Improvement of adhesion on polymer film, foil and paperboard by flame treatment

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Abstract

Flame treatment of film, foil and board is a well established method to improve adhesion. Passing the flame over a surface leads to an increase in surface energy and wettability, respectively, thus enabling a good contact between the fluids used for decoration and the surface. An improved process control together with new techniques of burners and air/gas control leads to a significant energy consumption reduction. Considering treatment effects as well as economical aspects flame treatment may be more convincing than Corona treatment applying high web speeds and large web widths. Latest developments include flaming with silane precursors.

Introduction

For decorating the surface with a paint, lacquer, glue or coating a good adhesion between surface and decorating fluid is necessary. Surface treatment is performed to increase the adhesion properties of surfaces. Among other methods physical treatment methods like corona, plasma or flame treatment are wide-spread. The advantages of these compact treatment units are that they can easily be integrated in the production line providing good treatment results even at high working speeds and that they do not produce any significant waste.

Which method is best-suited depends on the form of the part to be treated. Moulded parts are a domain for flame treatment. Small moulded parts or small working width are treated by atmospheric plasma devices. Corona treatment is mainly used for even surfaces like films and foils.

Surface properties corresponding to adhesion

For a good adhesion you have to fulfil two conditions in principle. The fluid which should be deposited onto the surface has to wet the surface for a good contact. And a good adaptation between the fluid and the surface material is needed to get an effective chemical link.

Surfaces on a technical level have low surface tensions leading to bad wettabilities of fluids. Polymer surfaces have low surface tensions by nature. Especially the polar parts of the surface tension are very small which may be explained by the long-chain molecular structure of polymer surfaces.

Surface tension is also influenced by additives which have been added to the polymers during the production process to design special properties. These additives (e.g. plasticizer) may diffuse to the surface forming a non-adhesive surface layer. Due to the production process you will find surface contaminations like oil, grease or other sliding agents. Dust and other components of ambient air may deposit onto the surfaces. This can be minimised by an appropriate storage or transport.

Surface roughness plays an important role, too. Roughening of surfaces increases the surface area thus enhancing the contact area between surface and coating. Due to an additional mechanical anchoring adhesion is intensified.

Measurement of the treatment effect

A measure for the treatment effect is the surface tension (or surface energy) of the surface. The standard method for measuring the surface tension is the contact angle. The angle between the surface and a drop of a fluid with known surface tension has to be determined. From this the surface tension of the surface can be calculated. Measuring with different fluids gives the polar and disperse part of the surface tension as well.

The main disadvantage of the contact angle method used in a production line is that it takes time to get a result. As a rule, a piece of the foil has to be cut out and brought to the contact angle device. For preliminary tests of the treatment effect it is suitable to use the test inks. These are fluids with known surface tensions. Dependent on the behaviour of a drop on the surface the surface tension can be estimated very quickly close to production. If the fluid which may be applied to the surface with a brush or a felt pen forms drops on the surface, surface tension of the ink is higher than that of the surface. On ther other hand, if the ink spreads on the surface, surface tension is higher than the surface tension of the ink.

For paperboards this method does not work. Best information on adhesion can be gained by performing an adhesion test. In any case this should be done for finally assessing the treatment result for all applications. High surface tension is necessary for a good contact between the surface and the coating material. But surface tension cannot guarantee a good chemical (or any other kind of) link between coating and surface. Both coating and surface material have to be matched with each other. If this has been done surface tension ensures good adhesion properties in most cases.

Properties of the flame

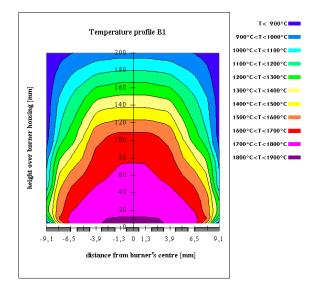


Fig.1: Measured temperature profile of a burner used for treatment of foils.

Using flame treatment you simply have to pass a flame over the surface. The flame consists of two parts: the primary and secondary part. Within the primary flame which is located directly above the burner nozzles the actual combustion takes place. In case of having propane you get

$$C_3H_8 + 5 O_2 \rightarrow 4 H_2O + 3 CO_2$$

Propane (or methane, butane or other hydrocarbons) burns with oxygen from air to water and carbon dioxid. Dry air has an oxygen content of about 21% and a nitrogen content of about 79%. So the combustion equation is

 $C_{3}H_{8} + 5 O_{2} + 18,8 N_{2} \rightarrow 4 H_{2}O + 3 CO_{2} 18,8 N_{2}$

For a stochiometric combustion you need an air/gas ratio of 23,8:1 in case of propane.

