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Molding of PVC Air Soles with Modified Formulation

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ABSTRACT

Molding of PVC Air soles are currently produced with the formulations of Resin (25 Kg), DOP/DBP (8+8 Kg), CPW (3 Kg), R9 (0.750 Kg), Ivamol (0.500 Kg), Stearic acid (0.500 Kg), Foaming ADC (0.350 Kg), MBR (8kg) and $CaCO_3$). Quality parameters investigated for such products have shown that internal microcellular structures were not uniform and durability was also weak. Hence the invention was undertaken eliminating CPW and Stearic acid. Instead of this Naphthenic oil was employed for molding the soles. Quality evaluations have shown the internal microcellular structures were quite uniform and had great impact on durability. The formulation was also found to be feasible for the regular production. High resolution pictures of the soles have exhibited the uniform polymeric network.

Keywords: Resin PVC, Molding, Naphthenic oil, Microcellular.

I. INTRODUCTION

PVC air soles are currently manufactured with the use of CPW and stearic acid, but the soles when exported, the consumers have complained about the crack in the soles due to the low temperatures in the Europe and foreign countries. After producing the soles when evaluated by cutting into the halves then it was observed that the soles were not composed of uniform microcellular network and hence were not compact. The probability of the absence of compactness may have caused the hardness in the soles and resulted in the cracks. Our invention has proven to be solved this particular problem due to excellent lubrication and synersis of Naphthenic oil with resin PVC and other ingredients.

Several authors have documented the historical developments of plasticizers and their use in PVC. (Sears and Darby [1]) provide an extensive review, including citations of the use of water and other liquids as “quasi-plasticizers” in non-polymeric materials. The use of plasticizers in PVC and other polymers originated as extensions from low volatility solvents. (Weinberg, Bailey, DM, Foltz SD, Rossiter WJ, Lechner, JA [2]) points out that Waldo Semon, of B. F. Goodrich, originated the use of plasticized PVC using plastisols (dispersion of PVC particles in plasticizers). Semon’s objective was to apply corrosion-resistant linings to metal storage tanks, which he accomplished via fused plastisol coatings on wire mesh secured to tank interiors. (Krauskopf [3]) reviewed plasticizers used in polymers, beginning with the use of camphor in nitrocellulose (1868) by the Hyatt brothers and Gresham’s patented use of DOP (di-2-ethylhexyl phthalate) in PVC (Diebel PW [4]) in the early 1940s.

The use of DOP prevailed as the preferred general-purpose plasticizer for PVC until the late 1970s. In 1968, more than 550 different materials were listed as commercial plasticizers, available from over 75 suppliers in the USA (Fayoux, D, Gousse F, Rummens F [5]). Changes in costs and availability of raw materials that serve as plasticizer feedstock have caused a significant reduction in the number of plasticizer suppliers and plasticizer products in use. Although there are still approximately 70 different plasticizers available, about 80% of the worldwide consumption is comprised of three plasticizers, di-2-ethylhexyl phthalate (DOP), diisononyl phthalate (DINP), and diisodecyl phthalate (DIDP).

1.1 Mechanisms of Plasticization

For a plasticizer to be effective, it must be thoroughly mixed and incorporated into the PVC polymer matrix. This is typically obtained by heating and mixing until either the resin dissolves in the plasticizer or the plasticizer dissolves in the resin. The plasticized material is then molded or shaped into the useful product and cooled. Different plasticizers will exhibit different characteristics in both the ease with which they form the plasticized material and in the resulting mechanical and physical properties of the flexible product. Several theories have been developed to account for the observed characteristics of the plasticization process. A significant review of the theoretical treatment of plasticization is described. In this treatment, plasticization is described by three primary theories, with some modifications.

According to the Lubricating Theory of plasticization, as the system is heated, the plasticizer molecules diffuse into the polymer and weaken the polymer-polymer interactions (van der Waals’ forces). Here, the plasticizer molecules act as shields to reduce polymer-polymer interactive forces and prevent the formation of a rigid network. This lowers the PVC Tg and allows the polymer chains to move rapidly, resulting in increased flexibility, softness, and elongation.

