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Technical

Titanium dioxide boosts sidewall compounds

By Steven Monthey, Jon Nienaber, Martin Saewe and Ronald McMullen
Rhein Chemie Corp.

Executive summary

Compounding white sidewall compounds is a difficult process. The difficulty comes not from the formulation or mixing procedure but from potential contamination. Since white sidewall compounds are mixed in locations where a significant amount of carbon black, antioxidants, incompatible polymers and other potential contaminates exist, the potential for discoloring and foreign material is extreme. The other problem with mixing white sidewall compounds is the dust generated by using powdered titanium dioxide.

This white powder is quite fluffy and is easily lost into the air and dust collection systems. Using dispersions of titanium dioxide can eliminate the dust level and save significant waste to the dust collectors and floor. This study will examine the physical and processing properties of a typical white sidewall compound using both rutile and anatase titanium dioxide and compare the results of powdered versus the dispersions of each.

Titanium dioxide dispersion can be made using a variety of binders for other applications. These dispersions have all of the same benefits as those seen in the white sidewall compounds. The dispersion can eliminate dust, waste, contamination and scrap, making titanium dioxide dispersions a cost-effective way to eliminate the problems incurred when dealing with a dusty powder.

The biggest reason customers use dispersions is to save money. Though the initial cost of dispersions is usually greater than that of the raw chemical, customers purchase them to save costs in other areas.

Before we can show the various ways that a customer can save money using dispersions, we need to examine the dispersion process in order to see the advantages of predispersing materials.

TECHNICAL NOTEBOOK
Edited by Harold Herzlich

The dispersion process for powder products starts with the breakdown of the larger particles into smaller particles.

Many powders are sold in pellets or granules that must be initially broken down so that the second step of dispersing, which is wetting, can be done either by the polymer or the processing oil. This initial wetting of the powder is the second step of the dispersion process.

After the powder goes through the first breakdown and the initial wetting, it then begins the incorporation into the polymer matrix.

The next step in the dispersion process begins when the shear of the mixing equipment breaks the small particles into micro particles. Also in this step the material may have reached its melting point, allowing it to be readily dispersed into the polymer matrix.

If the material has not or will not reach its melting point, it is further wetted by the polymer and any process oil until it is completely broken down and dispersed into the matrix. In the case of four incorporating titanium dioxide, this final dispersion step is completed without melting the product because the melting point of titanium dioxide is well above any mixing temperature.

Challenges of dispersing titanium dioxide in chlorobutyl white sidewall compound

There are two major challenges in incorporating titanium dioxide into chlorobutyl compounds. The first is the initial wetting of the powder with the polymer and the processing oil.

Since white sidewall compounds have little or no process oils, the initial wetting must be done by the polymer.

This requires a high initial shear to push the powder into the polymer matrix. If other powders are added during this step, the mixing challenge is even greater. The small particle size of the titanium dioxide causes considerable dust to escape into the atmosphere and ultimately into the dust collector.

Even though titanium dioxide has a higher specific gravity than the polymer, the relatively low bulk density allows this dust to escape causing material loss and housekeeping issues.

This also causes variations in the amount of titanium dioxide that goes into each batch, thus lowering the batch to batch consistency of the color rating. The other problem in completely dispersing the titanium dioxide into the polymer matrix is the fact that it does not melt, and so requires additional mixing time to completely incorporate it into the compound.

If the titanium dioxide incorporation is incomplete, then visual and physical defects can occur caused by undispersed titanium dioxide.

Advantages of using a polymer bound titanium dioxide dispersion

The biggest advantage in using polymer bound titanium dioxide dispersion is the removal of the dust. Pre-dispersing the titanium dioxide into a polymer matrix using the same polymer type as the white sidewall has benefits in cost reduction, improved housekeeping and worker morale.

