SESSION 6

THERMOSETTING COMPOSITES I: VOC REDUCTION TECHNOLOGY

6-A: No formal paper was submitted for this session.
6-C: No formal paper was submitted for this session.

The Effectivity of Styrene Suppressants

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1. Practical Concerns and Definition

Today, in the thermoset area of polyester resins, ever increasing regulations - health and safety as well as environmental - require us to take a closer look at styrene suppressants. These suppressants are additives which, when properly selected, can be utilized to reduce styrene monomer emissions in a broad array of thermoset resins, including:

-Orthophthalic Resins
-Isophthalic Resins
-DCPD Resins (Pure and Blends)
-Vinyl Ester Resins

Additives are best described as surface active liquids designed to be incorporated into liquid polymers in very small amounts under agitation. Their function is to bring about a specific improvement in the processing or final properties of a product without detrimental, secondary side effects. It should be understood that these suppressants are indeed additives which adhere strictly to the above definition.

The use of suppressants in polyester laminating applications – both hand lay-up and spray up – has been utilized for years to a certain degree. Indeed, in the spray up area (especially) such utilization is a wise choice since in such a process up to 13% of the styrene monomer can be volatilized from a non-suppressed resin. Switching to a suppressed resin can easily reduce the emissions from this same resin (using the same process) by 40-50%! Other factors that influence the styrene monomer emission include:

-Design of the working area (proper ventilation, carbon filtration)
-The styrene monomer content in the resin

It should be noted that while using a suppressed resin will significantly reduce emissions, lowering the styrene content will have a dramatic effect as well. Realizing the emission reduction such high solids resins yield explains their popularity! (See figure 1). Where do these styrene emissions originate? Styrene emissions sources from a typical laminating shop are many (See figure 2). The most notorious emissions occur during the resin application and when the resin is curing (on the mold). It is very important to note that styrene suppressant efficiency is low during resin application - especially spraying - but high during the curing stage.

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Figure 1
Styrene Monomer Emission Relative to the Styrene Content in the Resin

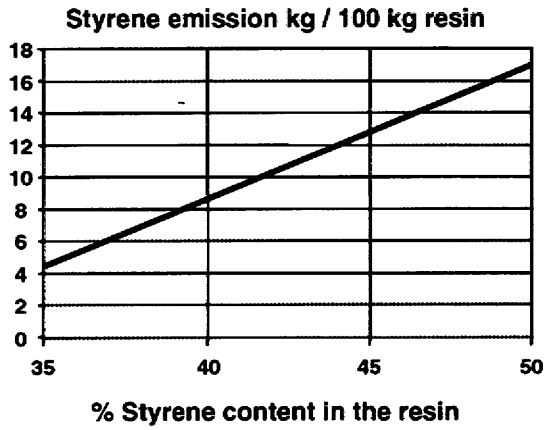
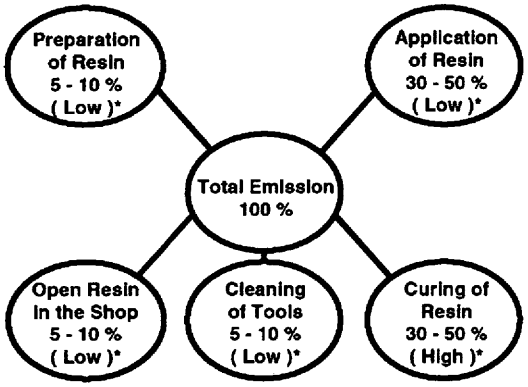


Figure 2
Styrene Monomer Emission Sources in the Work Place



* Styrene Suppressant Efficiency

2. Classification and Theory

This then brings us back to our original theme of styrene suppressant effectivity. These additives can be highly effective but, for maximum suppressing efficiency, the suppressant must be chosen depending on the type of resin that will ultimately be utilized in the fabricating process. It is fortunate to note that technology has yielded two different suppressants whose total suppressing capacity encompasses the broad range of polyester resins. One of these suppressants functions most effectively in the smaller grouping consisting of two polyester resins, these are:

-Orthophthalic Resins
-Isophthalic Resins

The other suppressant finds a broader application range consisting of four resins, these are:

-Isophthalic Resins
-DCPD Resins
-Ortho or Iso / DCPD Blends
-Vinyl Ester Resins

A. Suppressants for Orthophthalic and Isophthalic Resins:

What's out there today if you want to suppress emissions from Ortho or Iso resins? There's always been the old standby - paraffin wax, but there's also something more advanced - a specifically designed suppressant with adhesion promoter (designed per polarity and solubility parameters). Even though paraffin wax is effective in reducing emissions from Ortho and Iso resins, it is all too familiar what paraffin does to secondary bonding (See figure 3). Such problems with paraffin wax helped lead to the development of a Ortho/Iso suppressant which combines a special paraffin with a bonding and dispersing agent. Thus, each paraffin particle is surrounded by the bonding and dispersing agent during film formation on the resin surface. In this way, a closed paraffin surface is prevented and interlaminar adhesion is not reduced (See figure 4).