The primary flame has a conical shape. This conus is formed by two velocities: the flow velocity of the air/gas mixture out of the burner nozzle and the flame velocity. With this velocity a flame front moves towards the unburnt air/gas mixture.

The dark blue cover flame on the top of the primary flame is the so-called active area. It is used for the surface treatment. The maximum flame temperatures are located just above the dark blue cone. This temperature depends on the air/gas mixture. Highest temperatures occur near a stochiometric mixture. Flame is mainly cooled down by diffusion of ambient air into the hot flame. Due to the high temperature activated molecules are formed in the exhaust gases, mainly hydroxyl (OH) from the dissocation of water and oxygen (O). An oxygen content in the exhaust gas exists and may be adjusted if an air/gas mixture is used with excess oxygen. The concentration of the activated molecules depends on the temperature of the flame.



Fig.2: Example for a flame of a burner used for treatment of even surfaces like films, foils, paperboards.

Principle of flame treatment

The treatment of surfaces is simple. You have to pass a flame over the surface of the part to be treated. Choosing appropriate parameters the surface energy is increased. Alternatively the part may be moved through the active part of the flame not being in motion. The latest one is often used for treatment of foils. The impact of the flame on the surface depends on the properties of the surface and the flame.

As mentioned above thermal activated atoms and molecules are created in the hot flame. These activated species can be deposited into the surface leading to an increase in surface tension. As they form polar bonds with the long-chain hydrocarbons the increase in surface tension is mainly due to an increase in polar part of the surface tension.

Further effects influencing the surface is the cracking of the long-chain molecules in the surface. This improves the possibility of a chemical link between the decoring fluid and the surface. The activated molecules in the flame are preferentially deposited at the cracked surface molecules (oxidation).

Improvement of wettability may also be done by surface cleaning. If the layer thickness of the surface contamination is rather small flame treatment has a certain cleaning effect by burning the oil, grease or other contaminations. Micro roughening by flaming increases the surface area. Fluffy surfaces can be smoothed; loose material on the surface can be burnt or removed.

Flaming parameters

The treatment effect is essentially influenced by the flame characteristics and the flaming parameters. The flame pattern mainly depends on the geometry of the burner. The diameters of the burner nozzles and the number of nozzle rows play an important role. The type of burner which is most suitable for a given application depends on the handling of the parts and the materials to be flamed. For heat sensitive materials the heat power of the burner should be reduced to avoid melting or destruction of the surface. Moving the burner needs special arrangements for flame stabilisation. The required length of the active zone of the flame is determined by the moulded surface. Small flame length mostly are sufficient for even surfaces.

An important influence on the treatment results is given by the burning parameters. These are the mixing ratio, the distance between burner and surface, the heat power of the burner and the working speed. For a good treatment result it is often useful to have some excess oxygen in the exhaust gas which passes over the surface. This can be achieved by adjusting an air flow slightly higher than stochiometric air/gas mixing ratio.

The working speed which is the relative speed between surface and flame determines the impact time of the flame on the surface. To get the same treatment result you have to raise power or reduce distance when increasing the working speed. The heat deposition into the surface is given by the heat power of the burner and the distance. Too much heat deposition into the surface may destroy the surface layer leading to bad adhesion on the surface. Too less heat power has a negative influence on the treatment result. The ideal working distance is within the cover flame.

To get optimum treatment results the flame parameters have to be set to an optimum combination. As the various materials have different surface properties and the surfaces are influenced by additives and surface contaminations a commonly usable set of the flaming parameters cannot be given. They have to be found out by trials for each application.

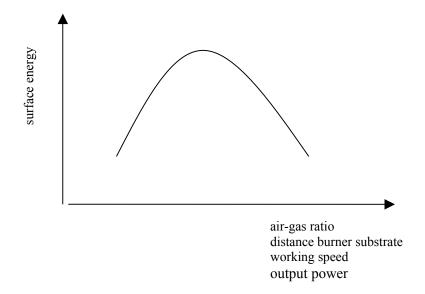


Fig.3: Schematic drawing showing the dependence of the surface tension from the flaming parameters

Flame treatment of films and foils

Flame treatment of films and foils is used in a wide range of applications: printing, glueing, laminating, pasting, coating... Increasing surface tension and improving adhesion on polymer films as well as on metal foils, paperboards or polymer-paperboard composites are possible.