The cost reduction comes from the elimination of waste going up the dust collector or winding up on the floor. Even if bulk loading systems are used,

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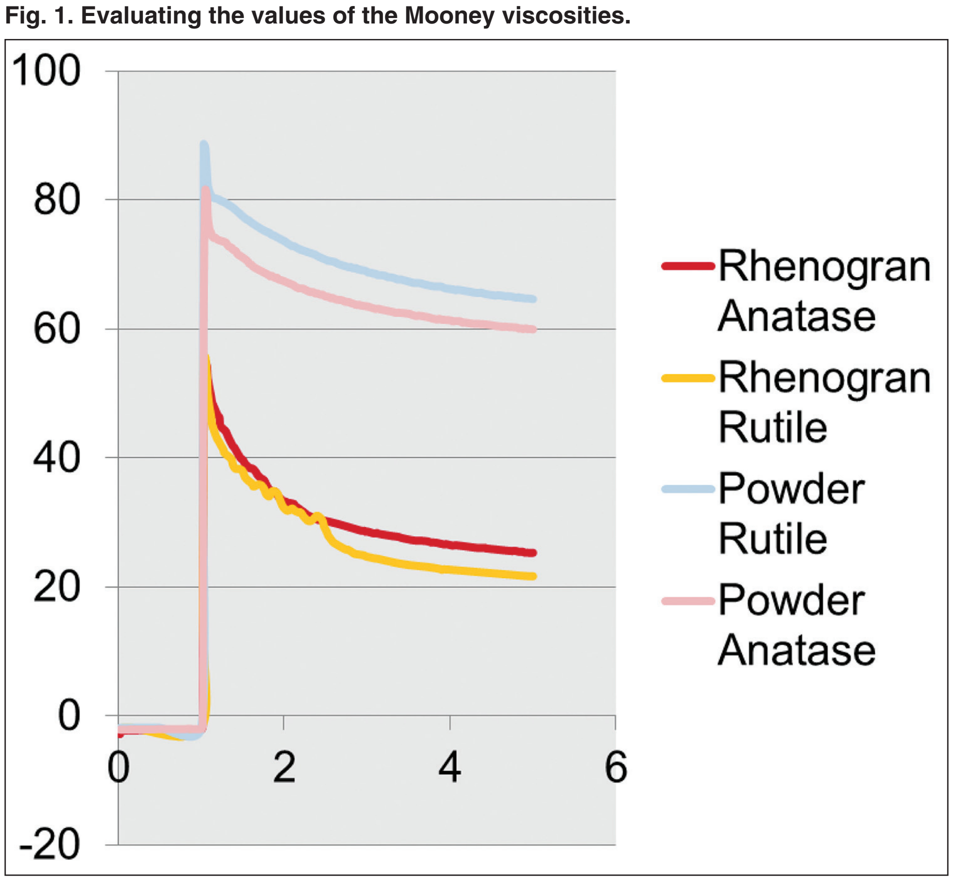
Table. I. Formulas with both types of powders and polymer dispersions.

Loadings	Anatase Powder	Rhenogran TiO2-80/CIIR Anatase	Rutile Powder	Rhenogran TIO2-80/CIIR Rutile
Compound	143.2	137.2*	143.2	134.2*
TiO2	40 phr	0	40 phr	0
TiO2 Disp	0	50 phr	0	50 phr
Total	183.2	187.2	183.2	184.2

Fig. 1. Evaluating the values of the Mooney viscosities.



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Sidewall

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the low bulk density of the unpelletized titanium dioxide allows it to be released into the atmosphere where it can be lost as waste and deteriorate housekeeping.

With the elimination of the dust, worker morale improves by working in a cleaner, healthier environment. Using polymer bound dispersions for all of the dry ingredients can improve the working environment significantly to a point that clean-up is quick and efficient.

Downstream scrap improvements also can be obtained by reducing undispersed titanium dioxide defects. This savings can become significant since the entire tire could be lost to a visual defect in the white sidewall.

Finally, the environmental footprint can be reduced by reducing the waste generated by the mixing operation. Since many of the powder chemicals are classified as hazardous, additional cost reduction can be realized by eliminating this source of hazardous waste.

Improving mixing efficiency by using polymer bound titanium dioxide dispersion

Predispersing a powder such as titanium dioxide in a polymer binder completes the five steps of dispersion before it is put into the mixer. This predispersing breaks down the titanium dioxide, wets it, breaks it down again, and then wets it with the polymer and finally fully disperses it into the compound matrix.

This process allows the combined dispersion to be incorporated into the polymer matrix faster than if the powder was mixed in directly.

