

AEROSIL[®] fumed silica and AEROXIDE[®] fumed metal oxides in hot melt adhesives

Technical Information 1323

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1 Introduction

1.1 Hot melt adhesives

According to the *ASC 2002-2004 Global Market Report*, hot melt adhesives were the second largest share by product category in North America during that period. These products are based on a variety of chemistries designed to be compounded at elevated temperatures, typically 120° to 175 °C, applied at these temperatures, and allowed to cool to achieve their final properties. Most are designed as pressure sensitive adhesives that are coated on to various sheet stocks with a release liner. These are separated and applied to a substrate. These may be compounded to act as a temporary adhesive, the ubiquitous "Hi my name is" label, or may be designed for a long service life under various environmental conditions, e.g. safety labels on mechanical equipment.



Pressure sensitive adhesive labels manufacturing

The largest application, approximately 60%, for hot melt adhesives is for paper, most often corrugated boxes. While package integrity is important in this application, the strength required tends to be somewhat low as the strength required to tear paper is relatively low. Other applications, such as building construction, woodworking, assembly and transportation, may require improved adhesion, and temperature and moisture resistance.

For these reasons, styrene block copolymers are chosen as the base polymer. Over the last forty years, these polymers have offered the combined adhesive properties of styrene with the flexibility of butadiene, isoprene, and ethylene-butylene. Natural and synthetic resins are added to modify these blocks to achieve specific formulating requirements.

1.2 AEROSIL® fumed silica and AEROXIDE® fumed metal oxide process

Flame hydrolysis is the method used by Evonik Degussa (hereafter Evonik) to produce AEROSIL® fumed silica and AEROXIDE® fumed metal oxides. The most common is AEROSIL® fumed silica in which silicone tetrachloride is mixed with hydrogen and oxygen in a flame with temperatures above 1,000°C. Other salts based on metals such as titanium, zinc, zirconium, etc, can also be used to produce high purity AEROXIDE® fumed metal oxides.

AEROSIL® fumed silica has long been known in the adhesives and sealants industry for not only its rheological, but also its reinforcing properties. The latter is most important for hot melts as viscosity and rheological properties are generally not a concern, though they must be monitored as they may affect coat weights.

AEROSIL® fumed silica is synthetic amorphous silica produced by a flame hydrolysis process that can be traced back to the Evonik chemist H. Kloepper. Through engineering controls, the primary particle size of the fumed silica may be controlled which affects the surface area of the fumed silica. The particle size and structure achieved in this process directly affect the rheological properties of the fumed silica. This process results in a sufficient amount of silanol groups on the surface to produce a hydrophilic material. Through hydrogen bonding of these sites, a matrix is set up to control the rheological properties of the final mixture.

AEROSIL® fumed silica may also be offered as a hydrophobic material. Chemical aftertreatment, most often a silane, is used to achieve this effect. Hydrophobicity is most often determined through ability of the fumed silica to disperse in a methanol and water mixture. The silane and amount of treatment determine the degree of hydrophobicity. These products may offer less thickening and reinforcement than hydrophilic grades, but the treatment offers selective compatibility with organic materials thus improving properties such as dispersibility, film formation and hydrophobicity of the final product.

1.3 Primary particles and structure

During the AEROSIL® process, silicon tetrachloride is combined with hydrogen and oxygen in a flame to produce pure amorphous silicon dioxide. Through engineering designs, a primary particle is produced in the flame, but these particles quickly begin to cool and collide with each other fusing to form tightly held aggregates and finally loosely formed agglomerates.

During the dispersion of AEROSIL® fumed silica, it is necessary to break up the agglomerates. With time, the resulting aggregates form a matrix within the mixture, which affects the rheology and reinforces the film. The reinforcement results in improved cohesive strength, improved tear resistance, higher modulus and reduced elongation. The loading level affects each of the properties and it is up to formulators to balance these with their individual requirements.

1.4 Hot melt testing

Most often, hot melt adhesives are used as pressure sensitive adhesives (PSA). The Pressure Sensitive Tape Council (PSTC) publishes various test methods for PSAs. Of these, three are often used to evaluate the properties of the adhesive, *PSTC-107 International Standard for Peel Adhesion of Pressure Sensitive Tape*, *PSTC-107 International Standard for Shear Adhesion of Pressure Sensitive Tape*, and *PSTC-16 Loop Tack*. The impact of the fumed silica on viscosity may be measured by a Brookfield Viscometer. Thermal stability testing was also conducted on various formulations using ASTM International D4499 *Standard Test Method for Heat Stability of Hot-Melt Adhesives*.

