HIGH-PERFORMANCE ELASTOMER BLACK PIGMENT from Post-Consumer Waste

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The coatings market faces increasing customer and consumer demands to offer products with a green advantage. A report cited by EnvironmentalLeader.com notes that 78% of consumers bought green or sustainable products in 2013, which is up from 69% in 2012.[1] While studies have shown that consumers will not pay more for a product that has the benefit of being environmentally friendly, companies are beginning to recognize that there is a longer-term potential economic benefit for products that offer environmental claims.[2]

In addition to customer pull, regulatory pressures are placing higher environmental impact standards on coatings. Many of these regulations are restrictive, and the need to identify materials that improve a company's sustainability portfolio is becoming much more critical. The pigment reported on in this article has not been assessed as a green or sustainable product, but one of the primary sources for the product is waste rubber materials, such as post-consumer tires. The pyrolysis process has been deemed beneficial to the environment, which is likely the minimum designation for this product.

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Over the last three decades, the amount of scrap tires being landfilled or stored in private piles has decreased as tires are finding a wide range of recycled uses. In 1990, the Rubber Manufacturers' Association reported that approximately 240 million scrap tires were generated, with 175 to 205 million, or more than 70%, being landfilled or stockpiled. In 2009, the number of scrap tires generated climbed to nearly 297 million, where approximately 37 million, or 12.6%, were landfilled. The current markets for scrap tires include tire-derived fuel, ground rubber, used tires, and civil engineering. Tire-derived fuel and ground rubber account for the largest volume of scrap tire usage at 40% and 26%, respectively.[3]

The pyrolysis process for converting tire to fuel results in a char that can be processed to obtain carbon black. This carbon black is then sold back into the rubber and plastics market, where it is often blended with virgin carbon black. However, the quality of this carbon black is not acceptable as a colorant for other applications, such as coatings. In addition, the extra processing adds cost to the product, only some of which is offset by the fuel production.

The second primary use for recycled vulcanized rubber is ground rubber, which is also known as crumb rubber. Crumb rubber is composed of ground tires that have been separated from the steel, other reinforcing fibers, and various other fillers and contaminants. Approximately 70% of the weight of a tire is recoverable rubber (or about 10 lb per passenger car tire). The ground rubber is typically ground to sizes between 9 mm and 400 µm. Further processing through wet milling or cryogrinding can obtain particles that are 75 µm or less, also commonly referred to as powdered rubber.[4] The crumb and powdered rubber obtained in these processes has uses in molded and extruded products, sports surfacing, playgrounds, mulch, animal bedding, and asphalt. While there are several publications reporting use of these products in coatings, commercialization has been limited since the primary benefit that they have provided is functional in nature. These functions include improved salt spray resistance, greater lap shear strength, and tactile properties.[5,6] Particles in the typical size ranges available with existing technology are too large to impart significant color value to a coating, and the film that is formed from these particles has a coarse texture.

Reported here is new technology for refined rubber or elastomer pigment that improves on powdered rubber for color value, spray application, and use in thin film coatings. The product can be formulated to produce a matte appearance without the use of matting agents, or, in the proper system, it can take on a semigloss look. While this colorant has unique tactile properties, the resulting film is typically smooth. The process for making the colorant is easily controlled so that a wide range of median particle sizes is obtainable, thus allowing for different texture options and effects. The physical and chemical properties of the refined rubber product at D50 particle size of 12 µm are provided along with preliminary application data.

CHEMICAL PROPERTIES OF ELASTOMER PIGMENT

Tire composition varies depending on the type and use of tire, but in general, tires have four main components: rubber (40–49%), carbon black (~20%), metal (15–30%), and textile (0–5%). Typically, there are a number of additives that provide a variety of functions used in the manufacture of tires, and zinc oxide is used as a catalyst in the vulcanization process. During the reclamation process, some of the metals and textiles are removed. However, these materials are inherent in the product, and complete removal is nearly impossible.

