not adhere to the PVC film as efficiently as the traditional solvent-based systems. In an effort to investigate the modification of the surface to accept the intrinsically different, more hydrophilic ink and coating systems, surface energy may be used to denote any differences in PVC films. As noted in Table I, the baseline for this study is traditionally plasticized PVC films whose surface energies are usually 33–36 dynes/cm. The additive system described here resulted in much more hydrophilic surfaces, that is, surface energies in the 40–43 dynes/cm range.

TABLE I
Comparisons of Plasticizers Neat

	1	**2**	**3**	**4**	**5**
Geon® 30 (PVC Resin)	100.0	100.0	100.0	100.0	100.0
Synpron® 0350 (Barium/Zinc PVC Stabilizer)	1.0	1.0	1.0	1.0	1.0

Paraplex® G-62 (Epoxidized Soybean Oil)	5.0	5.0	5.0	5.0	5.0
RX-13290 (Polyester Adipate)	67.0	--	--	--	--
Paraplex® G-30 (Mixed Dibasic Polymeric)	--	67.0	--	--	--
Paraplex® G-31 (Mixed Dibasic Polymeric)	--	--	67.0	--	--
Santicizer® 160 (Butyl Benzyl Phthalate)	--	--	--	67.0	--
Paraplex® G-54 (Polyester Adipate)	--	--	--	--	67.0
Variable	**RX-13290**	**G-30**	**G-31**	**S-160**	**G-54**
Surface Tension (dynes/cm)	**33**	**34**	**34**	**36**	**36**

It has been determined that RX-13705 in conjunction with a metal oxide (Calcium Oxide HP), unexpectedly increases the hydrophilicity of PVC sheets or films by factors of 25–33 percent.

With the additive package, vinyl sheets have been measured with surface energies greater than 40 dynes/cm. With this 25–33 percent increase in hydrophilicity, the PVC articles should be more amenable to coating with low or no VOC inks, coatings and adhesive systems.

Table II highlights data that shows characteristics of the suggested components neat or in dual combinations when compared to the complete system, RX-13705. This indicates the synergy that exists between the components for the ultimate increase in hydrophilicity.

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TABLE II
Comparison of Components of the Complete System

	1	2	3	4	5
Geon® 30 (PVC Resin)	100.0	100.0	100.0	100.0	100.0
Synpron® 0350 (Barium/Zinc PVC Stabilizer)	1.0	1.0	1.0	1.0	1.0
Paraplex® G-62 (Epoxidized Soybean Oil)	5.0	5.0	5.0	5.0	5.0
Paraplex® G-54 (Polyester Adipate)	--	67.0	53.6	65.0	--
Plasthall® 7050 (Dialkyl Diether Monomeric Glutarate)	67.0	--	13.4	--	--
RX-13705					65.6
Calcium Oxide HP	--	--	--	2	1.4
Variable	**7050 Neat**	**G-54 Neat**	**G-54/ 7050**	**G-54/ CaO**	**RX-13705 w/ CaO**

Surface Tension (dynes/cm)	38*	37	35	40	40-43

* PVC compound plasticized with Plasthall® 7050 is not stable and requires the addition of 1 PPHR of antioxidant to test the product. The effect of the antioxidant was not determined.

This paper will discuss the effect of each component on the recommended system and their results.

Reproducibility

Results from independent experiments are tabulated in Table III in an effort to measure the reproducibility of the surface tension data. Data indicates that a range of ±1.5 dynes/cm is reliable for compounds containing the necessary additive combination to fully improve the hydrophilicity of the PVC article.

TABLE III

Reproducibility

	1	2	3	4	5
Geon® 30 (PVC Resin)	100.0	100.0	100.0	100.0	100.0
Synpron® 0350 (Barium/Zinc PVC Stabilizer)	1.0	1.0	1.0	1.0	1.0
Paraplex® G-62 (Epoxidized Soybean Oil)	5.0	5.0	5.0	5.0	5.0
Paraplex® G-30 (Mixed Dibasic Polymeric)	67.0	67.0	--	--	--
RX-13705	--	--	65.6	65.6	65.6
Calcium Oxide HP	--	--	1.4	1.4	1.4
Variable	**G-30**	**G-30**	**RX-13705 w/ CaO HP**	**RX-13705 w/ CaO HP**	**RX-13705 w/ CaO HP**
Surface Tension (dynes/cm)	**35**	**34**	**40**	**40**	**42**

