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


## ***Abstract***

Typically, the measure of hydrophobicity in 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 which, 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.

The HallStar Company 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% to 33%.

This paper will discuss the use of RX-13705 in conjunction with Calcium Oxide HP to an increase of 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 V.O.C. (volatile organic compound) materials and formulate with lower V.O.C. or water-based systems. The “new” inks, coatings and adhesives formulated with these low or no V.O.C. 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, i.e. 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% to 33%.

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

TABLE II highlights data which 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.

*Geon® is a registered trademark of The Geon Company.*
*SYNPRON® is a registered trademark of Synthetic Products Company.*

**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 affect 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 compound 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 V.O.C. 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 of 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.

*Reofos® is a registered trademark of FMC.*

**TABLE IV**

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## 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) on 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 affects.

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

(PARAPLEX 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 provide 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 of 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 @ 50°C (122°F) and 90% RH. The parameters for soapy water immersions were 24 hours @ 90°C (194°F) with a dry out for 24 hours @ 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** |
| **Original Physical Properties** | | | | | |
| Stress @ 100% Elong., MPa | 9.1 | 8.4 | 6.6 | 10.5 | 9.8 |
| psi | 1325 | 1225 | 950 | 1525 | 1425 |
| Stress @ 200% Elong., MPa | 13.8 | 12.2 | 10.9 | 15.0 | 14.7 |
| Stress @ 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 @ Break, % | 320 | 325 | 330 | 320 | 320 |
| Hardness Duro A, pts. | 69 | 68 | 66 | 70 | 71 |
| **Humidity Aging, 1 wk @ 50°C (122°F), 90% RH** | | | | | |
| **Surface Tension** (dynes/cm) | **34** | **<32** | **32** | **32** | **32** |
| **Δ Change,** (dynes/cm) | **5** | **>1** | **5** | **1** | **2** |

| | | | | | |
|---|---|---|---|---|---|
| **Ivory Soap Immersion, 24h @ 90°C (194°F)** | | | | | |
| **Surface Tension,** (dynes/cm) | **39** | **32** | **32** | **<32** | **34** |
| **Δ Change,** (dynes/cm) | **0** | **0** | **5** | **>1** | **0** |
| **Ivory Soap Dry Out, 24h @ 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 article with water-based inks, coatings or adhesives is recommended prior to such exposure.