1. Summary

Adhesive tapes and self adhesive coated materials are used in various industries and in multiple applications. A multitude of applications further requires that the adhesive does, at least not impair the flammability behaviour of the complete system. In some cases the adhesive should even reduce the flammability. Due to their nature pressure sensitive hot melt adhesives are not particularly suitable for this purpose. The demand for halogenfree flame retardant adhesives, which do not emit toxic fumes during a fire, poses an additional barrier. The paper gives an update about recent developments and an outlook for opportunities with flame retardant pressure sensitive hot melt adhesives.

2. Introduction

Pressure sensitive equipped materials like polymeric films, foams, textiles, metal foils, woven or extruded hook & loop substrates are widely used in various industrial applications. The pressure sensitive adhesive layer adds a range of advantages to such materials:

- the material already has the adhesive pre-applied
- the adhesive layer is covered and protected by a liner
- to establish the bond no further adhesive application or application equipment is needed
- the bond can be established with pressure

Pressure sensitive hot melt adhesives further are especially suitable for the coating of materials with a structured surface. The typically required higher coating weights can be achieved with relatively high line speeds. This in contrast to liquid pressure sensitive adhesive systems (water or solvent based) where at high coating weights the formation of bubbles during the drying process can only be avoided with a drastic reduction in line speed.

The thermoplastic nature of pressure sensitive hot melts on the other hand is a disadvantage regarding flame retardant properties. Good flame retardant performance together with the required adhesion and cohesion characteristics are generally only achieved with halogenated flame retardant additives. Aim of our work was to formulate pressure sensitive hot melt adhesives that meet typical adhesion/cohesion profiles for tape applications, show good flame retardant properties without the use of halogenated additives.

3. Critical Aspects During a Fire

The request for flame retardant materials and thus adhesive systems comes mainly from construction
and transportation applications, with the purpose to protect life. In reference to flame retardant materials three critical aspects during a fire are considered:
- first: the ignitability, flammability and flame spread of materials with the corresponding release of heat
- second: the formation of smoke and the resulting smoke density
- third: the toxicity of the arising smoke

The importance of these criteria varies with the associated risk. In transport and building applications this risk is related to the available time to escape in case of a fire:
- for road vehicles the focus is on the flammability of materials to avoid a fire at all. Generally a car be stopped quickly and the passengers can escape easily
- for buildings the focus is stronger on the heat release and flame spread, where the fire can propagate to other materials, rooms, floors or houses. Heavy smoke further restricts the possibility to escape.
- for rail vehicles the limited escape route becomes, besides the flammability and fire spread, an important factor especially on longer tunnel routes.
- for ships this escalates with the limited “outdoor” space. Further smoke density and toxicity become important in view of its distribution through air conditioning systems
- in airplanes escape routes are naturally very limited, the sum of the three criteria have here be biggest importance

![Figure 1. Visualization escape route vs. critical fire criteria](image)

**4. Requirements for Flame Retardant Applications and Method for Flammability Evaluation**

Requirements or regulatory demands for fire resistance are extensive and covered in application specific standards. The standards cover the key aspects as described before: flame spread, smoke opacity and smoke toxicity. For the development of adhesives, these standards and the corresponding test methods are of limited use since they involve substrates and application specific constructions. For our work a simple, rapid, economical but reliable test procedure for the flammability of adhesives had to be established.
a. Flammability Test for Pressure Sensitive Hot Melt Adhesives
The internal screening method was developed based on a vertical burn test as described in 14CFR25 Appendix F, Part I--Test Criteria and Procedures for Showing Compliance with Sec. 25.853, or Sec.25.855.

The tested adhesive samples were coated typically at 200 g/m² and transferred to an inert glass fibre web as carrier. This sample was fixed vertically with two clamps in a ventilated chamber. Flame impingement was done at a 45° angle with a propane gas burner for 5 seconds. To assure consistent test conditions, the gas flame was tuned to a total flame length of 9-10 cm with a core length of 4.5 cm. After ignition the following criteria were observed and recorded: burn time, drip behaviour, burn time of dripping material, smoke formation and other observations.

![Diagram of test setup](image)

**Figure 2.** Setup for flammability testing

b. Determination of Limited Oxygen Index (LOI)
After the initial screening the promising adhesives candidates were further tested for their flammability by determination of the LOI (limited oxygen index). The LOI as described in EN ISO 4589-1: 1999 (Plastics-Determination of Burning Behaviour by Oxygen Index) or ASTM D 2862:00 (Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics) is a very useful method to determine the flammability of materials and thus can also be used as flammability characteristic for adhesives.