Sample ID	Fe (ppm)	Zn (ppm)
~140 µm Crumb rubber	23790	40940
12 µm Elastomer pigment	6700	9559

Table 1—Metals Analysis for Elastomer Pigment vs Powder Rubber

During each of the stages of crumb and powdered rubber production, the majority of reinforcing materials, such as steel and textile fibers, are removed. While large pieces of fiber and metal are fairly easily eliminated, the nature of the processes, which is most often mechanical dry grinding at ambient or cryogenic conditions, leaves many contaminants still embedded in the rubber. The elastomer pigment process results in an overall lower metal and fiber content due to the finer particle size and processing conditions allowing for more effective removal.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis, an analytical technique involving complete digestion of the entire particle in strong acid and quantitatively determining the trace metals content, confirms that the elastomer pigment has more than a three-fold decrease in *total* metal and contaminates content. The metals content is noted in *Table* 1. The higher purity is particularly important with regard to product consistency. In a textured finish, the metal and fiber particles in crumb rubber can be part of the overall appearance package, and in many cases are desirable. However, their levels can be challenging to control within the tight specifications required for most coatings applications.

A key consideration in the use of elastomeric materials in coatings systems is solvent resistance. Elastomers are well known to swell when exposed to various solvents. A preliminary evaluation of the chemical resistance has been conducted through a simple test of soaking the elastomer pigment in a solvent at 38°C for 48 hr. The solvent resistance is determined by measuring the particle size distribution before and after solvent exposure. The particle size distribution does not change after exposure. A Cilas laser diffraction particle size analyzer was used for this measurement, and the results of the change in the median particle size are displayed in *Figure* 1. Catastrophic failures were noted with mineral spirits and xylene. For coatings that use these types of solvents, the solubility could provide an added benefit in that the elastomer pigment may be solvated with the effect that the elastomer pigment flowed into a film. As such, this pigment can contribute to the film properties without added film formers. In fact, in our studies, a mineral-spirits-based alkyd coating provided a reasonable film without any formulation, and the solubility of

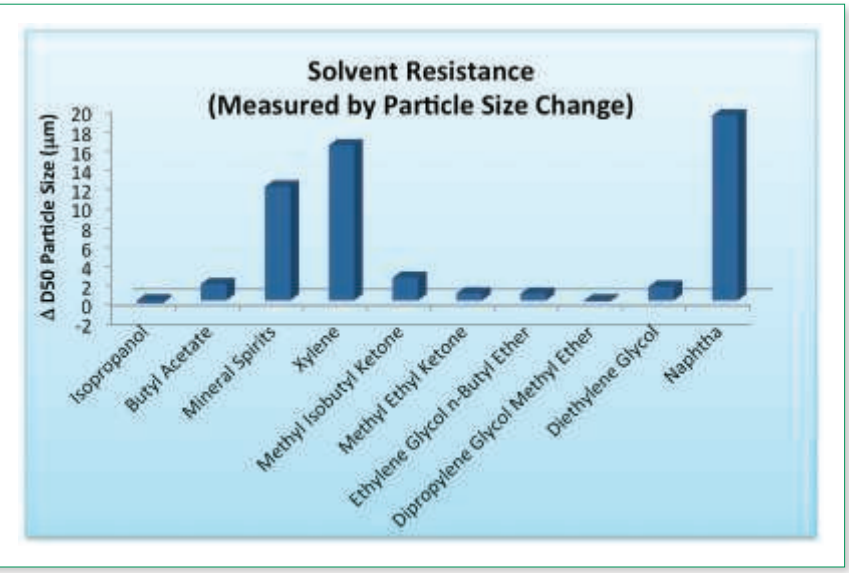

Figure 1—The change in the median particle size (D50) between the elastomer pigment before and after solvent exposure.

