MAJOR PROJECT

STUDY OF PIGMENTS ON PVC ARTIFICIAL LEATHER CLOTHS

A Major Project Report submitted in the partial fulfilment for the award of the degree

of

MASTER OF TECHNOLOGY (M. Tech)

In

POLYMER TECHNOLOGY

Submitted by

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July 2013

DECLERATION

I, hereby declare that the dissertation entitled "**Study of Pigments on PVC Artificial Leather Cloths**" being presented here in the partial fulfilment for the award of the Degree of Master of Technology (Polymer Technology), is an authentic record of own work carried out by me under the guidance and supervision of Prof D Kumar and Dr. Ram Singh, Department of Applied Chemistry and Polymer Technology, Delhi Technological University, Delhi.

I, further declare that the dissertation has not been submitted to any other Institute/University for the award of any degree or diploma or any other purpose whatsoever.

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CERTIFICATE

This is to certify that the major project report entitled '**Study of Pigments on PVC Artificial Leather Cloths**' which is submitted by **Neeraj Jindal** [2K10/PST/10] in the fulfilment for the award of the degree of Master of Technology (M. Tech) in Polymer Technology to the Department of Applied Chemistry & Polymer Technology, Delhi Technological University, Delhi – 110042, is the student own work carried out by him under our supervision during 2012-2013. The matter embodied in this project report is original and not copied from any source without proper citation and has not been submitted to any other university or institute for the award of any degree or diploma.

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Dated **(NEERAJ JINDAL)**
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Contents

CHAPTER 1

INTRODUCTION

1.1 Introduction

Solar energy is essential for human race. It spreads itself thin on the entire surface of the globe. The large buildings, which are now essential for the world's growing population, need to be made comfortable for its residents. In certain parts of the year these radiations are not required for the comfort of the residents. If the buildings are allowed to receive these radiations, the expenditure of cooling is excessive. Coatings that reflect the infrared radiation in the near IR region responsible for heat from the solar radiation are formulated with special pigments (Figure 1.1).

Pigments are inorganic or organic substances that are insoluble or substantially insoluble in water or the organic medium in which they are used as dispersions [1-4]. They impart color, opacity, mechanical rigidity and reinforcement to the continuous phase in which they are dispersed. Paint is a fine dispersion of pigments in binder(s) in the presence of solvent (s) and a small amount of additives. The final properties of the paint or coating depend on the properties of the binder, pigments or also on the additives. Pigments alter the appearance of the coating by selective absorption or by scattering of light. Pigments are classified on the basis of their performance as decorative pigments and protective pigments. Pigments also impart certain special properties to the coatings such as reflection of infrared radiation [5]. Light or electromagnetic radiation falling on any object meets three fates. It can be reflected, absorbed or transmitted. Any or all three can occur totally or selectively on the entire spectrum of electromagnetic radiation. (This means a substance can reflect in visible region, absorb in UV region and transmit in Infra Red region or any other combination of the three.) The development of infra red reflection phenomenon seems to have stemmed from the observation that radar frequency reflective pigments have been developed and used in the defence for making airplanes invisible to radar. For a common man, it is very difficult to comprehend this phenomenon since human beings cannot see radar waves. It is true for IR reflecting pigments also.

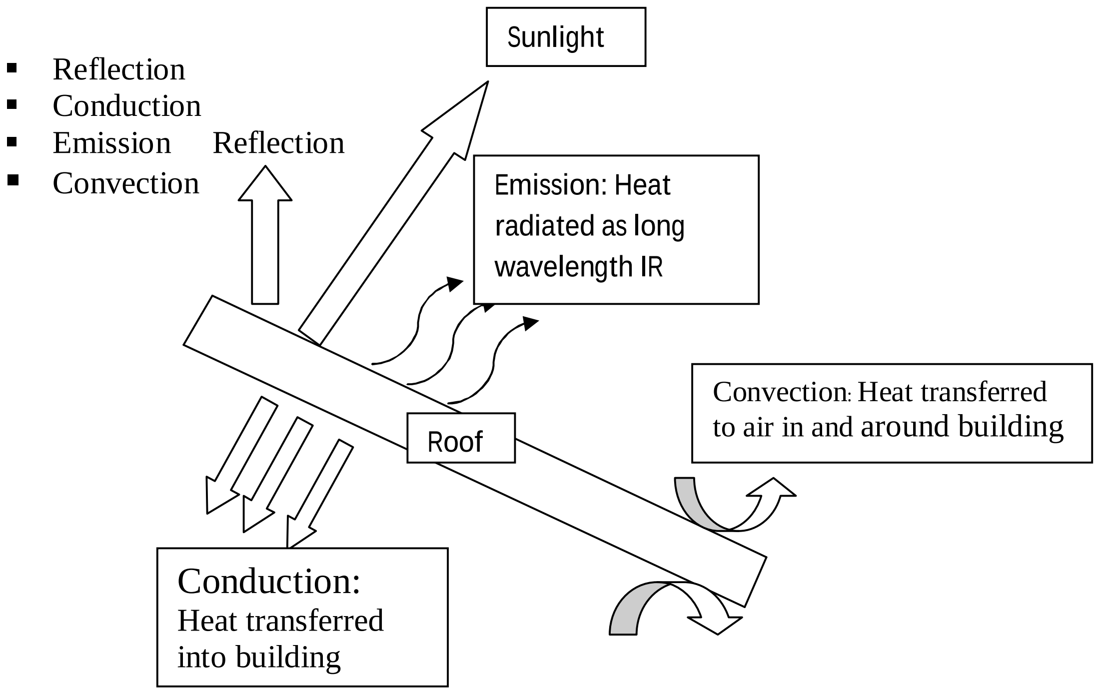


Figure 1.1

The conduction and convection draw heat from Sun into the building or home, increasing cooling costs (Figure 1.2) [6-8]. IR-reflective pigments minimize conduction and convection, by increasing reflection [6, 7]. Light energy from the sun spans a wide range of wavelengths. Much of the total energy is absorbed in our atmosphere and never reaches the Earth's surface [6, 9, 10]. The light that reaches the Earth's surface ranges from 295-2500 nanometres (nm) in wavelength. The human eye is sensitive to only a part of the electromagnetic spectrum. Apart from the visible region, pigments also interact with other wavelengths of light in the electromagnetic spectrum. These interactions can produce interesting effects on the coating properties.

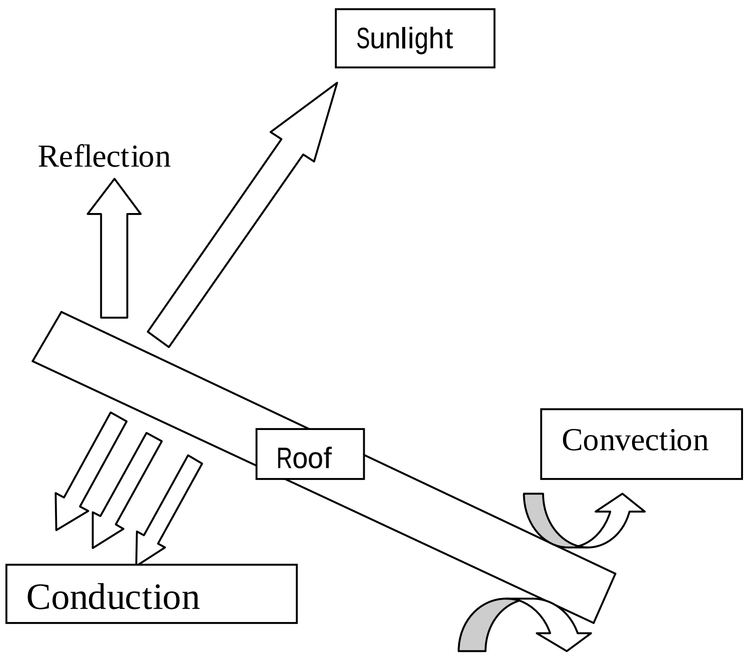


Figure 1.2

The sun's energy that reaches the earth's surface is divided into three main parts: (i) UV region; (ii) Visible region; and Infra-red resion [10].