Monomeric Component

Various monomeric plasticizers were evaluated in an effort to determine the best monomeric for RX-13705 to improve the receptivity of PVC articles toward low or no VOC systems. Major classes of monomeric plasticizer additives were evaluated, including:

- Ether Esters of two Diacids **(Plasthall® DBEEA, Plasthall® DBEA, Plasthall® DBES)**
- Dialkyl Ethers **(Plasthall® 7050, C_6 Diacid Ester, C_4 Diacid Ester)**
- Trimellitates **(Plasthall® TOTM)**

- Dialkyl Adipate **(Plasthall® DOA)**
- Dialkyl Azelate **(Plasthall® DOZ)**
- Linear Phthalates **(Plasthall® 6-10P)**
- Dialkyl Phthalates **(Plasthall® DOP)**
- Long Chain Phosphates **(Reofos® 65)**
- Benzyl Phthalate **(Santicizer® 160)**

All these materials when combined with the recommended system provide PVC with a surface tension of 36–38 dynes/cm, except for the Plasthall® 7050 and C_4 Diacid, as noted in Table IV. Plasthall® 7050 and the C_4 Diacid ester (a non-commercial product) provide PVC with a surface tension value of 40–43 dynes/cm. The difference between 36 and 40 dynes/cm is outside the range of experimental error and represents a significant improvement in increasing the hydrophilic nature of a PVC film or sheet.

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TABLE IV
Comparison of Monomerics Evaluated

	1	2	3	4	5	6	7	8	9	10	11	12	13
Geon® 30 (PVC Resin)	100	100	100	100	100	100	100	100	100	100	100	100	100
Synpron® 0350 (Barium/Zinc PVC Stabilizer)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Paraplex® G-62 (Epoxidized Soy Bean Oil)	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Paraplex® G-54 (Polyester Adipate)	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5
Calcium Oxide HP	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
Plasthall® 226 (DBEEA) (Dibutoxy Ethoxy Ethyl Adipate)	13.1	--	--	--	--	--	--	--	--	--	--	--	--
Plasthall® 207 (DBES) (Dibutoxy Ethoxy Sebacate)	--	13.1	--	--	--	--	--	--	--	--	--	--	--
Plasthall® TOTM (Trioctyl Trimellitate)	--	--	13.1	--	--	--	--	--	--	--	--	--	--
Plasthall® DOA (Dioctyl Adipate)	--	--	--	13.1	--	--	--	--	--	--	--	--	--
Plasthall® 6-10P (Mixed Normal Alkyl Phthalate)	--	--	--	--	13.1	--	--	--	--	--	--	--	--
Reofos® 65 (Aryl Phosphate)	--	--	--	--	--	13.1	--	--	--	--	--	--	--
C_6 Diacid Ester	--	--	--	--	--	--	13.1	--	--	--	--	--	--
Plasthall® 203 (DBEA) (Dibutoxy Ethoxy Adipate)	--	--	--	--	--	--	--	13.1	--	--	--	--	--
Plasthall® DOZ (Dioctyl Azelate)	--	--	--	--	--	--	--	--	13.1	--	--	--	--
Santicizer® 160 (Butyl Benzyl Phthalate)	--	--	--	--	--	--	--	--	--	13.1	--	--	--

Plasthall® DOP (Dioctyl Phthalate)	--	--	--	--	--	--	--	--	--	--	13.1	--	--
C_4 Diacid Ester	--	--	--	--	--	--	--	--	--	--	--	13.1	--
Plasthall® 7050 (Dialkyl Diether Monomeric Glutarate)	--	--	--	--	--	--	--	--	--	--	--	--	13.1
Variable	**DBEEA**	**DBES**	**TOTM**	**DOA**	**6-10P**	**Reo. 65**	**C_6 Diacid**	**DBEA**	**DOZ**	**S-160**	**DOP**	**C_4 Diacid**	**7050**
Surface Tension (dynes/cm)	**36**	**36**	**36**	**36**	**36**	**36**	**36**	**37**	**37**	**37**	**38**	**42**	**40-43**

The recommended monomeric component of RX-13705, Plasthall® 7050, provides PVC with the most improvement. In addition, PVC plasticized with Plasthall® 7050 neat, G-54 neat or either in combination with CaO HP provides surface tension readings outside the range of experimental error or on the lower end of the optimal results, as discussed previously (Table II), in terms of reproducibility.