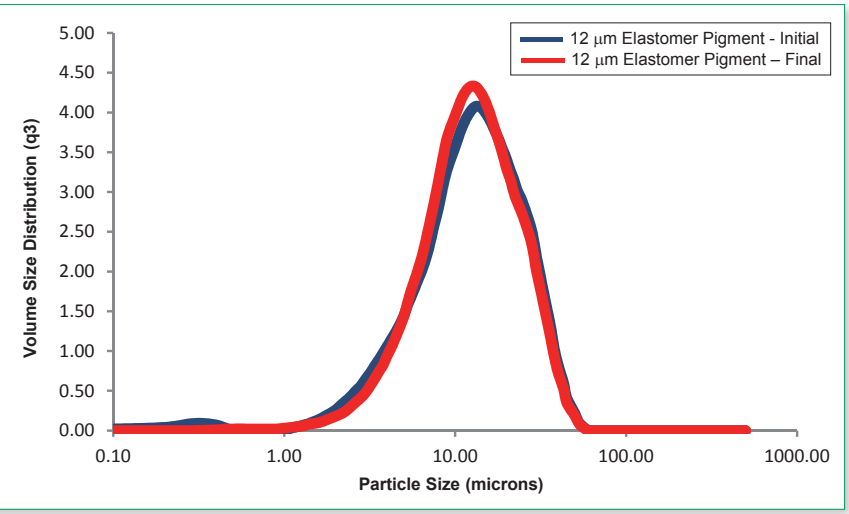

Figure 2—Particle size distribution of elastomer pigment in isopropanol comparing the initial to the seven-month-aged material.

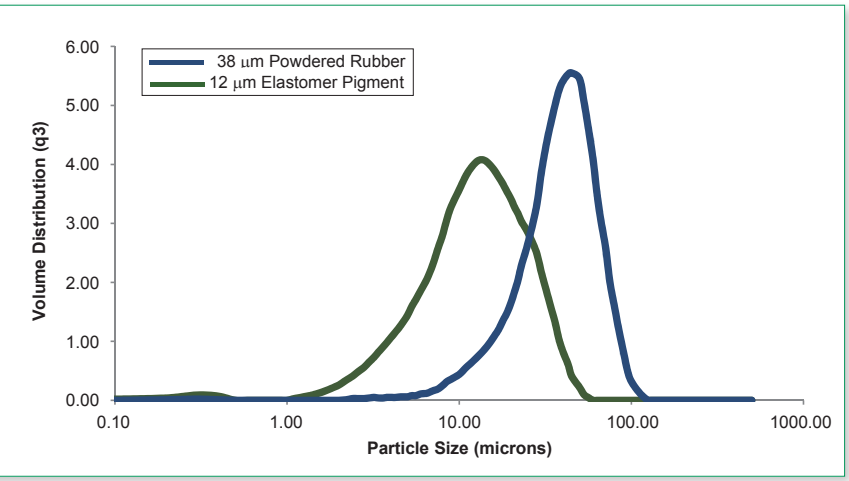

Figure 3—Particle size distribution curves comparing elastomer pigment at 12 and powdered market at 38 µm.

the elastomer pigment is hypothesized to be the key factor in the performance.

Elastomer pigment typically is available as a presscake in either water or isopropanol. As such, longer-term aging studies are available for these solvents. Of particular note, the elastomer pigment exhibits an especially high level of stability in isopropanol. Particle size analysis completed on a paste of rubber in isopropanol before and after seven months of aging indicated no measurable differences. The aging process was conducted at room temperature and at a solids content of approximately 50%. The particle size distribution curves for the initial and seven-month-aged samples are provided in *Figure* 2.

PHYSICAL PROPERTIES OF ELASTOMER PIGMENT

One of the most interesting features for the elastomer pigment is the degree of particle size control that is achievable. The smallest mean particle size of crumb rubber available on the market today is 38 µm. Elastomer pigment is defined as having a median particle size less than 30 µm, and the median particle size can be controlled down to approximately 10 µm. By controlling the particle size, more significantly, controlling the upper end of the size distribution, the film smoothness or lack of smoothness can be controlled, and as a result interesting tactile effects in a coating can also be attained. The particle size distribution curves for a particle size target of 12 µm is compared to the state-of-the-art 38 µm powdered rubber particle size distribution in *Figure* 3.