Flame treatment units can easily be integrated into a coating machine. Having large working width or high heat power, respectively, an exhauster is required. The flame should fire on a cooling drum. With this heat removal and a defined distance between flame and substrate is ensured.

Besides cooling drum and exhauster the flame treating unit consists of an air/gas controller and special burners. The controller together with a special mixing chamber provides the air/gas mixture by controlling the air flow and the gas flow. A rather exact and fast measure of flow rates can be carried out by mass flow meters. These devices measure the mass flow instead of the volumetric flow which is independent on temperature and gas pressure. Additionally a measurement of the oxygen content in the process air is feasible for monitoring reasons. As seen from Fig.5 the surface tension is nearly constant within a oxygen content of around 21%. Significant changes in surface tension occur at deviations of about 10%.

The burners are connected to the controller unit by special gas hoses or pipes. Due to a special design the burners create a homogeneous flame even at large working widths up to several meters in length. To avoid heating up burners should be cooled. On the other hand the temperature of the cooling water should not be too low to prevent the formation of condensed water. So it is advisable to use a cooling/heating unit for the burners and the cooling drum.



Fig.4: Burner which is used for large working widths

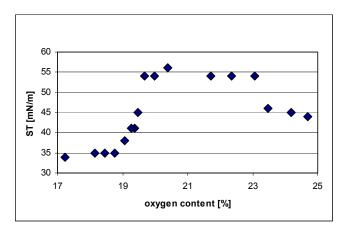


Fig.5: Dependence of the surface tension of a PE surface from oxygen content in the process air

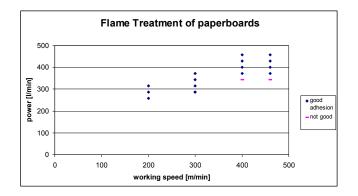


Fig.6: Adhesion of a paperboard-polymer composite. The drawing shows the dependence of the burner's heat power from the working speed.

Originally the main application field of flame treatment has been (heavily structured) moulded parts due to the large active zone of the flame enabling the treatment with varying distances between surface and burner. Corona treatment which have been widely used for many years for treating even surfaces like foils and films present some disadvantages

which make flame treatment interesting. Dependent on the special production process high working speeds together with large working widths could favour flame regarding costs for acquisition and operation. The flame always treats one side of the films while Corona treatment influences both sides of the film. Back side treatment often is not desired because of higher probabilities of the formation of wrinkles. Working with very thin films there are risks of perforation of the film due to inhomogeneous disruptive discharges. If long time stability of the treatment is required flame treatment often provides better results.

For optimal treatment results the flaming parameters should be set carefully. In general the working speed is given due to the following coating process and the allowed speed of the rewinding machine. The appropriate other flame parameters heat power, air/gas mixture, distance and type of burner should be find out by trials. Doing like this heat power and gas consumption could be reduced drastically. Further taking into account that the working speed of rewinding machine is increased step by step to maximum speed within several minutes a power regulation with speed.

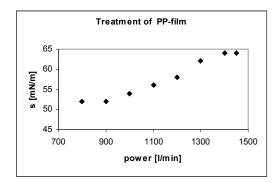


Fig.6: Dependence of the treatment effect from the heat power of the burner in case of pp-film. Surface tension without treatment is 28 mN/m.

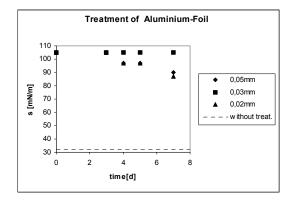


Fig.7: Longtime stability of the treatment effect on Al-foil with various thicknesses. Surface tension whefore treatment is 32mN/m.

could save further energy. An automatic burner deckling may be useful when working with varying working width of the films and foils. Considering all these items energy savings of more than 50% can be achieved.