(i) Ultraviolet Region (295-400 nm):

The ultraviolet region starts at 295 nm and this is the atmospheric cut-off point. This light is full of energy most suited to break several bonds, which hold the polymers, and is also responsible for sunburns. It is responsible for degradation of binder of the coatings because the energy level is enough to break down the primary bonds [10].

(ii) Visible Region (400-700 nm):

Around 50% of the sun's energy occurs in the visible region of the electromagnetic spectrum. Pigments selectively absorb the visible light and reflect the remaining. The visible region consists of wavelengths that give us the perception of color [10].

(iii) Infrared Region (700-2500 nm):

Forty-five percent of the total solar energy is in the nonvisible infrared region. Heat is a direct consequence of infrared radiation incident on an object. Infrared radiations range from 700 - 2500 nm wavelength. The heat-producing region of the infrared radiations ranges from 700 - 1100 nm. These radiations on absorption result in heating up of the surface [10]. A spectral distribution of solar power is given in figure 1.3 and 1.4 [6, 11].

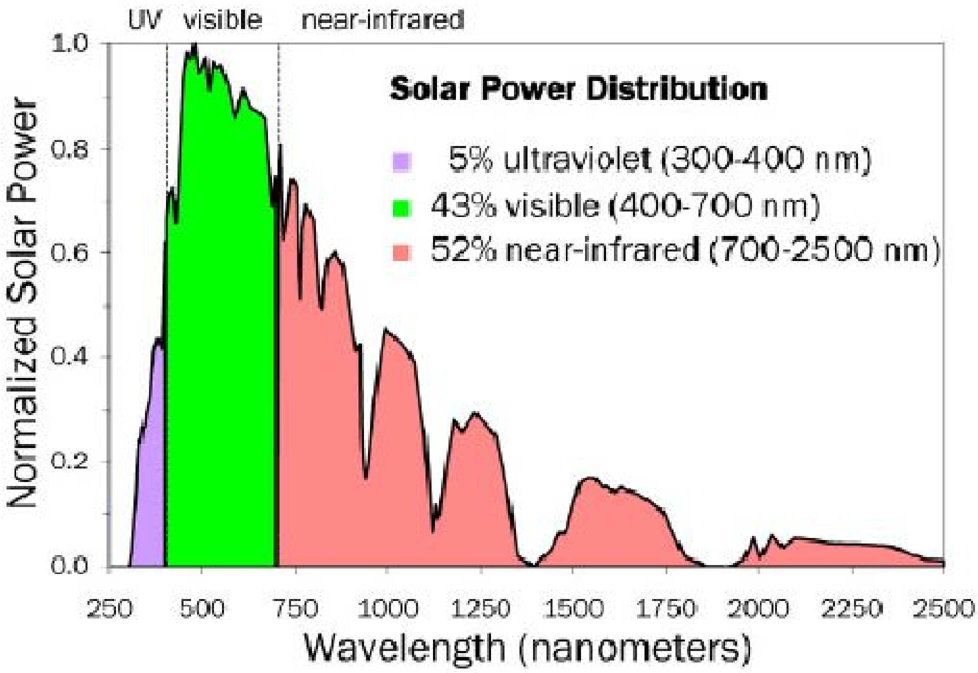


Figure 1.3

Infrared reflective inorganic pigments are complex inorganic color pigments, which reflect the wavelengths in infrared region in addition to reflecting some visible light selectively [10,12]. Inorganic NIR pigments are mainly metal oxides and are primarily employed in two major applications namely visual camouflage and reduced heat build-up applications. Most of the literature on NIR reflective pigments exists as patents [13,14] which indicate their vast potential application. These pigments are synthesized by subjecting mixtures of metal hydroxides, nitrates, acetates or even oxides, to very high temperatures in a process called calcination. Metal oxides or salts are blended together and strongly heated, generally at temperatures of over 1000°C. At the calcining temperature the solids themselves become reactive. Metal and oxygen ions in the solids rearrange to form new, more stable crystal structures such as spinel or rutile structures [15].

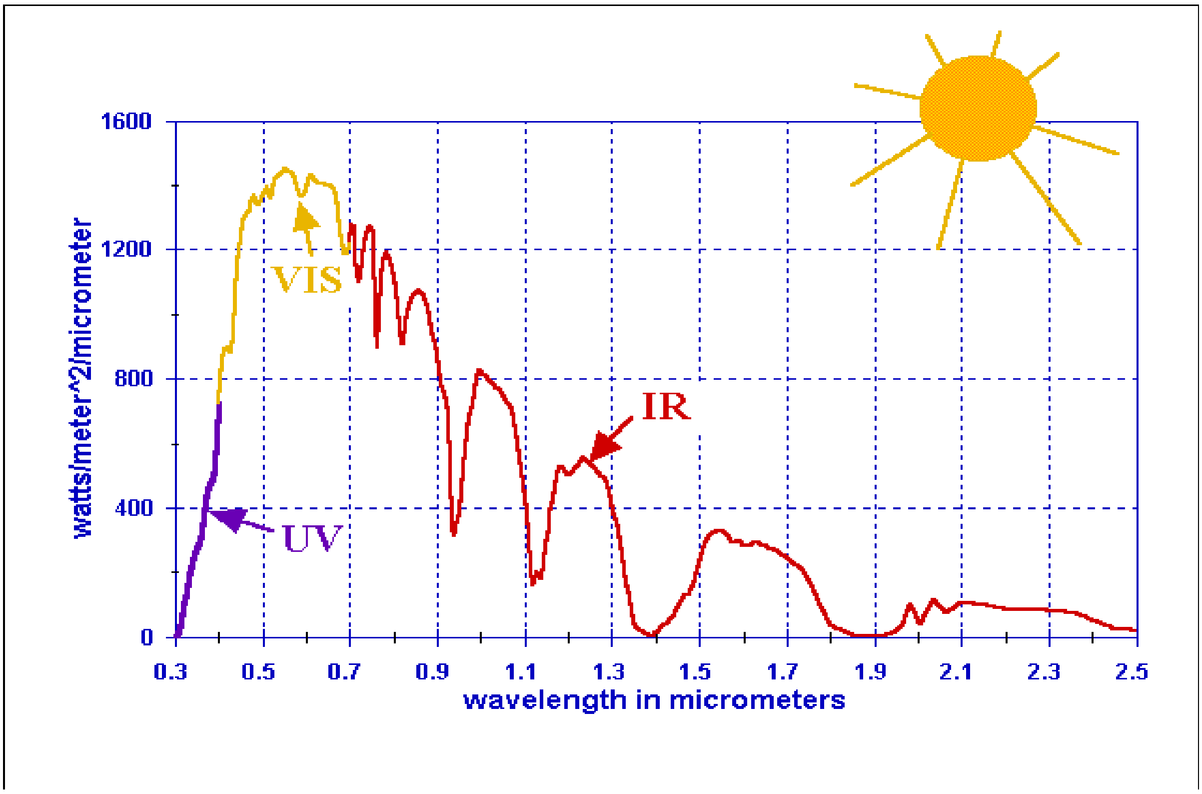


Figure 1.4

Pigments selectively absorb visible light (Figure 1.5) [6] and but can also absorb or reflect ultraviolet and infrared light (Figure 1.6) [6]. The effects of this absorption /reflection are invisible to the human eye.