In addition to the particle size control, the particle surfaces are unique compared to cryoground products. The cryoground products have very irregular, sharp edges, while the smaller-sized elastomer pigment reported here is smooth and more rounded. At these particle size ranges, smoother edges will lead to improved coatings characteristics. These smooth edges have an influence on the appearance properties by imparting a unique sheen to the coating system not seen with other gloss control materials. The optical images provided in *Figure* 4 demonstrate the differences between the cryoground products and refined rubber. In the image of the powdered rubber (*Figure* 4a), the large particles of the powdered rubber are not well distributed throughout the film, and the particles are noticeably protruding from the film as a result of the poor wetting characteristics of the powdered rubber.

In addition to the particle distribution of the powdered rubber in the white film, the presence of metals is clearly observed in most of the visible particles and prominently seen in the particle on the lower left of the image as the bright spot in the center of the rubber piece. This is corroborated by the metals analysis reported in *Table* 1. Comparatively, the refined rubber in *Figure* 4b is homogeneously distributed, fully wet out, and has no visible glints from metal particles.

It is well accepted that the tinting strength of a pigment is directly related to its particle size. This applies to rubber particles and can easily be observed by the differences in tint strength of crumb rubber and elastomer pigment. In fact, powdered rubber does not impart any color value to a white reduction. Elastomer pigment, although considerably stronger than crumb rubber, is still weaker than C.I. Pigment Black 7, typically requiring about four times the loading to achieve the same degree of hiding. When the loading of the elastomer pigment is increased to approximately equal strength of a C.I. Pigment Black 7 pigment in the white reduction, the color of the elastomer pigment has a comparatively unique blue hue, as noted in the reflectance curves of *Figure* 5. The blue hue is primarily due to the relatively lower amount of reflectance in the red region of the spectrum as compared to C.I. Pigment Black 7, which has a much flatter curve throughout the visible spectrum. The visual differences can be seen in *Figure* 6.

As a consequence of the smoother, more rounded particle morphology, the elastomer pigment has unique rheological properties for a coatings system, compared to other pigments. The viscosity at different shear rates was measured for the pigments incorporated into different coatings systems. The viscosities for the coatings at the P:B noted in *Table* 2 were measured on a Brookfield LVDV-1 at 25°C. Interestingly, the viscosity at low shear is significantly higher for the elastomer pigment as compared to the coatings made with C.I. Pigment Black 7. As the shear increases, the elastomer pigmented coating demonstrates shear thinning behavior. This behavior offers the advantage of good application properties, such as atomization and brush-out, while maintaining very good flow and leveling characteristics. Indeed, the appearance of brush marks in the C.I. Pigment Black 7 samples are obvious on all substrates tested, but there are minimal to no visible brush marks for the elastomer pigmented coatings.

APPLICATION PROPERTIES OF ELASTOMER PIGMENT

Elastomer pigment has successfully been evaluated in a number of different coatings systems on a variety of substrates. The coatings systems include CAB lacquer, water-based self-crosslinking acrylic, oil-based alkyd, polyester powder coating, and solvent-based acrylic. The substrates to which these coatings have been applied include steel, ABS, unprimed MDF, and wood.

For the purpose of application testing, commercially available coatings and bases were purchased. C.I. Pigment Black 7 is used as the control because the powdered rubber imparts only weak color value to a coating. Additionally, smooth films are not achievable with crumb or powdered rubber and valid comparisons would be difficult to achieve. Test samples were prepared in identical vehicles using elastomer pigment at the P:B indicated. To demonstrate the impact of powdered rubber, *Figure* 7 shows images of the powdered rubber added directly to a coating, blended with C.I. Pigment Black 7 (to achieve hiding), and the elastomer pigment in a coating. These coatings were formulated in an oil-based alkyd at P:B of 12. For the coating in