Polymeric Component

The data in Table V shows the effect of various polymeric plasticizers in combination with the suggested Plasthall® 7050 and Calcium Oxide HP.

TABLE V
Comparison of Polymerics Evaluated

	1	2	3	4	5	6	7
Geon® 30 (PVC Resin)	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Synpron® 0350 (Barium/Zinc PVC Stabilizer)	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Paraplex® G-62 (Epoxidized Soy Bean Oil)	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Plasthall® 7050 (Dialkyl Diether Monomeric Glutarate)	13.1	13.1	13.1	13.1	13.1	13.1	--
Calcium Oxide HP	1.4	1.4	1.4	1.4	1.4	1.4	--
Plasthall® P-7035 (Polyester Glutarate)	52.5	--	--	--	--	--	--
Plasthall® P-7046 (Polyester Glutarate)	--	52.5	--	--	--	--	--
Paraplex® G-41 (Polyester Adipate)	--	--	52.5	--	--	--	--
Paraplex® G-25 (Polyester Sebacate)	--	--	--	52.5	--	--	--
Paraplex® G-30 (Mixed Dibasic Polymeric)	--	--	--	--	52.5	--	--
Paraplex® G-54 (Polyester Adipate)	--	--	--	--	--	52.5	67.0

Variable	P-7035	P-7046	G-41	G-25	G-30	G-54	G-54 neat
Surface Tension (dynes/cm)	**32**	**34**	**39**	**39**	**40**	**40-43**	**35-38**

Major classes of polymerics were evaluated, such as polymeric adipates, glutarates and sebacates. Polymeric glutarates appear to negatively affect the results, while polymeric adipates and sebacates have positive effects.

As noted in Table I, PVC plasticized with polymeric plasticizers alone provided surface tensions of 33–36 dynes/cm. Table V demonstrates that a polymeric alone (Plasthall® G-54 neat) without the Plasthall® 7050 or Calcium Oxide HP is less preferable to the suggested combination of all three. The plasticized PVC compound containing all three components provides surface tension of 40–43 dynes/cm in comparison to 32–37 dynes/cm for other plasticizer combinations.

Metal Oxide Components

Metal oxides with oxidation states of plus two, three and four are exemplified in Table VI. Each compound was plasticized with RX-13705 in conjunction with a metal oxide. Groups IIA and IIB of the periodic table are represented. Two forms of calcium oxides, as well as calcium and magnesium hydroxides, were tested. While the addition of all the metal oxides decreased the hydrophobicity and increased the hydrophilicity of the PVC film, the data indicates that calcium oxide and calcium hydroxide are the preferred cation metal oxides (Table VI).

TABLE VI
Comparison of Oxides Evaluated

	1	2	3	4	5	6	7	8	9
Geon® 30 (PVC Resin)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Synpron® 0350 (Barium/Zinc PVC Stabilizer)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Paraplex® G-62 (Epoxidized Soy Bean Oil)	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Paraplex® G-54 (Polyester Adipate)	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5	53.6
Plasthall® 7050 (Dialkyl Diether Monomeric Glutarate)	13.1	13.1	13.1	13.1	13.1	13.1	13.1	13.1	13.4
MgO	1.4	--	--	--	--	--	--	--	--
MgOH	--	1.4	--	--	--	--	--	--	--
Fe_2O_3	--	--	1.4	--	--	--	--	--	--
TiO_2	--	--	--	1.4	--	--	--	--	--
ZnO	--	--	--	--	1.4	--	--	--	--
$Ca(OH)_2$	--	--	--	--	--	1.4	--	--	--
CaO (Technical Grade)	--	--	--	--	--	--	1.4	--	--
CaO - HP	--	--	--	--	--	--	--	1.4	--

Variable	MgO	MgOH	Fe_2O_3	TiO_2	ZnO	$Ca(OH)_2$	CaO-Tech	CaO - HP	no oxide
Surface Tension (dynes/cm)	**36**	**37**	**37**	**37**	**37**	**39**	**39**	**42**	**35**