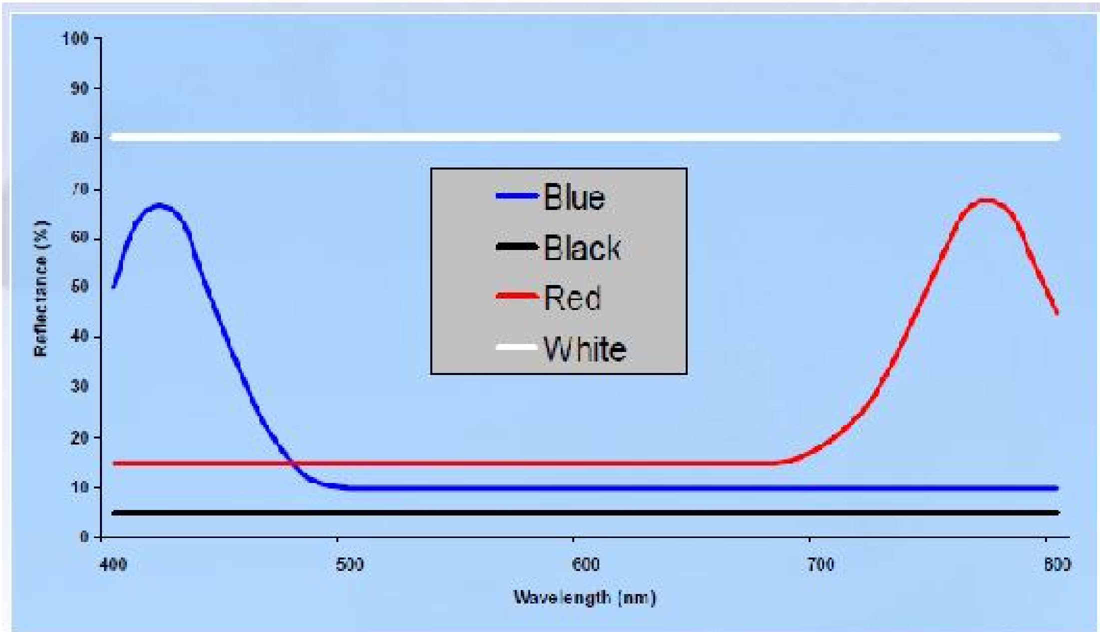


Figure 1.5

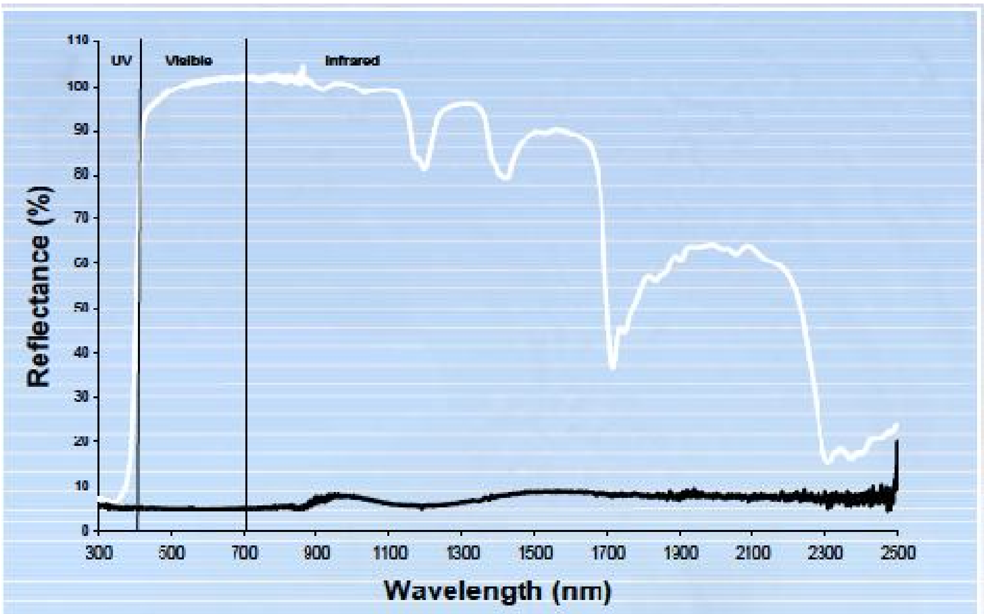


Figure 1.6

1.2 Reflection Mechanism of Infrared Radiations

In urban areas, the design of roofs has a major influence on the heat absorption of sunlight. The hot buildings also known as "concrete jungle" radiate heat and warm the air in the surrounding. If there are several such buildings in the vicinity, the combined effect leads to a phenomenon known as 'urban heat island effect' [10]. The infrared reflective pigments do not absorb in near infrared region. They either reflect it or transmit it [16]. Their refractive index is different from that of the binder in the infrared region. This causes diffused reflection in IR region [10]. Iif the refractive index of the pigments in the IR region is similar to that of the binder's refractive index in the IR region, the pigment would be transparent to near infrared light (NIR). In such a case, any reflection in the near infrared region would be due to the undercoat.

The absorption of light occurs when light energy promotes electrons from one bonding state to another. If light of a different wavelength is used to cause this energy transition, it will not be absorbed e.g. iron chrome blacks absorb light through the visible region. This means there are electronic transitions responsible for absorbing light with wavelengths of energy from 400 - 700 nm. Light of lower energy (>700 nm) is not absorbed. In this case, a beam of light with a wavelength of 1500 nm is too low in energy to cause any electronic transitions in the material. Thus it will not be absorbed, instead the 1500 nm light beam is refracted, reflected and scattered (depending on the refractive index) leading to diffuse reflection of NIR light [10].

1.3 Benefits of Infrared reflective Coatings

The general benefits of the Infrared reflective coatings have been mentioned by Malshe et al [10].

- Longer life-cycle due to less polymer degradation and thermal expansion due to lower temperature.
- Aesthetically pleasing colors.
- Cooler to touch for better handling
- Improved system durability and less thermal degradation.

In addition to the above mentioned benefits, the IR reflective coatings also have certain Roofing benefits:

- Less heat to transfer into buildings.
- Reduced ‘Urban heat island effect’.
- Low energy demand for air conditioning, particularly in equatorial regions.
- Reduction in air pollution due to low energy usage, power plant emissions, and reduction in urban air temperatures.
- Installation crews can work longer during the day before the roof gets too hot to work on.
- Very high durability coatings. Some coatings have been in use for as long as 25 years.

1.4 Typical Pigment Reflectance

When selecting an effective IR-reflecting pigment the most important factor is the TSR value. TSR means Total Solar Reflectance and is the integral total amount of solar energy that is immediately rejected by a surface material (e.g. coating). That means that it includes UV-, visible- as well as NIR-radiation and is thus a key figure to describe the heat build-up of surfaces.

Due to the fact, that the TSR covers the entire range of radiation between UV and NIR, e.g. black pigments show systematically lower TSR values compared to e.g. white pigments. Therefore only TSR values of similar pigments should be compared (Figure 1.7).

A high TSR value indicates efficient reflection - a low TSR value indicates a strong tendency to absorb NIR-light and therefore induce significant heat build-up. It is helpful to interpret the TSR value in relation to the matrix used and/or a reference pigment (e.g. titanium dioxide). Furthermore it should be considered, that even small amounts of impurities can negatively affect the TSR of the coating. Even fillers, which are usually added to the paint, can potentially reduce the resulting reflectance in the near infrared.

