Rubber metal bonding - Waterborne bonding agents - Solvent reduction - VOC legislation - Metal preparation

Rubber-Metal-Components are widely used for antivibration-, sealing- and rubber lining technologies. The production of such components requires normally the use of organic solvents for substrate cleaning, dilution of bonding agents and anticorrosion coatings. This paper refers to alternative cleaning agents and bonding agents which allow a reduction of organic solvents.

Waterborne bonding agents have reached the bonding activity of traditional solvent based ones. Bonding tests result frequently into 100 % rubber break. However, adhesion forces might not always reach the highest possible level. Certain combinations of waterborne products have shown advantages in respect to flexibility and fluid resistance of the bond.

Market shares of waterborne bonding agents have not yet reached 10 % in Europe. However, it is expected that this will change in 2007 when the European VOC rules. Have to be fully applied. There is no major barrier from the technical point of view.

Ein umweltfreundliches Verfahren zur Herstellung von Gummi-Metall-Teilen

Gummi-Metall-Bindung - Wässrige Haftvermittler - Lösemittelreduction - VOC-Richtlinie - Metalvorbehandlung


In Europa liegt der Marktanteil der wässrigen Haftvermittler noch unter 10 %. Es wird damit gerechnet, dass dieser Anteil bis zum Jahr 2007, wenn das europäische Luftreinhaltungsge- setz voll zur Anwendung kommt, deutlich steigt. Die technischen Vor- aussetzungen für eine die Steigerung des Anteils an lösemittelfreien Produkten sind gegeben.

Cleaning and degreasing of the metal

The foundation of a good bond is a clean and stable metal surface. Any protective oil or grease layer that may be present must be removed to ensure that the bonding agent achieves good contact and in particular optimal wetting of the metal.

Today, aqueous degreasing systems can replace the traditional solvents and are highly effective methods of surface preparation before the grit blasting. Neutral or alkaline systems can be used for metal preparation as also can acid phosphat- e systems.

The neutral system allows avoiding the rinsing phase because the residual thin protective film of organic products is removed during the blasting phase but in this process the grit is progressively contaminated. The alkaline cleaning is the more commonly used with success. The alkaline cleaner is a mixture of surfactant, builder and sodium or potassium hydroxide. The surfactant action is very important in assisting the degreasing because of the encapsulation of the oil or grease residues by the hydrophobic groups of the surfactant [1]. The builders are combinations of sodium carbonate, sodium silicate, borates or sodium gluconate [2]. The two main application processes are the dipping in heated baths (50 to 100 °C) sometimes with additional ultrasonic activation, and the spraying at 60 °C. The four main interrelated process variables must be well controlled: These are concentration, temperature, time and mechanical action. A failure of the rinsing is absolutely necessary in all cases.

Despite some difficulties, alkaline cleaning is an effective alternative to the solvent vapour degreasing, and in particular the spray system which is already used in the field of the rubber to metal bonding.

An Environment Friendly Process for Rubber-to-Metal Bonding

Solvents are commonly used in the rubber industry, for example for mould cleaning, adhesion of new tread in the tyre retreading process, rubber coating of fabrics, anti-friction coatings and of course the rubber to metal bonding which is the topic of this paper. Rubber to metal bonding is used for the manufacture of many components including vibration damper elements, gaskets, seals and rollers.

The solvents are used for two main process steps:

i) Cleaning and degreasing of the metal;

ii) Coating of the metal by the bonding agents.

The control of V.O.C. (Volatile Organic Compounds) emissions is more and more an important issue in the industry and the legislation concerning V.O.C. use is becoming increasingly severe. The European Union Directive of the 11th March 1999 gives the emission limit values for each of the activity sectors; the objective is the reduction of the solvent emissions by 1.5 million ton per year. For the “Rubber conversion” example, as the limit value of the waste gas emission is 20 mg/Cm². This European legislation will become fully implemented in 2007. For the past thirty years, many attempts have been made to substitute solvent based bonding agents by aqueous systems and increasingly some bonding agent manufacturers (Lord Corporation, Henkel, C.I.L., Chemetall and Morton) have accepted the difficult challenge for providing environment friendly alternatives in aqueous forms.

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Paper given at the IRC’03 in Nürnberg, 30.06.–03.07.03

1 Kautschuk Gummi Kunststoffe 56. Jahrgang, Nr. 11/2003

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Rubber to metal bonding with aqueous systems

**General principles**

The main steps of the bonding process with conventional solvent based systems are:
1. the coating of one or two layers which are the primer and the cover
2. the solvent evaporation
3. the over moulding of the metal by the uncured rubber in order to obtain simultaneous adhesion and the vulcanisation.

The primer contains phenolic resin and specific ingredients; the cover contains mostly halogenated polymers with specific additives or organosilanes for particular applications.

As in the case of solvent based bonding agents, the aqueous systems are generally composed of two components, the primer and the cover coat. In aqueous systems both top and cover coat are in emulsion form. An exception is being bonding agents for special rubbers as FKM or silicone which need only the cover containing organosilane.

The bonding agent manufacturers have had to overcome four major difficulties in the production of aqueous bonding agents:

- The preparation of active polymers in stable emulsion form; for this reason the chemical structure of the backbone polymers are not the same as for the solvent based agents and also the crosslinking agents are different.
- The application process of the aqueous agents onto the substrate to obtain a continuous layer with good film properties.
- The providing of specific grades for various chemical structures of elastomers leading to adhesive performances as high as those of solvent based agents.
- The cost.