For most polymer bound dispersions, the incorporation time is half that of the normal time for powders. Given the high loading of titanium dioxide in most white sidewall compounds, this time savings can be enough to allow the mixing of several more batches per shift, increasing the overall capacity of this equipment.

Processing and physical properties—formula

Four formulas were mixed and tested. The recipes were based on a standard three polymer white sidewall compound with a normal loading of 40 parts of titanium dioxide. Fifty parts were used for the 80 percent active polymer bound samples to compensate for the weight of the binder. Since there are two types of titanium dioxide, anatase and rutile, we ran formulas with both types of powders and polymer dispersions.

Processing tests

Since the main advantage of predispersing a metal oxide such as titanium dioxide is to improve the processing and housekeeping, we should see advantages in shorter mixing times and lower Mooney viscosity witch can be an indication of improved processing.

Both of the batches using the predispersed titanium dioxide incorporated faster and came together quicker than the two powder batches. **Fig. 1** shows that the two predispersed batches also had noticeably lower Mooney viscosity. All Mooney viscosities were run at 100°C using one minute warm-up and then testing for four minutes.

Evaluating the Mooney values in **Fig. 1** we can see why the predispersed batches incorporated faster than the powder. The initial of the two polymer bound products is 25-39 points lower than the powders, meaning that less energy would be needed to wet and break down the powder so it can be dispersed into the compound.

The predispersed samples already had gone through the incorporation process when dispersed into the polymer binder so they were able to be mixed into a finished product quicker.

The housekeeping is also dramatically improved as no powder fell into the pan during the dropping of the batches while the powder batches had small amounts of powder that came down with the batch. This can be a source of contamination in normal production as sweepings from the mill pan can also include foreign material which can cause visual defects.

Rheometer properties

Fig. 2 shows the comparison of the Rheometer curves of the two powder batches versus the two curves of the polymer-bound Rhenogran batches. The initial portion of the cure curves are lower for the two polymer bound batches showing the lower initial Mooney viscosity.

Next the cure rate of the two powders show a variation in speed and height indicating that they may have inconsistent amounts of titanium dioxide in them due to the loss of powder during mixing. The two polymer bound batches are closer together showing a more consistent weight of the titanium dioxide.

Also the powder batches show higher ending values indicating that their titanium dioxide may not have been fully incorporated into the compounds while the lower more consistent curves of the polymer bound batches indicate that complete dispersion has occurred.

Physical properties

Finally, physical properties were tested to see if there were any advantages or disadvantages in using predispersion of titanium dioxide. Normal tensile sheets of each polymer were cured and tested with the results shown in **Table II**.

Other than a slight increase in the reinforcement of the rutile form of the titanium dioxide, all of the physical were the same. This shows no loss in physical properties and demonstrates that polymer bound dispersions can replace powders with no negative effects while generating improvements in processing, quality, housekeeping and worker morale.

Conclusion

There are several problems in making white sidewall compounds. Contamination of carbon black and other foreign materials cause many batches and tires to be rejected or reworked. Housekeep-

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Fig. 2. Comparison of the Rheometer curves of the two powder batches versus the two curves of the polymer-bound Rhenogran batches.