Figure 1.7 (www.shepherdcolor.com)

1.5 Reflectance Spectra of Black Pigments

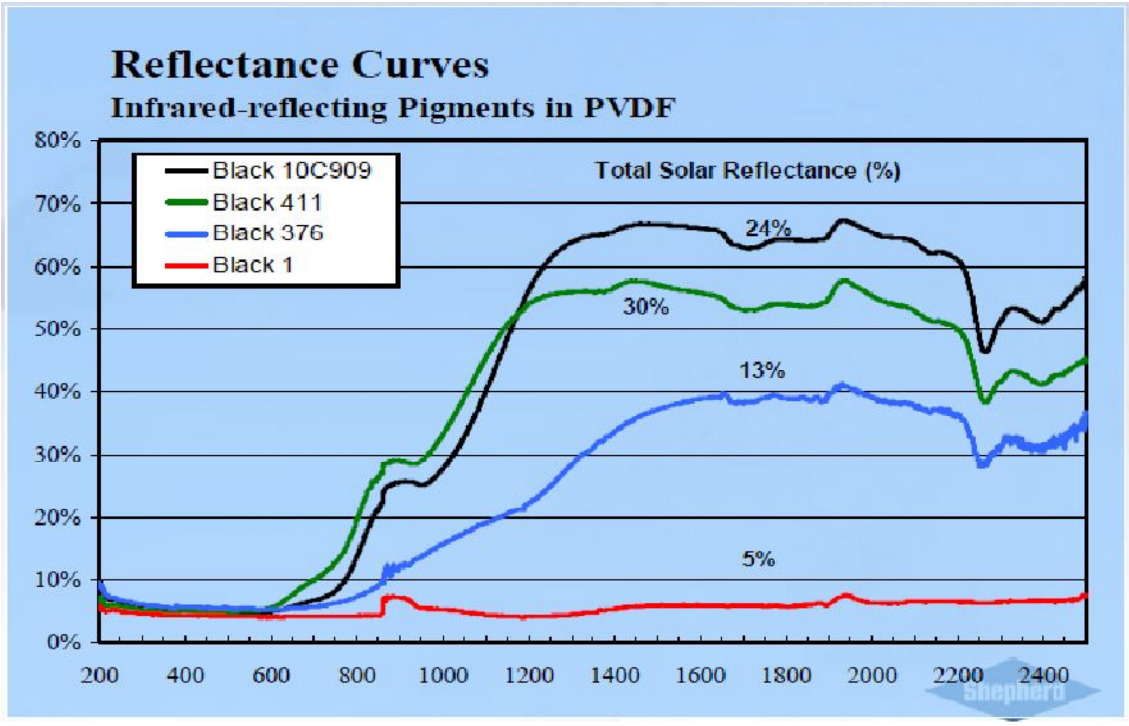


Figure 1.8

By using IR-reflective Pigments, the same visible color, can look very different to an infrared camera (Figure 1.9) [6]. The Infrared-reflecting (Arctic) formulation reflects the infrared light, which makes the surface (and interior spaces) cooler.

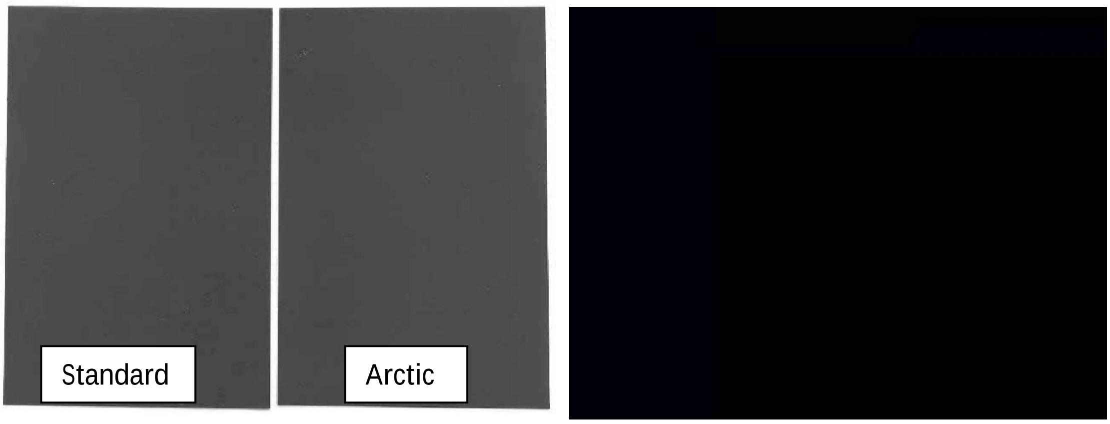


Figure 1.9

Darkness *vs* Reflectance

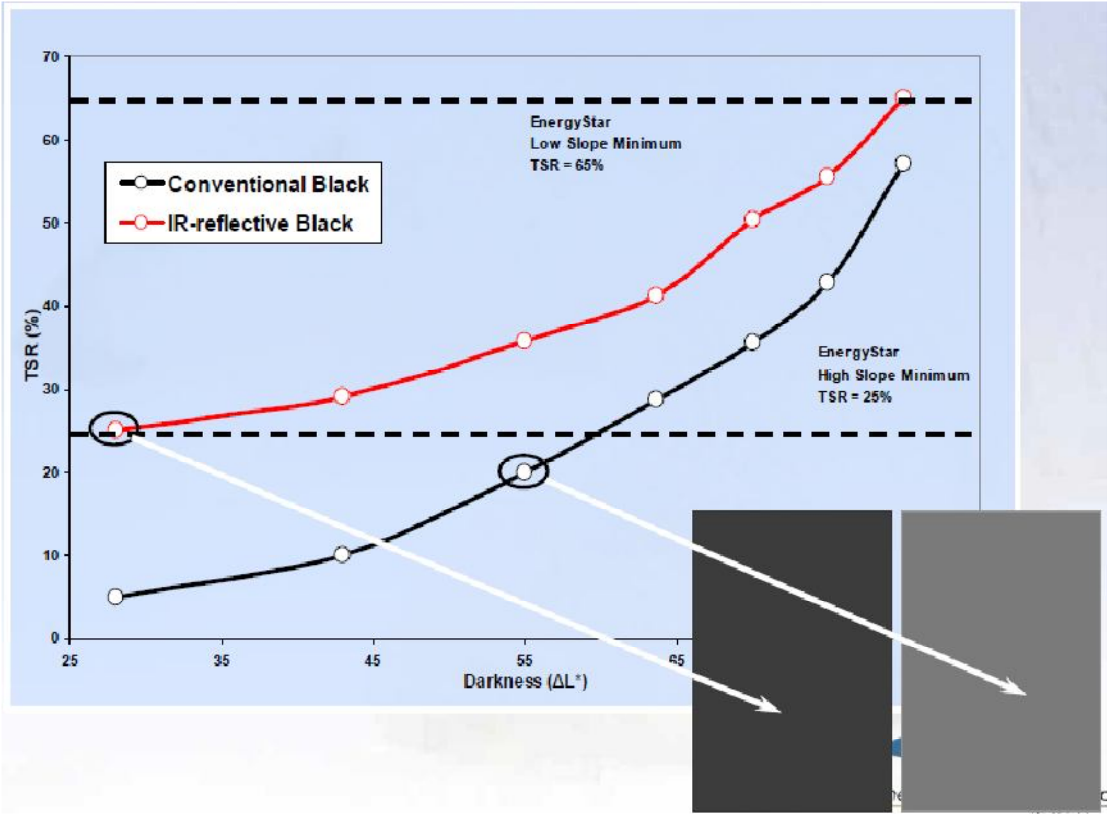


Figure 1.10 (www.shepherdcolor.com)

TSR is influenced by particle size as it is manufactured (Figure 1.11) [6]

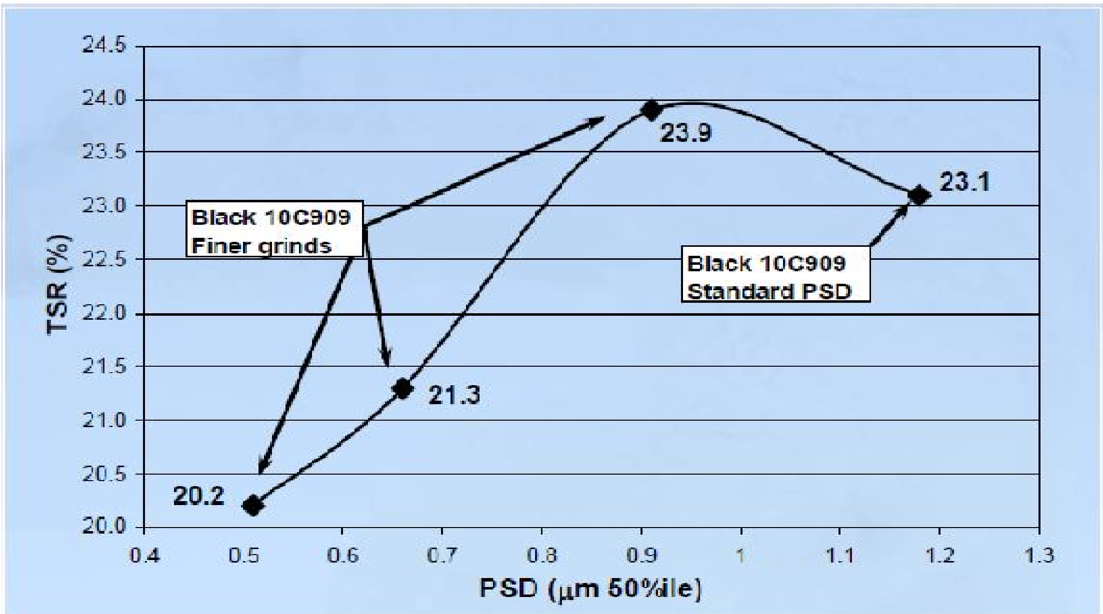


Figure 1.11

TSR is influenced by particle size during dispersion (Figure 1.12) [6]