Basically, the bonding process for both waterborne and solvent borne bonding agents uses the same principle of mechanism. This mechanism is based on the formation of three interfaces (Fig. 1):

1. Metal/primer interface consisting of polar adsorption with chemical reactions and physical links,
2. Primer/cover interface where occur the interdiffusion of the two types of polymers and the migration of the crosslinking agents,
3. Cover/rubber interface where the interdiffusion of the cover polymer with the elastomer macromolecules and the crosslinking agent migration must occur before the beginning of the rubber vulcanisation.

According to all these parameters, destructive bond failure will be either cohesive in the rubber (which is the desired goal) or adhesive failure at these different interfaces.

**Specificity of the application process of the waterborne agents**

When bonding agents using a solvent vehicle the principle of the film formation is very simple. The bonding agents deposited on a substrate surface form during the solvent evaporation a continuous elastic layer that has good mechanical strength and film properties in the uncured state.

For the aqueous systems, the principle of film formation is more complex (figure 2). The aqueous systems are emulsions of small particles called micelles. After air drying the uncured micelles are separate having only surface cohesion between particles. To obtain a dense and continuous elastic film in the layer, the micelles must coalesce to form a continuous film. If the waterborne agents are applied to cold substrates as in the conventional way, the film tends to crack and chip because there is no coalescence of the micelles. However by coating onto preheated surfaces (40–60 °C) the micelles coalesce and good film properties can be achieved. Several methods of application can be used: brushing (but excessive pressure can disrupt the latex stability), dipping, electrostatic, rollers and spraying. The latter is particularly recommended however spraying must be done with a not too high pressure as this will cause powdering of the bonding layer. A carrousel with appropriate guns at low pressure is the most convenient equipment. Electrostatic application is also a convenient process to minimise the overspray.

In all cases the coating thickness should not exceed 15 µm for the primer and 20 µm for the cover. After an air drying up to 80 °C; the primer must be dry before applying the top coat that should dry within a minute.

There are also specific recommendations for storage and handling. Transport and storage recommendations

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Fig. 1. Mechanism of rubber-to-metal adhesion with the bonding agents in solvent or aqueous phase: formation of the three interfaces.

Fig. 2. Principle of film formation with the waterborne agents.
storage temperature of 5–30 °C are recommended to avoid gel formation or coagulation. Before using the waterborne agents must be conditioned at 25–30 °C and carefully stirred to avoid vortex formation that would cause air inclusion and foam formation. Dilution with deionised water is often useful to adjust the viscosity for a particular application process. Another important point for the aqueous systems is the pre-bake resistance; that is the period of time the coated metal component resides in the heated mould prior to the rubber introduction. An excessive time in the hot mould before moulding can lead to a pre-cure of the bonding agent thus giving rise to bond failure. Various grades of waterborne agents were put on the market some years ago (1995–2001) by suppliers such as Lord Corporation, Henkel, C.I.L., Chemetall and Morton. Table 1 illustrates some examples of these commercial products. There were specific primers and covers for a wide range of rubbers: unsaturated (NR, NBR, CR), saturated (EPDM), polar (ACM, Vamac, hydrid rubber) and fluorinated also (FKM). Some systems can also be used as one coat. In 2003 Lord Corporation, Henkel, C.I.L. and Rohm & Haas (which has bought the Chemetall and Morton products), are still present on the market.

**Adhesive performance of waterborne Chemosils in comparison with solvent based Chemosil**

Waterborne products assist in compliance to solvent emission regulations. They also facilitate in the application of the bonding agents and furthermore can even outperform some of the typical bond characteristics in comparison to standard solvent products. These are strong arguments for the use of waterborne products provided that there is not any deficiency in:
- general bond security to various rubber compounds
- bond resistance to various fluids and temperatures
- underbond corrosion resistance
- handling of the bonding agent
- costs

It has been proved that the universal bonding capability can be obtained for the bonding of a wide range of NR, SBR, NBR and CR compounds to various mild steel and aluminium alloys. However, solvent based primers show some advantage on some substrates which are generally more critical in bonding such as cast iron or some plastics. Whereas some waterborne primers provide an excellent flexibility of bonded components. Waterborne bonding agents behave in respect to sweep resistance and mould fouling similar to standard covers which contain a high level of crosslinker but can’t reach the low mould fouling level of covers with a low level of crosslinker. Film build of waterborne bonding agents is excellent when applied as recommended onto pre-warmed substrates. Correctly prepared substrates and correctly applied waterborne products will not show deficiency to solvent based products in respect to under bond corrosion (e.g. 1000 h salt spraying test). Bond resistance in typical fluids such as hot glycol or hot brake fluid is excellent. General bond security is the key parameter for component selection in the automotive industry. A wide range of components bonded with waterborne products have been produced for more than 10 years without any significant difference when compared to traditional bonding agents. It is assumed that the total process costs with waterborne bonding agents are similar to those with solvent based products when the new European solvent emission regulation is fully implemented in 2007 latest.

**Conclusion**

Waterborne bonding agents have the potential to replace large market segments that currently use solvent based products. At the present time they have not yet reached 10% market share in Europe. This will however change when the European VOC legislation becomes fully implemented in 2007.

**References**


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