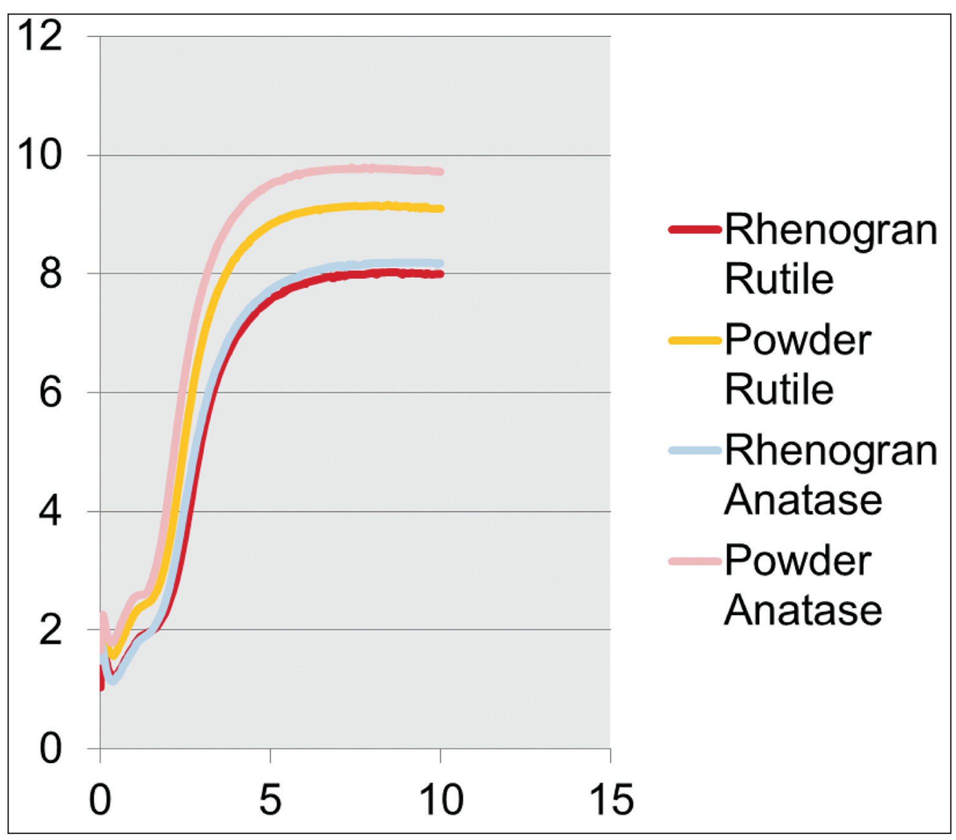

Table II. Normal tensile sheets of each polymer, cured and tested.

Properties	Anatase Powder	Rhenogran TiO2-80/CIIR Anatase	Rutile Powder	Rhenogran TIO2-80/CIIR Rutile
Tensile mPa	13.13	12.67	13.74	13.63
100% Mod	1.13	1.05	1.08	1.24
200% Mod	1.66	1.48	1.61	1.78
300% Mod	2.25	1.95	2.15	2.33
Elongation %	934	926	922	907

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Expansion

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tomotive parts that are integral in vehicle transmission through both compression and injection molding, which includes seal rings, thrust washers, pistons and assemblies.

The firm said the facility maintains nearly perfect statistics in the areas of quality, delivery and customer retention. Duclos said the plant is mostly automotive-focused, but it does have a small portion of product that serves other industry.

"Most of our plants are relatively specific to a type of industry or a type of product," Duclos said. "The Findlay facility is relatively unique with the types of products that it makes."

Roy Schroeder, Findlay's lead center manager for fluid power automotive, said the facility utilizes high temperature thermoplastics, primarily polytetrafluoroethylene (PTFE). The expansion is in response to the automotive industry transitioning from six-speed transmissions to eight-, nine- or 10-speed transmissions.

> **"The Findlay plant is relatively unique with the types of products that it makes."**
> **Theodore Duclos**

Duclos said the purpose for the transition is to improve fuel economy, and as the number of speeds in vehicle transmissions increase, Freudenberg-NOK's market should continue to grow.

"As that trend continues, it gives us the chance to have increased product going into those transmissions," Schroeder said.

Duclos said the firm still is finalizing incentive programs with the state and local governments. Freudenberg-NOK said that the expansion will create new jobs, but the final number is still to be determined. The firm's release said the expansion could result in about 148 jobs being retained and the creation of about 25 new ones.

The company said it worked with JobsOhio, state and local officials on incentives to support the expansion. The firm said it will host a formal groundbreaking celebration on June 19.

Findlay has become Freudenberg-NOK's lead facility in adopting its single cavity net shape molding manufacturing approach, which Schroeder said began at the plant in 2010. The approach uses compact, custom-engineered one cavity injection and compression molding machines instead of multi-cavity machines to produce thermoplastic parts.

Freudenberg-NOK said the process improves part quality while reducing scrap and waste. Duclos said the new approach is still in the early stages of being adopted in other facilities.

"We have machines in other facilities that are practicing it, but we're still in a relatively introductory phase where we're refining the technology," Duclos said.

Freudenberg-NOK Sealing Technologies is an Americas joint venture between Freudenberg and Co. in Germany and NOK Corp. in Japan. It manufactures advanced sealing technologies for the aerospace, agriculture, appliance, automotive, construction, diesel engine, energy, food and beverage, heavy industry and pharmaceutical industries.