These tests are used to compare the performance of various types and levels of AEROSIL® fumed silica and AEROXIDE® fumed metal oxides produced by Evonik. Peel adhesion is perhaps the only true adhesive test in this set. The tests for shear adhesion and loop tack are more indications of the flow characteristics of the adhesive film. The ability of the system to flow and wet the substrate as well as its resistance to deformation has more of an impact on the results of these test methods.

2 Hot melt formulation

2.1 Raw materials

Typically, hot melt adhesive formulations are comprised of various combinations of synthetic rubber(s), natural resin(s), synthetic resin(s), oils, plasticizers, and antioxidants to achieve properties based on the specific application.

2.1.1 Synthetic rubber

A common type of synthetic rubber used in hot melt adhesives requiring higher performance is styrene block copolymers. This type of synthetic rubber is made through a closely controlled polymerizations step to form blocks of specific monomers. Two types of monomers are chosen based on their glass transition temperature (T_g). Styrene is typically chosen as the higher T_g monomer that has more effect on the adhesive properties, while a variety of lower T_g monomers are chosen and which affect the cohesive properties.

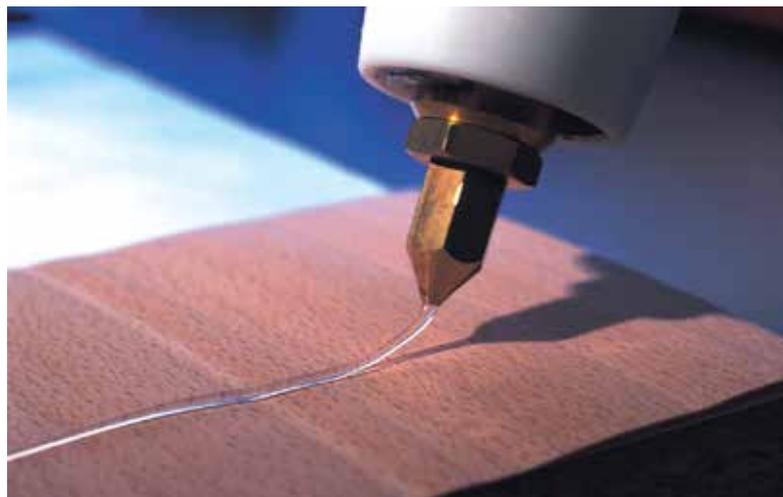
These polymers are typically sold as “diblocks”, in which two different monomers form discrete blocks; as various forms of “triblocks” usually with the harder, high T_g monomer on the ends of the polymer chain and a more flexible chain in the middle; or as blends of “diblocks” and “triblocks” to balance performance properties. Other structures are possible and the formulator should consult suppliers of these materials for further information.

Two styrene block copolymers were used in the evaluations and were obtained from Kraton Polymers LLC. Kraton® D 1161 K is a linear block copolymer of styrene and isoprene with 15% total styrene content and 19% diblock. The diblock is mobile enough to provide improved surface wetting and tack. Kraton® 1113 P is also a styrene and isoprene copolymer with 16% total styrene but with 55% diblock for improved tack.

2.1.2 Natural and synthetic resins, and oils

Organic resins added to hot melt adhesive formulations modify the properties of the rubber, such as strength and tack. These are typically chosen based on their melting or softening point, color, thermal stability, etc. As a general guideline, higher melt point resins enhance the properties of the styrene block, while lower melt point resins enhance the softer segment. The polymer used in this study is based on isoprene.

In this study several resins and oils were evaluated. Among these, the higher melt point materials were Sylvares® TR 1085 from Arizona Chemical Inc., and Piccotac 1095 from Eastman Chemical. Sylvares® TR 1085 is a polyterpene tackifier with a Ring and Ball softening point of 85°C. Piccotac 1095 is an aliphatic C 5 resin with a Ring and Ball softening point of 94°C. Both products modify the styrene portion of the SIS polymer.



Hot melt adhesive being applied to wood substrate

Piccotac® 1020 from Eastman Chemical was evaluated. This is a liquid hydrocarbon resin with a Ring and Ball softening point of 5 °C. This is used to increase tack and reduce viscosity.

Nyflex® 222 B is naphthenic oil from Nynas Group that acts as a plasticizer. This increases tack and reduces viscosity in a hot melt adhesive.