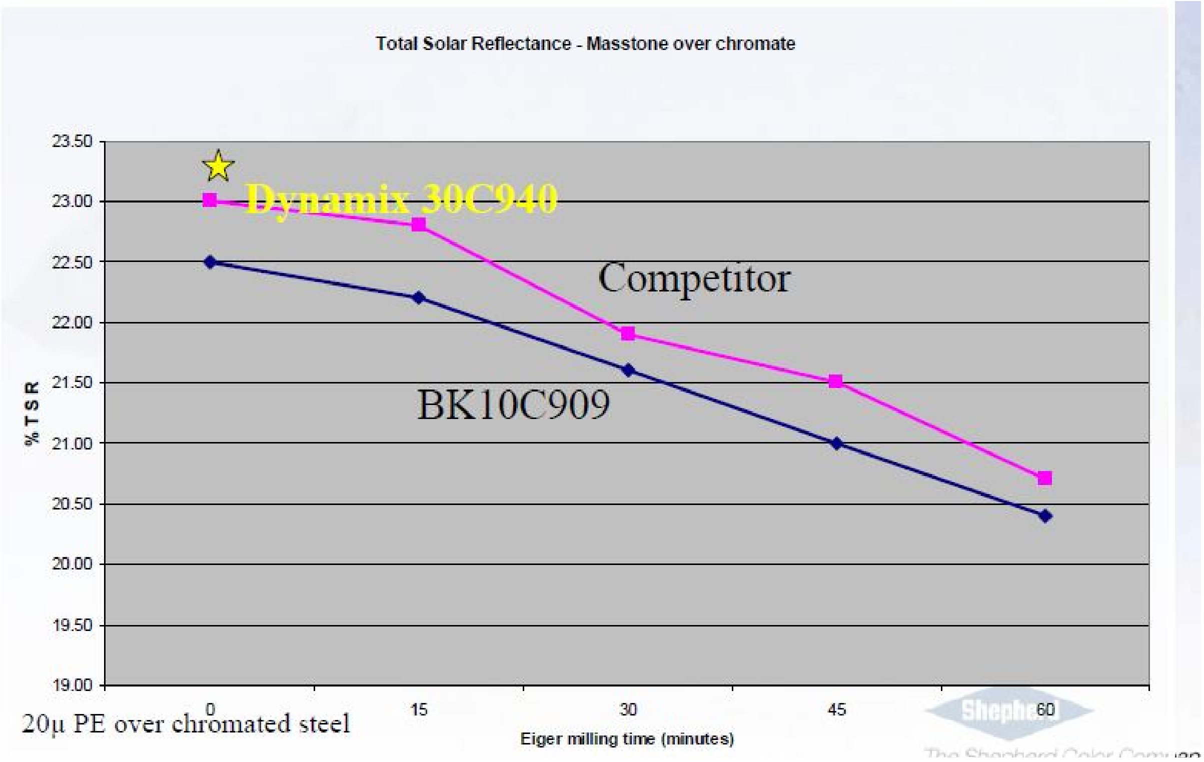


Figure 1.12 (www.shepherdcolor.com)

Coil Coating Application

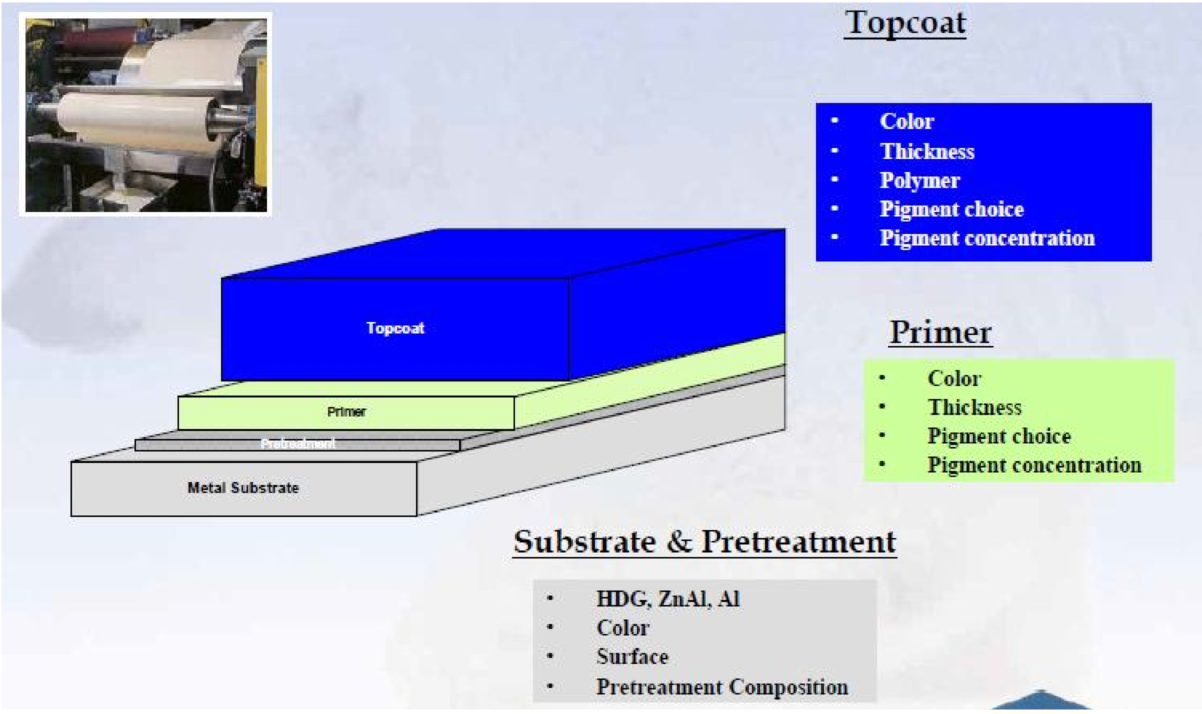
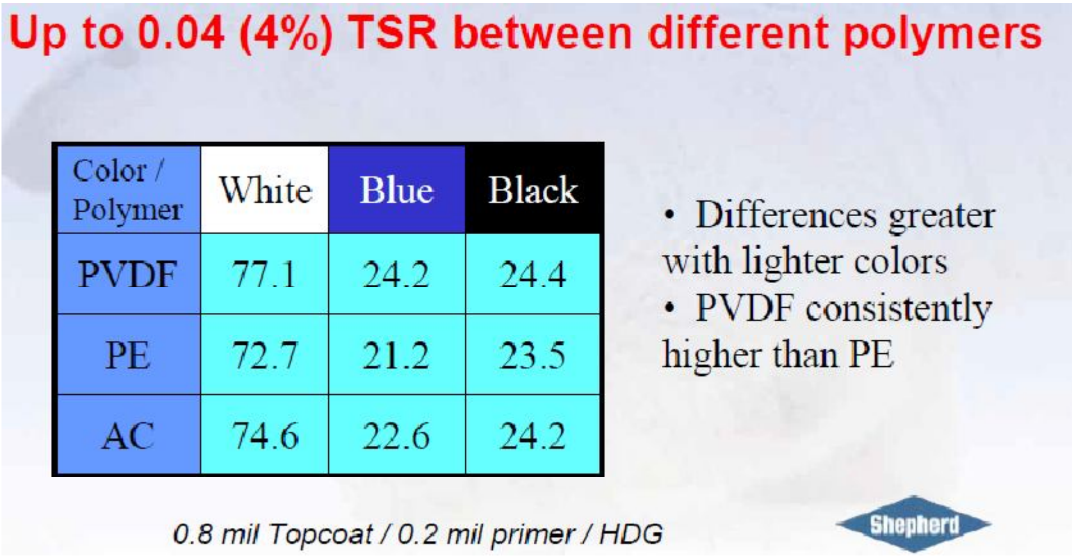