The Gel Theory considers the plasticized polymers to be neither solid nor liquid but an intermediate state, loosely held together by a three-dimensional network of weak secondary bonding forces. These bonding forces acting between plasticizer and polymer are easily overcome by applied external stresses allowing the plasticized polymer to flex, elongate, or compress.

Free Volume is a measure of the internal space available within a polymer. As free volume is increased, more space or free volume is provided for molecular or polymer chain movement. A polymer in the glassy state has its molecules packed closely but is not perfectly packed. (Giroud JP [6]) (Giroud JP, Tisinger LG [7])

The free volume is low and the molecules cannot move past each other very easily. This makes the polymer rigid and hard. When the polymer is heated to above the glass transition temperature, Tg, the thermal energy and molecular vibrations create additional free volume which allows the polymer molecules to move past each other rapidly. This has the effect of making the polymer system more flexible and rubbery. Free volume can be increased through modifying the polymer backbone, such as by adding more side chains or end groups. When small molecules such as plasticizers are added, this also lowers the Tg by separating the PVC molecules, adding free volume and making the PVC soft and rubbery. Molecules of PVC can then rapidly move past each other. If the plasticizer uniformly went into the PVC, it would behave similarly to an uncured rubber, with lots of creep and high compression set. For example, uncured tires do not hold their shape; they require a cross linking cure to give them dimensional stability. Likewise, a thermoplastic elastomer such as PVC requires physical cross links which are melt able to make them thermoplastic. These melt able cross links are the PVC crystallites which give PVC a physical cure. Therefore, the plasticizer must not be a powerful solvent for all the PVC parts, but must be selective in entering the amorphous PVC part and must not enter and destroy the crystalline part of PVC. (Hammond MHG, Mackey RE, Levin SB [8])

The mechanistic explanation of plasticization considers the interactions of the plasticizer with the PVC resin macromolecules. It assumes that the plasticizer molecules are not permanently bound to the PVC resin molecules but are free to self-associate and to associate with the polymer molecules at certain sites such as amorphous sites. As these interactions are weak, there is a dynamic exchange process whereby, as one plasticizer molecule becomes attached at a site or centre, it is readily dislodged and replaced by another. Different plasticizers yield different plasticization effects because of the differences in the strengths of the plasticizer- polymer and plasticizer-plasticizer interactions. At low plasticizer levels, the plasticizer-PVC interactions are the dominant interactions, while at high plasticizer concentrations plasticizer- plasticizer interactions can become more significant. This can explain the observation of " anti plasticization", wherein low plasticizer levels (< 15 phr) increase rigidity in PVC, as measured by modulus, tensile strength, elongation and low temperature properties.(Hawkins WL [9])

For a plasticizer to be effective and useful in PVC, it must contain two types of structural

Groups viz. polar, and apolar. The polar portion of the molecule must be able to bind reversibly with the PVC polymer, thus softening the PVC, while the non-polar portion of the molecule allows the PVC interaction to be controlled so it is not a powerful solvate as to destroy the PVC crystallinity. It also adds free volume, contributes shielding effects, and provides lubricity. (Holzmann I [10])

Examples of polar components would be the carbonyl group of carboxylic ester functionality or, to a lesser extent, an aromatic ring; the non-polar portion could be the aliphatic side chain of an ester. The balance between the polar and non-polar portions of the molecule is critical to control its solubilizing effect; if a plasticizer is too much polar, it can destroy PVC crystallites; if it is too non-polar, compatibility problems can arise. Useful tools in estimating plasticizer compatibility are the Apolar/Polar Ratio method developed by Van Veersen and Meulenberg and the solubility parameter methods.