2.1.3 Other raw materials

Other raw materials such as antioxidants are added to maintain thermal stability of the hot melt adhesive. These products are used to tie up free radicals generated when high heat and oxygen are in the presence of organic materials.

Irganox® 1010 from Ciba is a sterically hindered phenol that acts as a primary antioxidant. This class of antioxidant reacts quickly with peroxy radicals, ROO●, to break the cycle of degradation.

2.2 Compounding and coating

A one-quart sigma-blade mixer was used to compound the formulations and a HLC-101 Hot Melt Laboratory Coater, ChemInstruments, was used to apply the adhesive to 2-mil thick biaxially oriented polyester (BOPET) film. The coater was adjusted to achieve coat weights of 20 to 25 g/m². Formulations were made, coated and tested within one week.

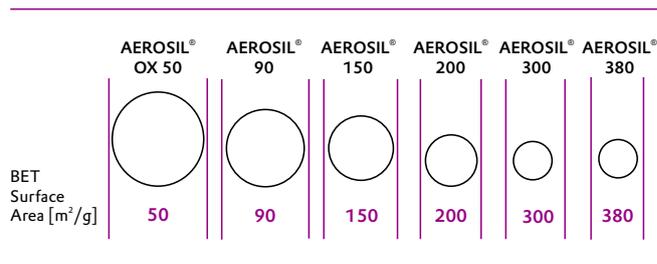
The resin and antioxidant were added to the mixer and the resin was allowed to melt. The styrene block copolymer was added and allowed to melt before the liquid hydrocarbon resin or oil was added. This was mixed to an even consistency before any AEROSIL® fumed silica was added. It is necessary to do this as AEROSIL® fumed silica may coat a partially melted resin mass and interfere with the processing.

3 AEROSIL® fumed silica and AEROXIDE® fumed metal oxides

3.1 Hydrophilic AEROSIL® fumed silica

The most commonly used fumed silica is AEROSIL® 200, a 200 m²/g specific surface area material. Based on an equal degree of dispersion, fumed silica with a surface area less than this provides less thickening for equal weight loading, while those above provide more thickening. In this study, AEROSIL® 200 and 150 were used.

Difficulties in dispersion arise with high surface area fumed silicas. More energy is required to disperse high surface area particles. Equipment engineering may limit the surface areas from which a formulator may choose.



3.2 Hydrophobic AEROSIL® fumed silica

Evonik offers the widest variety of surface treated AEROSIL® fumed silica. Each treatment type has a direct effect on the rheological properties of the system and the degree of reinforcement achieved.

One common treatment uses dimethyldichlorosilane to treat part of the AEROSIL® fumed silica surface. AEROSIL® R 972 fumed silica has a BET surface area of 110 m²/g and is treated with dimethyldichlorosilane. The carbon content, a relative measure of the level of treatment, is nominally 0.90%. Though treated, there still are a number of silanols on the surface to affect rheology and the reinforcing properties of the silica. For higher surface area (increased rheology), AEROSIL® R 974 may be used. Additionally, AEROSIL® R 104 and R106 provide higher surface areas. These are treated with octamethylcyclotetrasiloxane (D4 silicone oil) and still result in dimethyl groups on the surface of the fumed silica.

Another method of treatment is to use polydimethyl-siloxane, PDMS silicone oil. AEROSIL® R 202 is the most hydrophobic grade of fumed silica and is commonly used in the adhesives and sealants industry when a high degree of water resistance is needed in the fumed silica.

AEROSIL® R 805 is an octylsilane treated fumed silica. This offers a high amount of carbon on the surface, but due to the steric hindrance, it does not react with all of the surface silanol groups.

3.3 AEROXIDE® TiO₂ P 25 for heat stability

Through the same AEROSIL® fumed silica process, TiCl₄ is used to produce fumed TiO₂. AEROXIDE® TiO₂ P 25 consists of approximately 80% anatase and 20% rutile crystal structure. Compared to pigment grade TiO₂, AEROXIDE® TiO₂ P 25 produces less color due to the particle size difference.

Improved heat stability of a hot melt adhesive may allow for improvements in efficiency during the coating process. An adhesive that resists thermal degradation may be kept in a heated tank longer thus reducing the number of cleaning processes.

4 General purpose formulation and test results

An adhesive formulation suitable for a broad use was used as a base to evaluate various AEROSIL® fumed silica products. It is up to the individual formulator to evaluate the suitability of using fumed silica in each specific recipe.