Silicoating

Further improvements on adhesion may be achieved by the new silicoating technique. A silane precursor is mixed into the flame. The silane burns to silicate which is deposited on the surface forming a thin invisible silicate layer on the surface to be treated. The amorphous structured layers have thicknesses of about 20 nm. By the silicate layer the surface tension and the adhesion properties are improved. Specific requirements on adhesion can be fulfilled such as stability against moisture, protection against corrosion, diffusion barrier. Long time stability of the surface activation is improved.

Like conventional flaming the silane containing flame has be passed over the surface to be treated within the active region of the flame. Preliminary investigations of the treatment effect can be done by measuring the increase in surface tension with the test inks. Adhesion tests give more precise results.

The silicoating method is used for dental applications since more than ten years. Up to now only small parts have been coated. Latest developments in burner technology and silane dosages made it possible to expand the applications to higher working width and working speeds. Systems with working widths up to one meter and more are available.

The silicoating flame treating device consists of a conventional flame treating system supplemented with a silane dosage. The silane dosage which evaporates the silane fluid is connected to the flame treater via a pipe. Typically the silane consumption is below 1% of the air consumption. Though, in principle, it is possible to use standard burners, special silane burners with special air/gas flow characteristic should be used to reduce the probability of burner contamination. Flame colour of the cover flame is changed from dark blue to slightly red colour which can be used for an optical proof of the presence of silane in the flame.

Applications of the silicoating method is conceivable in the area of film and foil treatment. Metal foils like copper, aluminium or steel could be coated for protection against corrosion as well as for improving adhesion. In case of copper the silicoated copper surface is protected against oxidation which could be demonstrated easily by flaming different parts of the surface with and without silane. The silicoated parts do not change colour at temperatures around 300 °C while the non-silicoated parts change colour to black indicating an oxidation of the surface. This effect can also be used for proofing the silicoating.

Conclusions

Flame treatment is a well-established method for increasing surface tension and adhesion properties. Further developments in technique and a better understanding of the processes ensure product quality and demands in future. Finding out appropriate sets of flame parameters by trials and by experience energy savings of more than 50% are possible. Silane precursors dosed into the flame may lead to further improvements of adhesion. In principle other precursors are conceivable creating layers with custom-designed properties.





Improvement of Adhesion on Polymer Film, Foil and Paperboard by Flame Treatment

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content

- •surface properties
- •principle of flame treatment of films, foils
- •results
- •silicoating
- •conclusion

Adhesion of paint, lacquer, glue...

•wettability

- •surface tension $\sigma[mN/m]$, surface energy
- •contact ancle, test inks

•chemical link

•match surface material \Leftrightarrow coating

•adhesion tests

Properties of surfaces influencing adhesion

- •low surface tension, wettability
- •surface contaminations, dirt
- •additives, fillers
- •roughness
- •fluffy surfaces

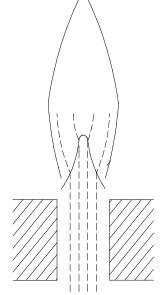
Surface treatment \Rightarrow increase in wettability

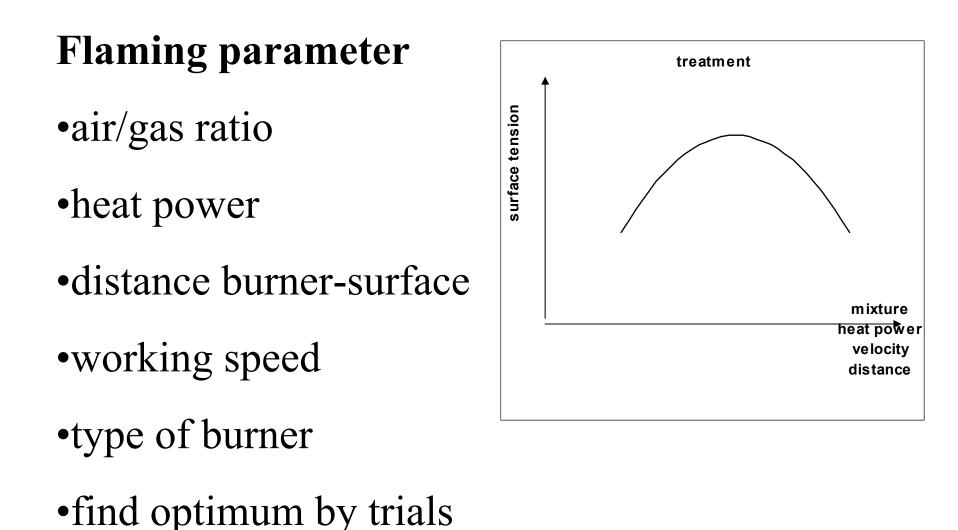
- •increase in surface tension (polar part)
- surface oxidation (O, OH)
- •cracking of long molecular chains
- •roughening
- •(Micro)cleaning
- •smoothing (flurry materials)