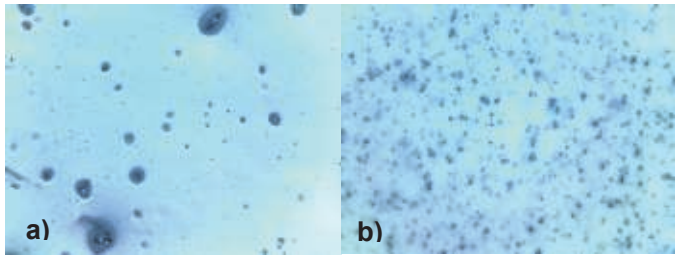

Figure 4—99:1 White reductions showing particle size differences between (a) powdered rubber and (b) elastomer pigment. The images are optical micrographs taken in reflection mode at 50X magnification on a Nikon Optiphot-2.

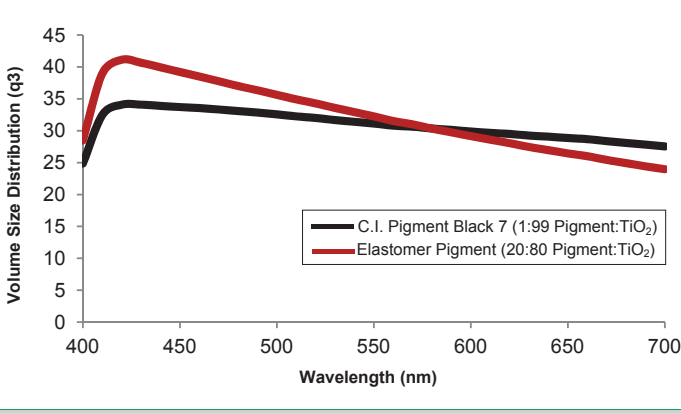

Figure 5—Reflectance spectra of white reductions of pigment elastomer black and C.I. Pigment Black 7.

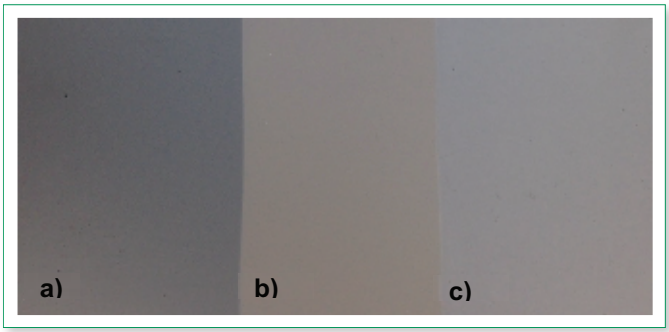

Figure 6—White reductions of (a) elastomer pigment P:B 33:67, (b) C.I. Pigment Black 7 P:B 1:99, and (c) elastomer pigment P:B 20:80.

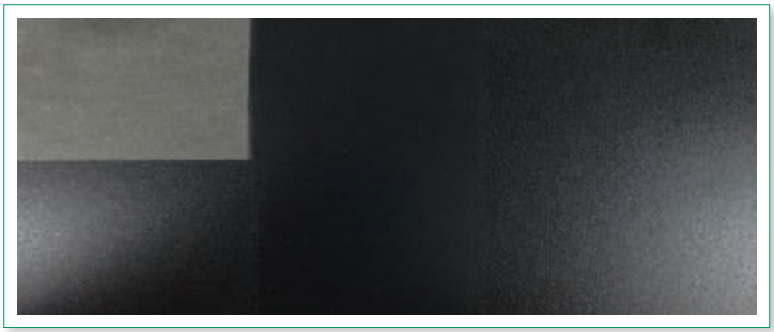

Figure 7—Comparison of (a) powdered rubber, (b) elastomer pigment, and (c) powdered rubber blended with 10% C.I. Pigment Black 7 of the total black pigment in an oil-based alkyd coating all at a P:B of 12.