Plasticizers have a strong affinity for PVC polymers, but do not undergo a chemical reaction that causes bonding, or grafting, to the polymer. Note, however, that epoxy plasticizers are an exception, in that they undergo chemical grafting onto PVC in their role as stabilizers, replacing labile chlorides in addition to their role of acid absorption. Other functional additives are known to graft and/or polymerize in the PVC matrix, but these are generally not considered as traditional "external" plasticizers. Copolymers for example, can lower PVC's *Tg* as plasticizers do. But at the same time, any significant level of co-monomer will disrupt the syndiotactic PVC structure and disrupt the ability to form crystallites. The crystallites are the physical cross-links that hold the structure together as a thermoplastic elastomer. Thus with copolymers, creep increases, compression set increases, and long-term elasticity is lost. Thus, the plasticizers, when not grafted or copolymerized, may be separated from the PVC matrix due to extraction by solvents, oils, water, surface rubbing, volatility, migration into adjacent media, or degradation mechanisms. (Kampouris EM [11])

2. Materials and methods

Resin (25 Kg), DOP/DBP (8+8 Kg), CPW (3 Kg), R9 (0.750 Kg), Ivamol (0.500 Kg), Stearic acid (0.500 Kg), Foaming ADC (0.350 Kg), MBR (8kg) and $CaCO_3$) were purchased from the leading manufacturers in India. All the raw materials were pretested in the QC laboratory before employed for the production.

2.1 Blending and drying of the formula

The raw materials as stated earlier were poured into reacting vessels with agitation, heating and discharge manhole. It was then agitated and heated at 100 ^{O}C for about 45 minutes. Later it was discharged into the carrots and allowed to cool at room temperature before it was taken for the molding. Once it was cold then it was charged into the hopper attached to 20 station molding machine along with purge of air into the mould. The molded soles were put into the baskets and were allowed to cure for 24 hour. It was then sent for the quality evaluation to quality control laboratory. 2500 Paris of air soles were produced.

2.2 Quality control

2.3 Benn wart Flex Testing

The soles produced on the shop floor are sent to the quality evaluations. The first quality parameter is Flex Testing where the soles are tightened at the both end and allowed to rotate at 90 ^{o} by putting a cut on the soles. 1, 00,000 cycles are run as a standard specification. During these cycles if the soles get cracked at the cut point then the soles are rejected.

2.4 Tensile testing machine

The strip of the sole is tied at both the end and stretched by the machine unless it is broken from the centre. The point at which it breaks, is noted and the measure is matched to the standards.

2.5 Din Abrasion Testing

The soles are tested for the percent abrasion as per standard norms set by Bata and SATRA. The lesser the measure of the abrasion the more is the life of the soles.

3. Results and Discussion

The soles manufactured on the shop floor with the employment of CPW and stearic acid shown to have less elongation (175%) and tensile strength (23 Kg^{-1}), more abrasion resistance 105 mm^3), specific gravity of 0.88 and hardness of 42 Shore A. (Table 1) Inventing the formulation by employing Naphthenic oil shown to have compatible quality parameters and found more durable as compare to the regular formulation. The results of the soles with Naphthenic oil shown to have elongation (235%), tensile strength (33 Kg^{-1}), abrasion resistance (70 mm^3), specific gravity (0.86) and hardness Shore A (44). (Table 2) With the view of the quality results the formula with Naphthenic oil was found at par for the production scale. Cutting the soles with two equal halves with the Naphthenic oil has shown to have a uniform network of microcellular (Figure 1) unlike that with CPW and stearic acid. (Figure 2) The concern of spill of oil with the Naphthenic oil on analysis shown to have negative result (Table 3) as it was mostly concern while bonding the soles with shoe upper. (Table 4) (Levin SB, Hammond M [12])

Table 5 and 6 presented the data that were evaluated in the company's quality control laboratory. The elongation was 60% better than that with old formula and the most important part of the sole performance was the abrasion which was 35^ less in case of new formula. Though plasticizers play an important role on sole finish but it was found that plasticizers gave great impact in the presence of Naphthenic oil than that with CPW and stearic acid. Not only that the rejections, in case of Naphthenic oil were only 5% but with the use of CPW and stearic acid the rejections were 30%. Hence it was a great achievement on the shop floor as far as feasibility of the process and rejections were concerned. The spill of the resin by side of the moulding station was also at minimum as was observed more in case of old formulation. Rejections of resins were used to recycle in the fresh batches as high as of 15% but this percentile use to have shown to bring quality of the soles down. In case of 5% of rejection the exercises of blending would be at least so have the soles quality at the best. Since most of the complaints comes from peeling of the soles that remain quite weak in the peel strength. (Mark HF, Gaylord NG [13]) Messadi D, (Vergnaud J, Hivert M [14]) (Morrison WR, Starbuck JG [15])