Figure 1.13 (www.shepherdcolor.com)

The Top coat is a thermally enhanced elastomeric coating (Figure 1.17) [17]. It uses ceramic nano-technology beads originally developed for the space shuttle re-entry tiles to significantly increase its insulation properties. It has a reflective R-value of up to 12.82 for a 12 mil thick application. In addition, it uses true elastomeric resins not plasticizers [17].



Color / Polymer	White	Blue	Black
PVDF	77.1	24.2	24.4
PE	72.7	21.2	23.5
AC	74.6	22.6	24.2

Figure 1.14 (www.shepherdcolor.com)

Different polymers generate different reflectance curves

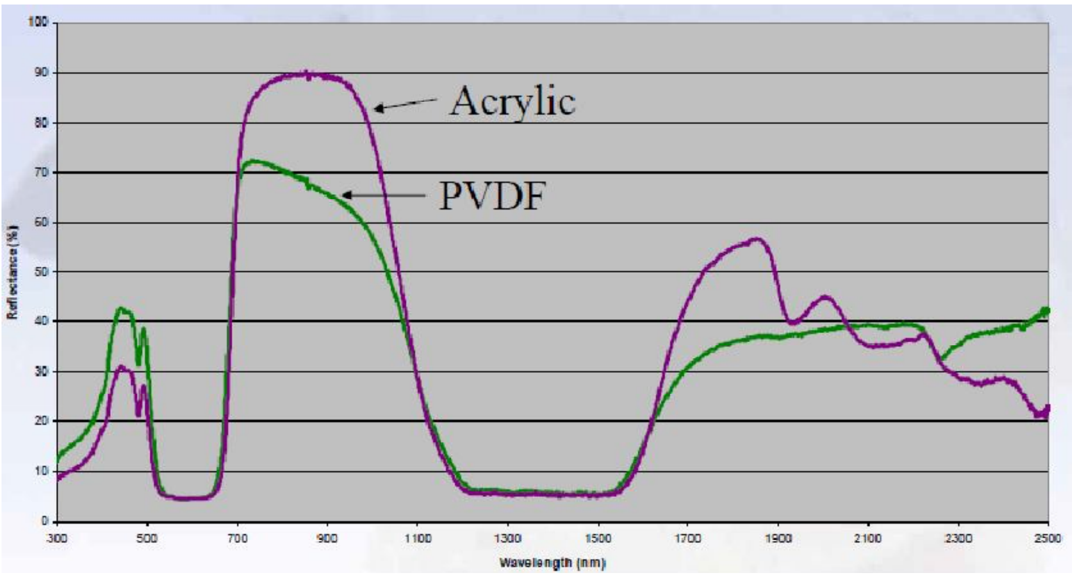


Figure 1.15 (www.shepherdcolor.com)

CHAPTER 2

EXPERIMENTAL Work

2.1 Methods for Indirect coating (transfer coating)

2.1.1 Preparation Methods for Plastisols

This is done by using the high speed mixture (Figure 2.1).

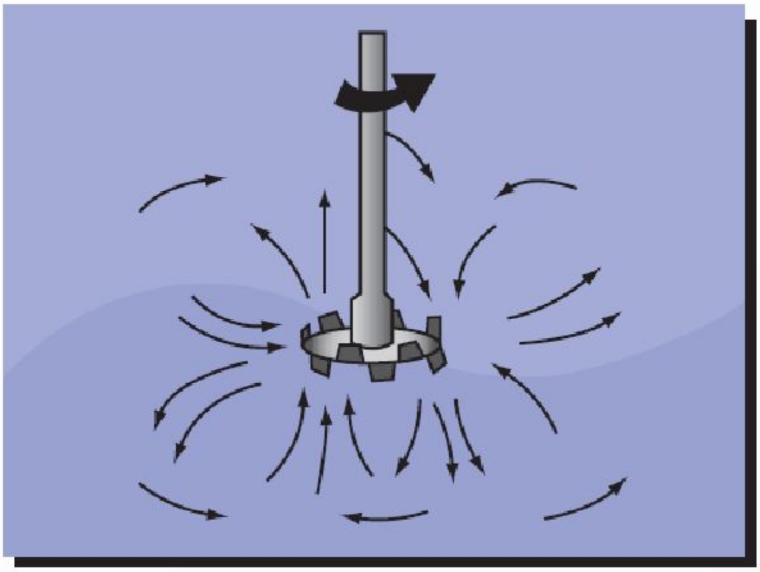


Figure 2.1 High speed Mixer

The normal sequence of operations is as follows:

- Introduction of all the liquid into the mixing tank,
- The liquid ingredients are plasticisers, stabilisers, diluents
- This liquid mixture is mixed at medium speed with slow addition of the fillers,
- When the added fillers were well dispersed, slow addition of the PVC resin takes place,
- Homogenisation at high speed.

The solid ingredients are added in the course of the mixing process. If the high speed mixer is fitted with a suitable device, the final mixing phase can be done under vacuum conditions. The overall time for the mixing operation does not exceed 20 minutes in industrial processing. Temperatures above 30 to 35 °C are not recommended (if necessary, use a double sheath vessel).

Homogenisation

It may happen that, for some applications, the dispersion of ingredients is incomplete and lumps remain in the plastisol. If the viscosity of the paste allows it, the lumps should be removed by filtration in a vacuum or at normal pressure.

It is also possible to reduce agglomerates in the plastisol by putting it through a triple roller mill. The mill rollers rotate at different speeds, creating a shear effect which reduces agglomerates. Impurities accumulate between the first two rollers and are easy to remove. The rollers must be cooled to prevent the paste from gelating due to friction heat. Additives such as solid stabilisers, fillers, pigments, blowing agents and thickening agents are generally incorporated into the plastisol as a masterbatch. This masterbatch is homogenised by putting it through a triple roller mill.

Coating

In the "transfer" technique, it is not the fabric itself but an auxiliary substrate that is coated. This is often a "release" paper (e.g. silicone coated paper) from which the coating material can easily be detached after gelation or drying. Glass fibre fabrics coated with elastomers or steel belts can also be used as auxiliary substrates.

The principle of transfer coating is as follows: the plastisol is spread over the auxiliary substrate with coating head no. 1 (when the item is completed, this plastisol will be the top coat or wear layer). After pregelation and cooling, the intermediary layer is deposited using coating head no 2 (for instance, a foam layer) which, in turn, is pregelled and cooled. Finally, the third coating head deposits a thin adhesive layer, on which the substrate is placed. The leather cloth and release paper then pass into the main oven, where gelation is completed (and expansion in the case of foam layers). After cooling, the leather cloth is separated from the paper and wound.

The release papers can be glossy or matt, even embossed. They can be used several times, reducing production costs. To determine the ideal production temperatures, initial trials should be carried out taking into account the formula, the coating weight and the speed of the substrate. The gloss, which increases with the gelation temperature, can also be used as an indicator of the quality of the gelation. Operating speeds can vary considerably, from 1 to 5 m/min for high coating weights (carped backing) up to 30 m/min when producing light qualities of leather cloth (Figure 2.2). In practice, the coating rate is often limited by the length of the gelling oven.