Figure 7c, C.I. Pigment Black 7 is added at approximately 10% of the total black in the coating while the same pigment-to-binder ratio is maintained. The powdered rubber in *Figure* 7a is clearly weak with very large amounts of texture, and when it is blended with C.I. Pigment Black 7 for enhanced color, as in *Figure* 7c, the surface of the film remains too rough. However, the elastomer pigment in *Figure* 7b, is very smooth with full hide.

Following conventional wisdom, the dispersing energy to incorporate pigments into a coating is much higher for smaller particles. For example, transparent perylenes require significant amounts of energy to disperse, but larger organic pigments, such as opaque C.I. Pigment Yellow 74, can be dispersed with much lower amounts of energy. Mica pigments and glass spheres can often be stirred directly into the coating. Although glass spheres are similar in size and morphology to the elastomer pigments, a more intensive dispersion process is required for this new pigment. The optimal dispersions require dispersing energies similar to that of TiO_2. See *Table* 3 for the recommended dispersion method. It has also been found that drying the pigment results in a highly aggregated product that cannot be redispersed. As a result, alcohol- or water-free versions for powder coatings, 2K isocyanates, and ultra-low-VOC solvent coatings require conversion to a preparation in an appropriate resin carrier.

As noted in the previous section, the color strength of the elastomer pigment is lower than that of a coating formulated with C.I. Pigment Black 7 at the same pigment-to-binder ratio. However, the elastomer pigment can be loaded to much higher P:B as compared to the carbon black while maintaining acceptable rheological properties. In some systems, the elastomer pigment has been formulated at a P:B as high as 25 to impart unique effects. In a study of the pigment-to-binder ratio in a glossy polyester powder coating, the refined rubber has a pronounced effect on the coating appearance. As can be seen in *Figure* 8, the lowest P:B of 8, shown in *Figure* 8a, results in a glossy coating; the mid-range P:B of 12.5 (*Figure* 8b), has a matte appearance; and the highest P:B of 25 (*Figure* 8c), has a very flat, highly textured appearance while having excellent hiding power. This textured coating has a much softer, more uniform feel compared to the corresponding powdered rubber.

Table 2—Viscosity Measurements for Various Coatings Systems (results in centipoise)

	0.5 RPM	50 RPM	100 RPM
Oil-base satin–C.I.[a] Pigment Black 7 P:B[b] 3:100	3599	719	599
Oil-base satin–Elastomer pigment P:B 12:100	11997	839	641
Multipurpose self-crosslinking acrylic latex–C.I. Pigment Black 7 P:B 3:100	2399	1225	995
Multipurpose self-crosslinking acrylic latex–Elastomer pigment P:B 12:100	8398	1896	1410
CAB[c] lacquer–C.I. Pigment Black 7 P:B 3:100	9598	1644	1416
CAB lacquer–Elastomer pigment P:B 12:100	17996	2599	2106

(a) Color Index
(b) Pigment to binder ratio
(c) Cellulose acetate butyrate

Table 3—Recommended Dispersion Procedure

Equipment:		
High speed disperser:		
Saw tooth blade		
4000 ft per min tip speed		
Formula:	**Amount:**	
	825 g	Vehicle @ 35% resin solids
	175 g	Elastomer pigment presscake 50% in IPOH
Procedure:		
Add pigment to vehicle with lower speed agitation to mix		
Increase speed to 4000 ft per min tip speed and mix 30 min		

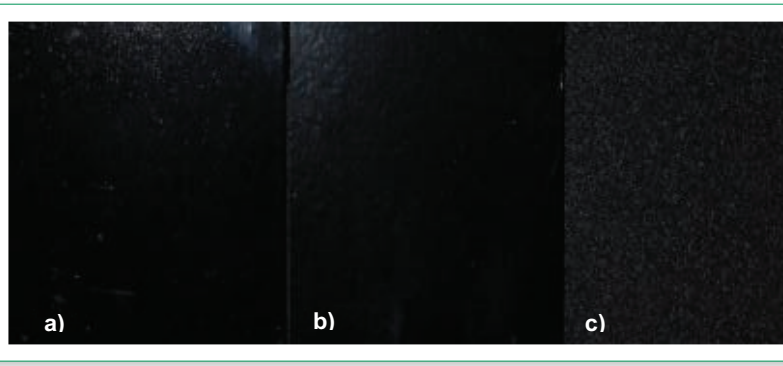

Figure 8—Elastomer pigment in polyester gloss powder coating at different P:B: (a) P:B–8, (b) P:B–12.5, and (c) P:B–25.