Table 1 GP base formulation

Raw material	phr.	pct.
Sylvares® TR1085	110.0	43.47
Irganox® 1010	3.0	1.19
Kraton® D1161 K	100.0	39.53
Piccotac® 1020	40.0	15.81
AEROSIL® fumed silica	1.5–3.0	0.5–1.0

As mentioned, the properties of Loop Tack and 180° Shear Adhesion are more related to the flow properties of the adhesive. These are both tested at room temperature conditions. Results of the test should indicate if the AEROSIL® fumed silica has a more positive impact on the resistance to flow during removal than during the wetting. This would be an advantage when trying to improve the permanency of the adhesive bond.



A 150, A 200, R 202, R 805, R 972, R 974 =
AEROSIL® 150, 200, R 202, R 805, R 972, R 974

With the exception of 3.0% loading of AEROSIL® R 202, the addition of fumed silica increases the loop tack properties of the system. In this test, the 1.5% loading of AEROSIL® R 972 proved to show the greatest increase in loop tack. As the dwell time of contact is very short, the rheology of the adhesive film likely has more effect on this test. The addition of fumed silica has long been known to impart a thixotropic behavior. The increase of viscosity at low shear rates will allow the adhesive to resist flow more, while a lower viscosity at higher shear rates will not significantly impact coating.

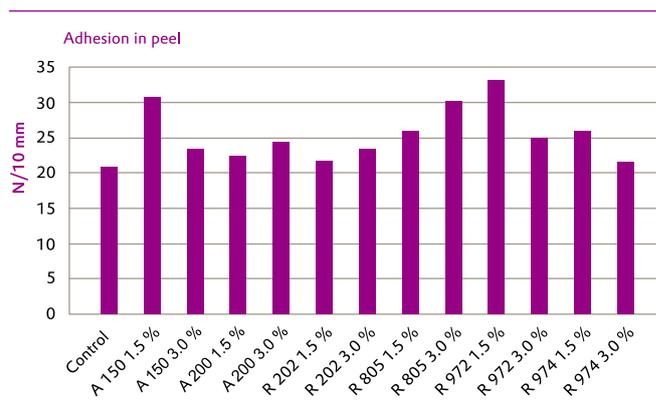
With the exception of the 1.5% loading of AEROSIL® 200, the 180° Shear results were higher in all cases. The largest increase in Shear results is seen in the 3.0% loading of AEROSIL® R 805.



A 150, A 200, R 202, R 805, R 972, R 974 =
AEROSIL® 150, 200, R 202, R 805, R 972, R 974

The 1.5% loading of AEROSIL® R 972 (that did well in loop tack test) was still quite good with an increase in shear time by over twice the control.

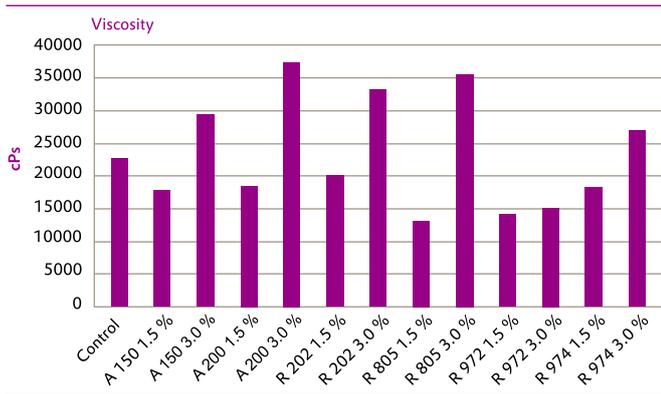
As adhesion in peel is more of a true adhesion test, a comparison of the results indicates that these properties are improved by AEROSIL® fumed silica addition. The largest increase in this property is seen in the 1.5% loading level of AEROSIL® R 972.



A 150, A 200, R 202, R 805, R 972, R 974 =
AEROSIL® 150, 200, R 202, R 805, R 972, R 974

For adhesion testing, the AEROSIL® R 972 at 1.5% loading proved best in two of three tests and showed a significant improvement in the third. The option of adding a small amount of surface modified AEROSIL® fumed silica gives the formulator options to improve performance without radically changing raw materials especially in relation to higher styrene content polymers or higher melt point resins.

However, the addition of AEROSIL® fumed silica is always a concern for increasing the viscosity of the system as it acts as both a rheology modifier and reinforcing agent. A comparison of the viscosity at 350 °F (177 °C) was made. A Brookfield HAT head with a SC4-21 spindle was used at 5 rpm. Testing was conducted within 4 hours of adding the adhesive to the melting chamber.