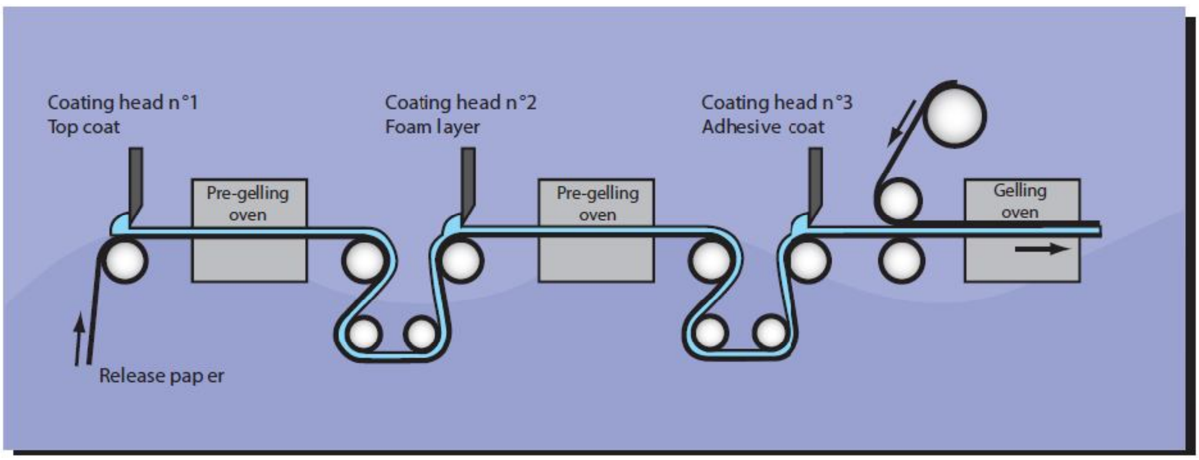


Figure 2.2

Embossing

Embossing improves the appearance of smooth surfaced leathercloths, for instance, by imitating the grain of natural leathers. Embossing is done using a cooled embossing roll made of steel on which is engraved the pattern to be reproduced and with a generally rubberised backing roll (Figure 2.3). Contact pressure is around 5 N/mm^2.

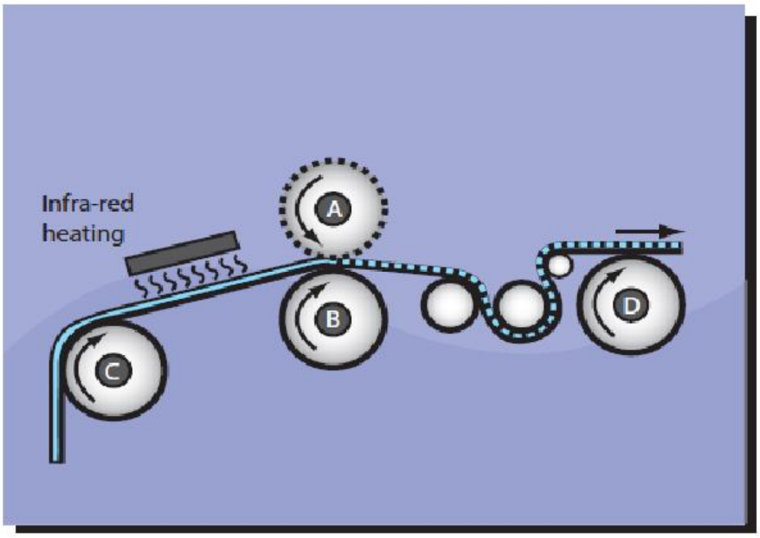


Figure 2.3: Embossing

After roll C, the coated fabric passes under an infra-red heater, where it is heated so that the surface temperature reaches 150 °C. It is then moved between the embossing roll A and the backing roll B. As the pattern is being printed, the embossing roll (cooled with water) cools down the PVC layer thereby fixing the pattern. Operating speed depends on the type and depth of the embossing pa

2.2 Method for Formulation and Lab Trial:

- Pour first liquid in the beaker and then powder and mix it well,
- Stir the material for few minutes,

- Filter the plastisol,
- Apply first Coat (Top Coat) on the release paper and then baked around 120 - 140 ^{o}C temperature in oven,
- Apply second coat (foam coat) on the release paper and baked around 120 - 140 ^{o}C temperature,
- Apply adhesive and then fabric and final curing around 180 - 190 ^{o}C temperature,
- Remove the product from the release paper after cooling down,
- Measure the temperature,

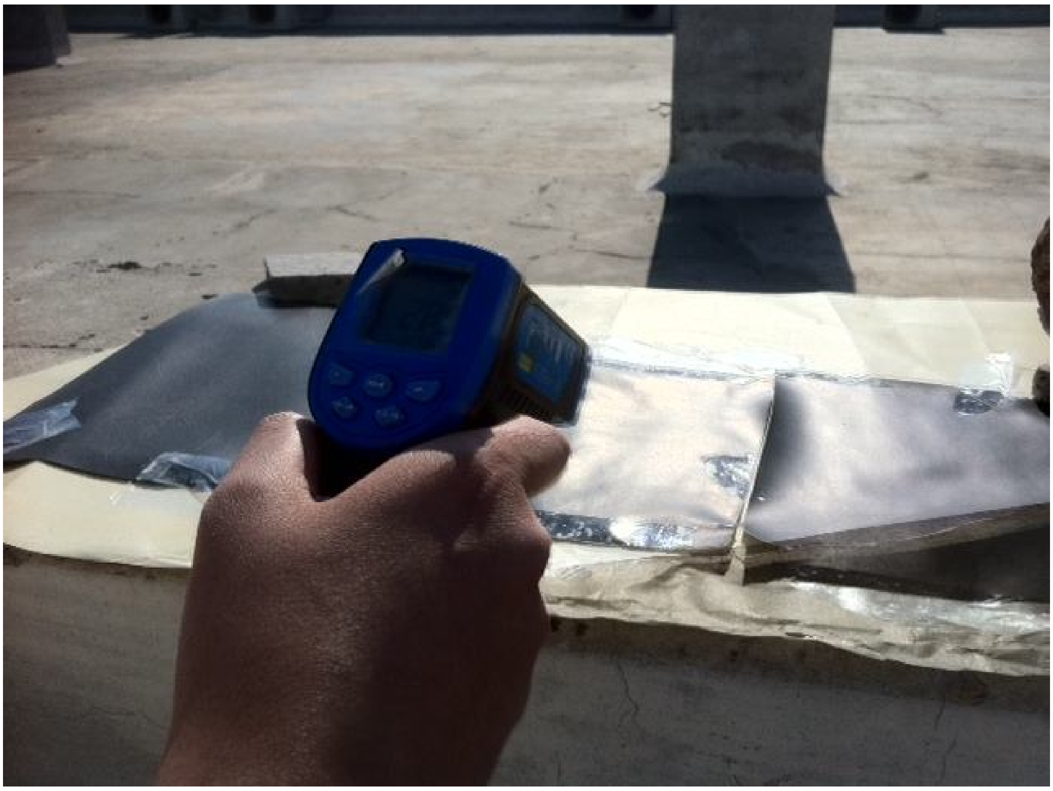
Dispersion:

DOP absorption of black pigment: 2 gm pigment : 1 gm of DOP (Table 2.1)

Table 2.1

S. No.	Raw Material Name	NO 1	NO 2	NO 3	NO 4
		PHR	PHR	PHR	PHR
1	PVC	100	100	100	100
2	DOP	70	70	53	70
3	Epoxy	05	05	05	05
4	Stabilizer (602)	2	2	2	2
5	Black 999	6	9	12	-
6	Black Normal	-	-	-	10