The joint venture is headquartered in Plymouth, Mich., and operates more than 20 facilities across the Americas.


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The authors

Steven Monthey is a technical service chemist at Rhein Chemie Corp.

He has 44 years of experience in the rubber industry, with Goodyear, Bandag, Dayco, Cabot and Hercules before joining Rhein Chemie in Chardon, Ohio.

His current assignments include the development and marketing of new and unique Rhein Chemie products for use in automotive, industrial and tire applications.

Monthey's background includes work in compound and product design for hose and belt applications, tires and retreads, vibration isolation, medical components and other rubber segments.

Monthey graduated with a bachelor's degree from Washburn University in Topeka, Kan.

He is chairman of the SAE Non Hydraulic Hose Committee and a member of the SAE Classification of Automotive Rubber Specifications (CARS) Committee.

Jon Nienaber formerly served as the technical service manager at Rhein Chemie.

He began his career at the facility as an intern in 2007 and was hired full time as an application technologist in 2008.

Nienaber is an active member of ACS Rubber Division and former president chair for the Michigan Rubber Group. He graduated from Ferris State University in 2008 with a bachelor's degree in rubber engineering technology.

Martin Saewe has worked at Rhein Chemie since 2002, serving in changing roles within research and development, technical sales and marketing.

In 2012 he moved to the U.S. with the responsibility for the tire customer segment. In October 2014, he moved back to Germany into his position as head of the Business Line Lube Additives.

Saewe has a doctorate in rubber crosslinking systems.

Ronald McMullen works as a product development and applications technologist for Rhein Chemie Additives, where his assignments include compound and product design, analytics and process engineering.

He has been with Rhein Chemie for five years, and is experienced with rubber processing and lab equipment.

He holds chemistry and mathematics degrees from Kent State University.

AirBoss

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military and first response forces globally for more than 40 years.

Part of the AirBoss Engineered Products division, the defense operation produces and supplies hand wear, footwear and respiratory protection products.

In September 2014, the Newmarket-based company was awarded an order for a little more than 400,000 pairs of CBRN over-boots. That pact's estimated value was about $15.3 million.

Deliveries of the boots began in the latter part of 2014 and will continue through December, Swartzman said. AirBoss also landed an order for 40,000 pairs of protective gloves and another for 30,000 pairs of boots from England in early 2014.

Awards that the defense operation received in 2014—especially the $15.3 million U.S. DoD order—were key reasons the engineered products division exited the first quarter with stronger financial results than the previous year.

For the remainder of 2015, the continuation of the over-boot contract combined with the new U.S. DoD glove award will benefit defense sales and earnings when compared to 2014, Swartzman and Gren Schoch, the firm's chairman and CEO, said in the company's quarterly report.

Overall, net sales for AirBoss rose 7.6 percent to $76.9 million for the quarter while net income increased 28 percent to almost $3.2 million from $2.4 million in last year's period.

In addition to engineered products, the firm gained momentum across all of divisions. Rubber compounding volumes, in terms of pounds, increased about 1.6 percent over the like period in 2014. The automotive business continued to perform well, benefiting from the strong automotive manufacturing environment as well as increased customer penetration, Schoch and Swartzman said.

They expect the automotive parts business to perform well for the remainder of 2015.

Sidewall

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ing is also an issue as the white titanium dioxide powder has a rather low bulk density causing dust to settle on the equipment, floor, and be wasted into the dust collector.

Incorporating this dust also slows down the mixing and reduces the capacity of the white sidewall mixing equipment. The loose powder also lowers the morale of the workers that have to work in the dusty environment.

Eliminating this dust also can improve the worker's safety and productivity by reducing their exposure to the irritating powder. Replacing the powder titanium dioxide with a polymer bound product can show considerable improvements and savings in a variety of areas.

Housekeeping is dramatically improved along with worker morale. Dust collector and floor sweeping waste are eliminated along with a major source of foreign material contamination. Other quality improvements include lower defects by having a more consistent color reading and the elimination of undispersed powder in the final tire.

Finally the mixing process can be speeded up, resulting in increased capacity and improved efficiency. All of this can be accomplished with additional improvements in processing due to lower Mooney viscosities and without any loss in physical properties.

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