A 150, A 200, R 202, R 805, R 972, R 974 =
AEROSIL® 150, 200, R 202, R 805, R 972, R 974

All loading levels at 1.5% surprisingly showed no significant change in viscosity. The error of the test is $\pm 2,000$ cPs. Loading levels of 3.0% AEROSIL® fumed silica showed a significant increase in viscosity which in some cases may render the adhesive unusable. Again, all such changes need to be evaluated by the individual formulator and is equipment dependent.

5 Thermal stability

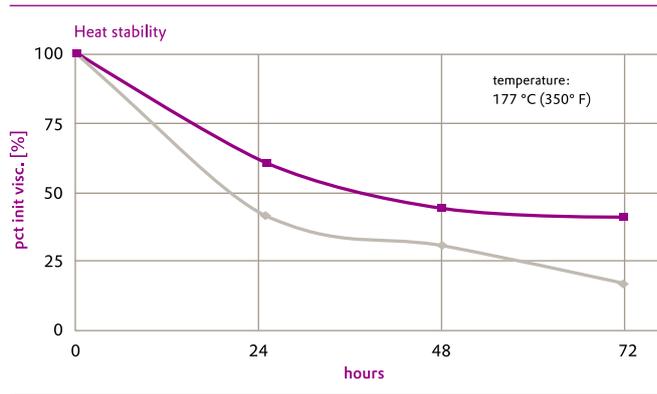
The viscosity stability of a hot melt adhesive maintained at operating temperature is an indication of the usable life of the adhesive when kept at high temperatures. ASTM International D4499 *Standard Test Method for Heat Stability of Hot-Melt Adhesives* was used to determine the melt viscosity at 24, 48 and 72 hours and compared to the starting, time zero (t_0), viscosity.

In this study, a more typical label formulation was used. This is made up of the following:

Table 2 Label base formulation

Raw material	phr.	pct.
Kraton® D1113 P	100.0	34.93
Piccotac® 1095	142.9	49.92
NyFlex 222 B	42.9	14.98
Antioxidant (e. g. AEROXIDE® TiO ₂ P 25)	0.5	0.17

Irganox® 1010 and AEROXIDE® TiO₂ were added at 0.5 phr loading level and is typical of such products. Sample specimens were kept at 177 °C (350 °F) and viscosity was tested at 24, 48 and 72 hours and compared to the initial viscosity. A plot of the results is shown on the chart.



— AEROXIDE® TiO₂ P 25, 0.5 phr. — Irganox® 1010, 0.5 phr.

The initial viscosity of each material was approximately 20,000 cPs indicating that the fumed TiO₂ does not have a significant effect on rheology. The use of the AEROXIDE® TiO₂ P 25 may allow the user to extend the time the adhesive is kept at melt temperature. Using a 25% drop in viscosity as a benchmark, a similar drop is seen at about 16 hours for the fumed TiO₂ and about 12 hours for the standard antioxidant tested. For a five day production cycle of three shifts, this would require 7.5 cleaning steps for the fumed TiO₂ versus 10 for the standard.



Hot melt adhesive being applied to wood substrate

6 Conclusions

The use of AEROSIL® fumed silica and AEROXIDE® fumed metal oxides offers the formulator a number of options in formulating hot melt adhesives. The choice of silica and loading level can positively affect the properties typically studied when making pressure sensitive adhesives. AEROSIL® R 972 at 1.5% loading appears to be the optimal choice, for the system evaluated in this study. The use of AEROXIDE® TiO₂ P 25 can also enhance the pot life of these adhesives thus extending time between costly cleanups.

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EVONIK
INDUSTRIES

Europe / Middle-East /
Africa / Latin America

Evonik Resource Efficiency GmbH

Business Line Silica
Rodenbacher Chaussee 4
63457 Hanau
Germany

PHONE +49 6181 59-12532

FAX +49 6181 59-712532

ask-si@evonik.com

www.evonik.com

North America

Evonik Corporation

Business Line Silica
299 Jefferson Road
Parsippany, NJ 07054-0677
USA

PHONE +1 800 233-8052

FAX +1 973 929-8502

ask-si-nafta@evonik.com

Asia Pacific

Evonik (SEA) Pte. Ltd.

Business Line Silica
3 International Business Park
#07-18, Nordic European Centre
Singapore 609927

PHONE +65 6809-6877

FAX +65 6809-6677

ask-si-asia@evonik.com

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