Visuals of the Experiments

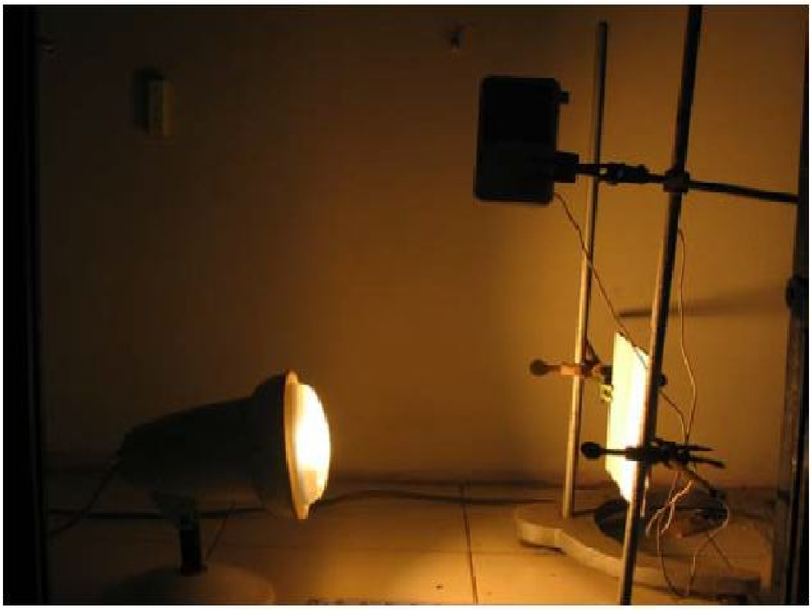


Date: 09.04.2013	**Quality: Cool Black**	**Fabric: Black Loop Knit**
	Dimension: 1.1-1.2 x 54"	**Emb./Paper:E-189**

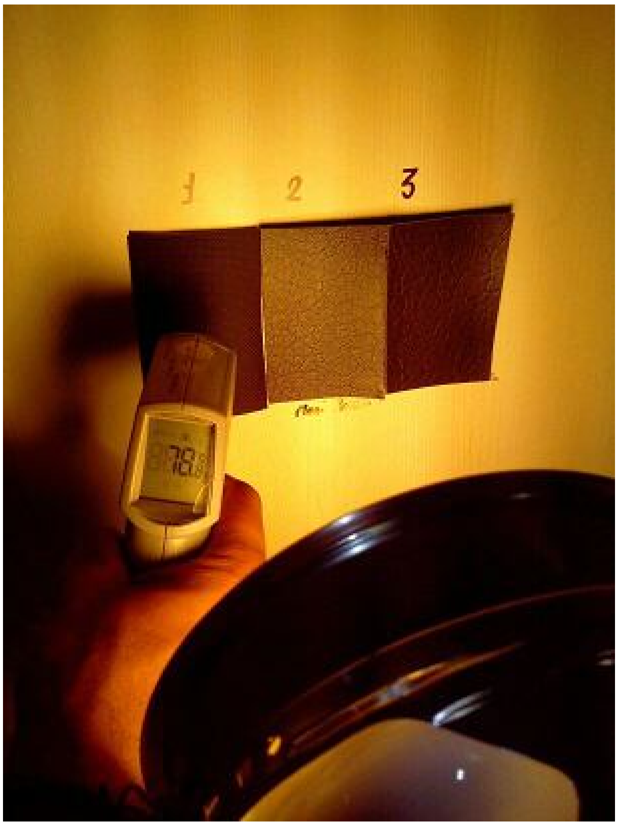
S. No.	**Raw Material Name**	**Top Coat 1**	**Top Coat 2**	**Foam Coat**	**Adhesive Coat**
		Parts (Kg)	**Parts (Kg)**	**Parts (Kg)**	**Parts (Kg)**
1	PVC	100	100	100	100
2	DOP	65	78	53	70
3	Epoxy	5	5	5	5
4	Filler	0	0	25	10
5	Stabilizer (602)	2	2	0	1
6	ADCL (MB)	0	0	3	0
7	Black 999	10	0	3	1.5
8	TiO2	0	20	15	0
9	ATO	4	4	1.5	3

S. No.	Item	Weight (Kg)
1	Top 1	0.300
2	Top 2	0.275
3	Foam	0.375
4	Adhesive	0.145
5	Hosiery	0.155
7	PU Lacquer	
8	Post Emboss	

Visuals of the Experiments



Experimental setup for measuring the infrared reflectivity of pigments




1 2 3


68.6 °C

CHAPTER 3

RESULTS AND DISCUSSION

The work has been done on the four samples (Table 3.1). The primary purpose of IR-reflective coatings is to keep objects cooler than they would be using standard pigments. These pigments show IR reflectivity, as the pigment dosages increases, IR reflectivity increases and the temperature measure in the open atmosphere. Hence one application of pigments is use for making PVC Artificial leather cloth for two wheeler seat covers for cooler effects.

Table 3.1

Sample	**Temperature of Untreated Sample (^oC)**	**Temperature of Treated Sample (^oC)**	**Temperature Difference (^oC)**
1	42.0	41.5	0.5
2	42.0	40.0	2.0
3	41.0	37.0	4.0
4	41.0	0.0	0.0

The sample 1 has an untreated temperature of 42 ^oC that on treated cooled down 0.5 ^oC to 41.5 ^oC. The sample 2 has an untreated temperature of 42 ^oC that on treated cooled down 2.0 ^oC to 40.0 ^oC. The sample 3 has an untreated temperature of 41 ^oC that on treated cooled down 4.0 ^oC to 37.0 ^oC. The sample 4 has an untreated temperature of 41 ^oC that on treated cooled down 0.5 ^oC to 41.5 ^oC. Hence, sample 3 has shown good potential.

The Shepherd Color Company

4539 Dues Drive

Cincinnati, OH 45246

Technical Support Laboratory Test Results

Request Number: 71189

Date: 5/9/13

Submitted by: Russell Pemberton

For Customer: Best Dye / Veekay Polycoats

TS Lab Staff: L. Branam

Test or Measurement: Total Solar Reflectance

Instrument: Device and Services, Solar Spectrum Reflectometer, Model SSR-ER

ASTM Reference: C1549 and E903-96

Shepherd Test Method Reference: SCTM 340

Test Results:

	%TSR
Sample A	25.3
Sample B	25.6
Sample C	3.9

CHAPTER 4

CONCLUSION AND FUTURE PROSPECTS

4.1 Conclusion

The formulation of IR-reflective coatings for various applications depends on many factors, some of which cannot be seen with the naked eye. There are two main keys to formulating these coatings.

1. Individual pigment selection: Select IR-reflective pigments.
2. Milling and dispersing: Do not over grind and degrade IR properties.
3. Mixing IR-reflective pigments: Be aware of the invisible interactions of different pigment types in the IR region.
4. Opacity: Use an IR-reflective substrate/primer if possible, or manage the pigment-to-binder and film thickness to minimize effect of absorptive substrates.
5. Contamination: Inclusion of even small amounts of IR-absorbing pigments can greatly reduce TSR.

The second key is to work with a partner with the products, research, and most importantly, technical support to allow you to formulate, test and validate your IR-reflective coatings. The IR range is invisible to the human eye, not covered by standard spectrophotometers, and measurable only by expensive and specialized equipment. A partner who can shepherd you in pigment selection, color matching and testing, along with guidance in the different regulations and programs can be an invaluable aid in formulating, marketing and supporting differentiated IR-reflective coatings.

4.2 Future Prospects:

1. These pigments use in the PVC artificial leather cloth for two wheeler seat covers and this product more effective in the summer season to get cooler effect.
2. These pigments use for refrigerated transport containers, roofs of the buildings are already in use.
3. Use of these coatings in petroleum refinery to reduce evaporation losses of hydrocarbons is being explored.

4.3 Benefits:

1. Longer potential life-cycle due to less polymer degradation and thermal expansion due to lower temperature
2. Aesthetically pleasing colors
3. Cooler to the touch for better ergonomics
4. Improved system durability and less thermal degradation

CHAPTER 5

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