The unique particle morphology, size distribution, and surface chemistry of elastomer pigment results in an interesting viscosity profile of the coating, as noted in *Table* 2. The shear thinning nature of the coatings affects the application properties of the coating, which manifests itself as a much smoother film on different substrates. An example of the improved flow during the coating application on unprimed MDF is provided in *Figure* 9. The refined rubber coating has a much more consistent film and sheen compared to the C.I. Pigment Black 7 panel.

These unique properties also result in a more consistent sheen on unsealed birch substrate. The elastomer pigment particles impart improved hold out, and the resulting coating has a more uniform gloss level across the grain. *Figure* 10 shows the differences between the elastomer pigment in water-based self-crosslinking acrylic as compared to the commercially available black coating.

To assess the durability, a stone chip test was performed according to a modified ASTM method where nuts and bolts are projected at the panel fastened to a holder at a prescribed angle. The panels were prepared as a polyester powder coating with a P:B of 12.5 with a 170°C bake for 30 min. Neither the elastomer pigment nor the C.I. Pigment Black 7 resulted in chips larger than 3 mm (as noted by the C and D ratings) or chips smaller than 1 mm (as noted by the A rating). Both coatings had the chips in the range of 1 to 3 mm, with the refined rubber coating being slightly better than the C.I. Pigment Black 7 coating. The overall values as assessed by the method are provided in *Table* 4. Visually, the elastomer pigment coating did not appear to penetrate the coating to the steel substrate, whereas the C.I. Pigment Black 7 panel chips appear to show metal. The images in *Figure* 11 show the two panels after the stone chip test.

Additional testing included mar resistance of a solvent-based acrylic flat coating against Windex®. The test was conducted by soaking a paper towel with 4 g of Windex, and placing the sample on a

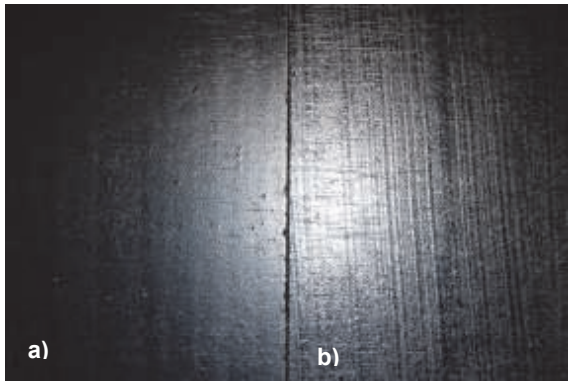

Figure 9—Water-based self-crosslinking coatings applied to MDF by brush: (a) elastomer pigment and (b) commercially available coating based on C.I. Pigment Black 7.

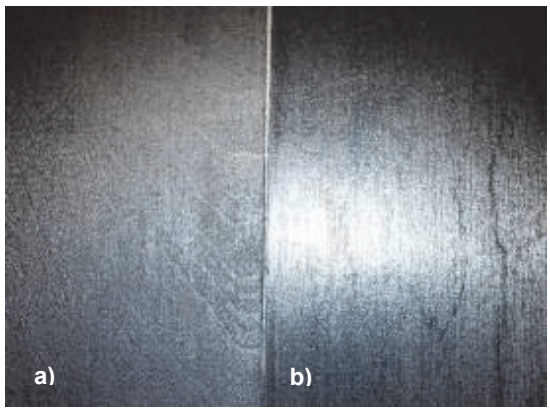

Figure 10—Water-based self-crosslinking coatings applied to unsealed birch panels applied by brush: (a) elastomer pigment and (b) commercially available coating based on C.I. Pigment Black 7.