Humidity Agings and Soapy Water Immersions

Compound containing the recommended additive of RX-13705 together with Calcium Oxide HP was aged under humid and soapy water conditions. The parameters for the humidity agings were one week at 50°C (122°F) and 90 percent RH. The parameters for soapy water immersions were 24 hours at 90°C (194°F) with a dry out for 24 hours at 60°C (140°F). Data, as compared to PVC film containing only a monomeric or polymeric plasticizer at the same part level, indicates a decrease in surface tension of 2–5 dynes/cm after humidity agings. The highest decrease in surface energy is observed after humidity agings versus soapy water changes (Table VII). For soapy water immersions, the increase in hydrophilicity is only slightly lower after testing than before, decreasing 0–2 dynes/cm. In addition, only the hydrophilic additive package maintains a higher degree of hydrophillicity compared to controls after soapy water testing. While surface energy decreases after humidity or soapy water conditions, data indicates that the application of water-based inks, coatings or adhesives should be carried out prior to such exposure.

TABLE VII
Humidity and Soapy Water Immersion Data

	1	2	3	4	5
Geon 30 (PVC Resin)	100.0	100.0	100.0	100.0	100.0
Synpron® 0350 (Barium/Zinc PVC Stabilizer)	1.0	1.0	1.0	1.0	1.0
Paraplex® G-62 (Epoxidized Soybean Oil)	5.0	5.0	5.0	5.0	5.0
RX-13705	65.6	--	--	--	
Calcium Oxide HP	1.4	--	--	--	--
Plasthall® DIDP (Diisodecyl Phthalate)	--	67.0	--	--	--
Santicizer® 160 (Butyl Benzyl Phthalate)	--	--	67.0	--	--
Paraplex® G-30 (Mixed Dibasic Polymeric)	--	--	--	67.0	--
Paraplex® G-54 (Polyester Adipate)					67.0
Variable	**RX-13705 w/ CaO HP**	**DIDP**	**S-160**	**G-30**	**G-54**
Original Surface Tension (dynes/cm)	**39**	**32**	**37**	**33**	**34**
<u>Original Physical Properties</u>					
Stress at 100% Elong., MPa	9.1	8.4	6.6	10.5	9.8
psi	1325	1225	950	1525	1425
Stress at 200% Elong., MPa	13.8	12.2	10.9	15.0	14.7
Stress at 300% Elong., MPa	16.9	14.8	15.2	17.8	17.4
Tensile, Ultimate, MPa	17.6	15.5	16.7	18.1	18.1
psi	2550	2250	2425	2625	2625
Elongation at Break, %	320	325	330	320	320
Hardness Duro A, pts.	69	68	66	70	71

<u>Humidity Aging</u>, 1 w at 50°C (122°F), 90% RH					
Surface Tension (dynes/cm)	**34**	**<32**	**32**	**32**	**32**
Δ Change, (dynes/cm)	**5**	**>1**	**5**	**1**	**2**
<u>Ivory Soap Immersion</u>, 24 h at 90°C (194°F)					
Surface Tension, (dynes/cm)	**39**	**32**	**32**	**<32**	**34**
Δ Change, (dynes/cm)	**0**	**0**	**5**	**>1**	**0**
<u>Ivory Soap Dry Out</u>, 24 h at 60°C (140°F)					
Surface Tension, (dynes/cm)	**37**	**33**	**<32**	**<32**	**<32**
Δ Change, (dynes/cm)	**2**	**1**	**>5**	**>1**	**>2**

Conclusions

- RX-13705 with Calcium Oxide HP was found to significantly improve the hydrophilicity of PVC film.
- Any one component without the other is not sufficient to decrease the hydrophobicity when compared to the combination of all three components. All components are needed to raise the surface tension of the PVC article from 32–34 dynes/cm to a value of 40–43 plus dynes/cm.
- One component of RX-13705 is a polymeric plasticizer, most preferably Paraplex® G-54 (a polymeric adipate), which is needed in combination with the other ingredients to have PVC sheet with a surface tension value of 40 plus dynes/cm.
- A monomeric plasticizer, primarily C_5 or less diacid (i.e., Plasthall® 7050), is the second component of RX-13705 needed to improve the hydrophilicity of a PVC film.
- The addition of a metal oxide (i.e., Calcium Oxide HP) is the third of three components needed for improved hydrophilicity.
- Surface energy decreases following humidity or soapy water agings. As is normally the case, treatment of PVC film or articles with water-based inks, coatings or adhesives is recommended prior to such exposure.