![Diagram of LOI test setup](image)

**Figure 3.** General setup for LOI testing according ASTM 2863
Sample preparation was made according scheme (V) for flexible films or sheets. The test adhesives were coated to an inert glass fibre web at a thickness of 100 microns (100 g/m²). The total test sample thickness was approx. 0.3 mm and had an overall area weight of 220 g/m². The test samples were 140 mm long and 55 mm wide, the adhesive coating had a width of 50 mm.

The test result gives the minimum concentration of oxygen that will just support flaming combustion of plastics. Limited oxygen index results can be classified as:
- LOI < 23 combustible
- LOI 24-28 limited flame retardancy
- LOI 29-35 flame retardant
- LOI > 36 especially flame retardant

5. Flame Retardant Additives

The world wide demand for flame retardant additives is approx. 1.4 million tons per year with a growth rate of 3.5%. In Europe the demand is 460’000 tons and can be divided in the main categories: Aluminiumtrihydrate, chlorinated and brominated compounds, halogenated phosphor compounds, halogenfree phosphor compounds and others.

**Figure 4. Flame Retardant Additives**
6. Results

![Flammability vs. FR Content](image1)

**Figure 5.** Flammability vs. Content of FR additive

Five flame retardant hot melt pressure sensitive adhesives (B-F) have been compared with the standard non flame retardant adhesive A regarding qualitative flammability and Limited Oxygen Index (LOI) depending on type of FR additive and FR content. Adhesive B equipped with Aluminium trihydrate shows only a minimal improvement in flammability and LOI. Adhesive C with a non halogenated phosphor compound 1 reaches an LOI of 23.2, also only a minimal increase. Much better results are achieved with the non halogenated phosphor compound 2, where adhesive D reaches an LOI of 29.2 which is considered flame retardant. Adhesive D also employs the highest add-on of FR additive, in adhesives E and F this content has been reduced by 21% respectively by 64%, the corresponding LOI values drop to 27.5 and 24.5.

![Processing Characteristics vs. FR Content](image2)

**Figure 6.** Processing Characteristics vs. Content of FR additive
To assess the suitability of the FR adhesives for hot melt coating, melt viscosity and softening point have been compared to the standard product A. Already a relatively low content of Aluminium-trihydrate increases the melt viscosity of adhesive B dramatically (230’000 mPas at 160°C), together with the poor flammability results this direction does not promise success. Adhesive C shows an increase in viscosity (73’000 mPas) and softening point (130°C) but can still be considered suitable for hot melt coating. The addition of phosphor compound 2 is very promising since also the highest content in adhesive D does not lead to an increase in coating viscosity (27’300 mPas). Adhesives with phosphor compound 2 show a softening point in the range of 105 – 110°C.

**Figure 7. Adhesion Characteristics vs. Content of FR additive**

Adhesion characteristics as the 180°-peel adhesion to stainless steel and as loop tack to glass were evaluated with a 100 g/m² adhesive coating on 50 micron polyester. As expected, the high adhesion of benchmark adhesive A (79.1 N/25mm) can not be achieved with the FR modified adhesives. The adhesion of adhesive C drops below 20 N/25mm and makes its suitability for many tape applications questionable. Phosphor compound 2 in adhesives D-F maintains very high loop tack values of 67-73 N/25mm. Peel adhesion of adhesives D-F is between 31.8 and 37.3 N/25mm and although significantly lower than the benchmark, can still be considered as moderate to good for many tape applications.

**Figure 8. Cohesion Characteristics vs. Content of FR additive**
To measure cohesion the shear adhesion failure temperature (SAFT) was utilized. The bonded area was 12.5x25mm, the shear load 1kg and the heating rate 0.5°C/min. The benchmark adhesive A shows a SAFT of 64°C, the value of adhesive C drops slightly to 53°C. The addition of phosphor compound 2 even increased cohesion of adhesives D-F to some degree to good 67-73°C.

7. Summary and Outlook

The demand for flame retardant pressure sensitive adhesive solutions is growing; the use of the hot melt technology brings various advantages. The use of non halogenated flame retardant additives is desired for toxicology and environmental reasons. Our work shows that it is possible to formulate pressure sensitive hot melt adhesives without halogenated flame retardant additives, such products show a high Limited Oxygen Index (LOI) of >29 together with an interesting adhesion/cohesion profile: peel adhesion >30 N/25mm and shear adhesion failure temperature >65°C. These products are an excellent basis for application specific flammability testing. Since involved materials, required adhesive coating weight and testing standard have a crucial effect, we believe there is further room to optimize end use specific properties like: adhesion/cohesion profile, flammability and cost.
TECH 31 Technical Seminar Speaker

Recent Developments in Halogenfree Flame Retardant Pressure Sensitive Hotmelt Adhesives (HMPSA)

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