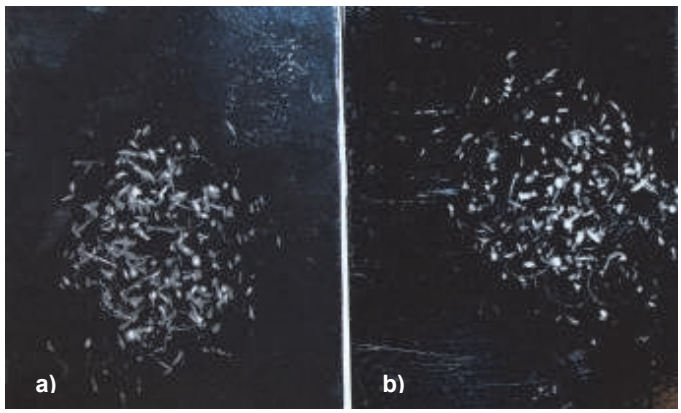

Figure 11—Stone chip test on powder coating panels: (a) elastomer pigment at P:B of 12.5, (b) C.I. Pigment Black 7 at P:B of 3.

Table 4—Stone Chip Test Results for C.I. Pigment Black 7 and Elastomer Pigment

C.I. Pigment Black 7 P:B 3	A1	B5	C10	D10
Elastomer pigment P:B 12.5	A1	B6	C10	D10

Sutherland Rub Tester. The control is a commercially available flat acrylic black coating made with C.I. Pigment Black 7, and the sample is the elastomer pigment formulated in the same acrylic bases as the control at a P:B of 12. Both the sample coating with elastomer pigment and the control were subjected to 100 cycles of the paper towel using a 900-gram weight. Visually, the control coating showed a higher gloss after the mar test was complete. Measuring the gloss on a 60° glossmeter, the gloss of the control coating increased by 3.3 units, while the experimental sample based on rubber did not change at all.

To assess lightfastness, ultraflat water-based acrylic coatings were subjected to weathering in a Xenon Weather-Ometer for 1000 hr, according to test cycle SAE J1960. The control coating is a commercially available black coating with a P:B of 3:1, and the elastomer pigment is tested at three P:B ratios: 15, 20, and 25:1. The coatings were tested for gloss differences using a 60° gloss reading. The elastomer pigment imparts a lower gloss value to the coating, and the gloss change is reported in *Table* 5. It is clear that the gloss decreased substantially for the control but remained much more constant for the different refined rubber coatings. While chalking was not evident in these ultraflat coatings, the data suggests that elastomer pigment is best suited for applications without high UV-resistance requirements.

CONCLUSIONS

Elastomer pigment is a unique product that offers many application advantages over the existing crumb and powdered rubber technologies, with the primary advantage being that it can provide coloration to a wide range of coatings. The pigment

Table 5—Gloss Change Due to Simulated Weathering

	Δ Gloss
Control WB acrylic coating P:B 3:100	4.2
Elastomer pigment coating P:B 15:100	1.1
Elastomer pigment coating P:B 20:100	0.3
Elastomer pigment coating P:B 25:100	0.2

can be tailored to meet the specifications of the application by controlling the particle size and the formulation as seen in the P:B study in powder coatings. In addition, the elastomer pigment can be incorporated into many commercial coating formulations, and it is quite readily formulated to a pigment loading that achieves full hide.

Elastomer pigment has shown performance benefits beyond being a recycled and possibly a sustainable pigment. It has shown potential to be a performance pigment with improvements in mar, sheen, flow, and holdout whose benefits warrant further investigation and usage independent of its ecological benefits.

Other potential functions include use as a sound dampening coating, electrical-resistive coatings, and antisag and antisettling additives. CT

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