The most widely used fillers in flexible and semi-rigid PVC are grades of dry-ground, wet ground, or precipitated calcium carbonate derived from limestone or marble, which are predominantly calcite. This is the stable crystal structure of $CaCO_3$ at ordinary temperatures and pressures. Marble consists of small, interlocking crystals of calcite. Calcite is soft, having a Mohs hardness of 3. Therefore, pure calcium carbonate fillers are low in abrasivity to processing equipment. Grades which contain significant fractions of hard silicates are much more abrasive. Recent work carried out in a PE carrier resin confirms this long-accepted fact and shows that coarser grades are more abrasive than fine particle size fillers The principal advantages of inorganic fillers in flexible PVC include cost reduction, stiffening, reducing coefficients of thermal expansion, and contributing to better flammability behavior. Specific heats per unit volume are comparable for most filler and many polymers. The disadvantage of using high levels of fillers, in flexible PVC, is the reduction of tensile and tears strength, elongation at failure, toughness at low temperatures, abrasion resistance, and resistance to attack by moisture and chemicals.(Figure 3) High filler levels also compromise process ability by increasing melt viscosity. (Nass LI, Heiberger CA [16]) (Orem JH, Sears JK; 17]) (Papakonstantinou V, Papaspyrides CD [18]) (Sears JK, Darby JR [19]) (Stark TD, Newman E, Rohe, FP [20])

4. Conclusion

On the basis of the quality evaluations the soles invented with naphthenic oil were found to have superior qualities as compare to the one with CPW and stearic acid. The results also have shown that the customers would certainly prefer to buy the soles with low abrasion, high elongation and tensile strength. The test performed in the central laboratory have also shown to have less volatility of 0.7% and 3.7 Kg^{-1} of peel strength which by no means is lesser than that the required 4.00Kg^{-1} pressure. (Stepek J, Daoust H [21]) (Wilson AS [22])

These exercises were not performed earlier in the company laboratory so the understanding of the soles performance was uneasy and unproductive. Since this is an industry R&D hence these technicalities would be very helpful for the soles manufactures in the world.

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TABLE 1 Previous formulation for molding PVC Air soles

Raw materials	Weight (Kg)
Resin PVC	25
DOP/DBP	8+8
CPW	3
R9	0.750
Ivamol	0.500
Stearic acid	0.500
Foaming ADC	0.350
MBR	8
CaCO$_3$	1

TABLE 2 Modified formulation for molding of PVC Air soles

Raw materials	Weight (Kg)
Resin PVC	25
DOP/DBP	8+8
R9	0.750
Ivamol	0.500
Naphthenic oil	1.500
Foaming ADC	0.350
MBR	8
CaCO$_3$	1

Figure 1Non uniform microcellular structure with the use of CPW and stearic acid

Figure 2Uniform microcellular structure with Naphthenic oil

Figure 3upper sole bright (Naphthenic oil) and lower dull bright (CPW & stearic acid)

TABLE3 Peel strength (between sole and split leather) Laboratory environment: Temperature: 20±2 ^{O}C; Relative humidity: 65±5%

Value	Requirement
3.6 Kg^{-1}	4.00 Kg^{-1} (min.)

Sample preparation: sole was halogenated properly. One coat PU adhesive with hardener was applied on the sole. On the leather two coats of PU adhesive were applied at an interval of 15 minutes.

The test pieces were reactivated at 85 °C for 10 seconds and bonded under pressure.

TABLE 4 % Volatile loss (@130 °C for 3 hour)

Value	Requirement
0.7	2.0% (max.)

TABLE 5 Quality evaluation of air soles with old formulation

Elongation	**Tensile Strength**	**Abrasion Resistance**	**Specific Gravity**	**Hardness**
175 %	23kg/cm²	105 mm³	0.88	42 Shore A

Weight of sole: 224 g

TABLE 6 Quality evaluations of soles with new formulation

Elongation	**Tensile Strength**	**Abrasion Resistance**	**Specific Gravity**	**Hardness**
235 %	33kg/cm²	70 mm³	0.86	44 Shore A

Weight of sole: 222 g

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