Flame structure

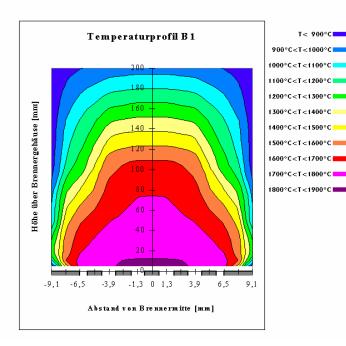
- •primary flame, conical form
- • $CH_4 + 2O_2 + 8N_2 - > CO_2 + H_2O + 8N_2$
- •secondary flame, active zone
- •flame plasma (O, OH)
- •activated molecules O, OH

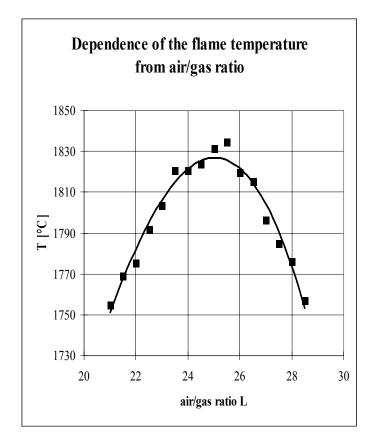






flame temperature





burner technique

- •burner length up to 3000 mm
- •homogeneous flame
- •water cooled
- •burner deckling
- •adjustable distance burner surface



Flame treater technique

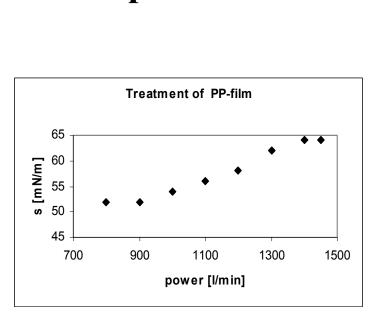
- air/gas measurement by mass flow meters
- electronically controlled system
- special mixing chamber
- power regulated air supply
- speed controlled power regulation

Web application

- •speeds -> 600m/min
- •firing on a drum
- •cooled drum
- •cooling/heating unit

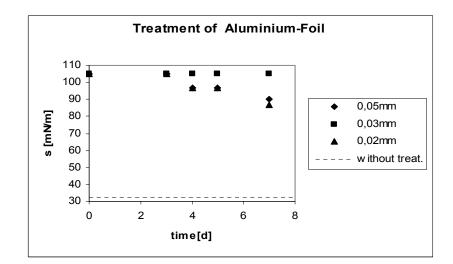


- •appropriate set of parameters
 - savings in gas consumptionenergy savings 50%

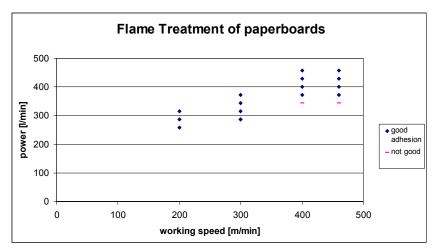


Examples

PP-film



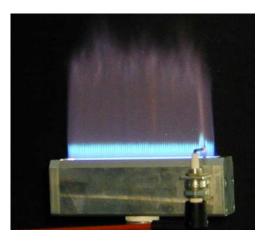
Aluminium foil



Paperboard-polymer composite

Silicoating

- •Silane \Rightarrow Silicate
- •thin invisible layer
- •applications:
 - •Materials difficult to treat
 - •Longtime stability
 - •Humidity resistent paintings
 - •Protection against oxidation



Test of treatment effect

- •increase in surface tension
 - •contact angle
 - •test inks
- •special adhesion tests

Corona

- films,foils
- less moulded parts
- small speeds
- small working width
- heat sensitive materials

Flame

- foils (no disruptive discharge, puncture)
- Moulded parts
- High speeds
- Large working width
- Longtime stability