B. Suppressants for Isophthalic, DCPD Types (Pure and Blends), and Vinyl Ester Resins:

In these resins paraffin wax is still occasionally incorporated. Paraffin wax is much less effective in this group of resins (compared to Ortho/Iso) and the problem of secondary bonding is even more ominous. Development of a more effective suppressant was a must and was ultimately successful with a suppressant designed specifically for Iso, DCPD types, and Vinyl Ester resins. This (Iso, DCPD type, and Vinyl Ester) suppressant combines a special wax with polar components. This special wax and polar component surface together during film formation and form a suppressing film which does not detract from secondary bonding (See figure 5).

Figure 3
Resin Surface with Paraffin Wax

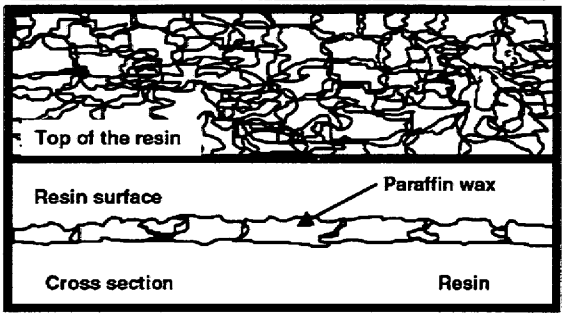


Figure 4
Resin Surface with Special Orthophthalic / Isophthalic Resin Suppressant

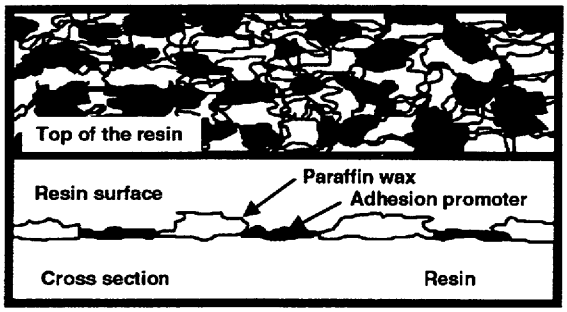
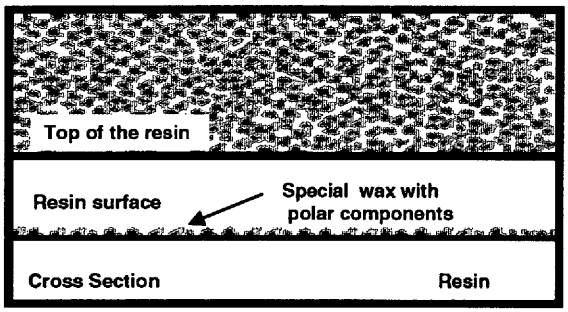


Figure 5
Resin Surface with DCPD, Isophthalic and Vinyl Ester Resin Suppressant



3. Practical Benefits

A. Styrene Suppression

Both the suppressant designed for (Ortho/Iso) resins as well as the suppressant designed for (DCPD types, Iso, and Vinyl Esters) can reduce emissions up to 70%, though reductions in the 50% range are more common (See figures 6 and 7). It should be noted that the maximum recommended dosage of either suppressant is 1%, based on resin weight. Efficiency checks should be run at lower levels as well since, quite often, lower dosages are effective in meeting suppression requirements.

Figure 6
Styrene Monomer Emission of Orthophthalic Resin

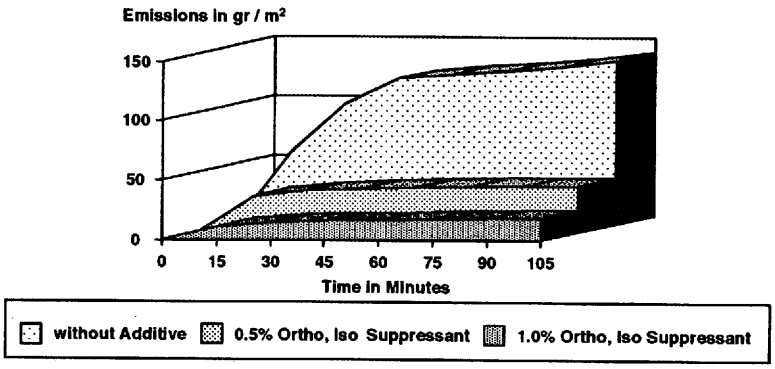
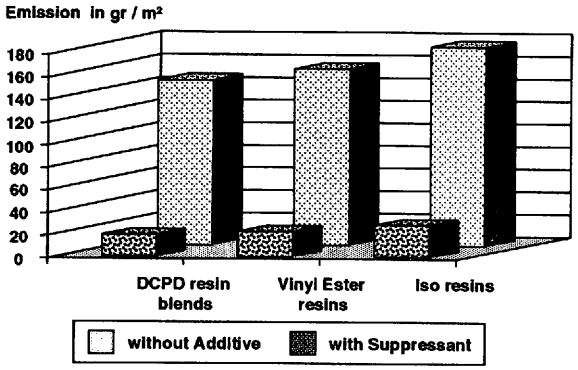


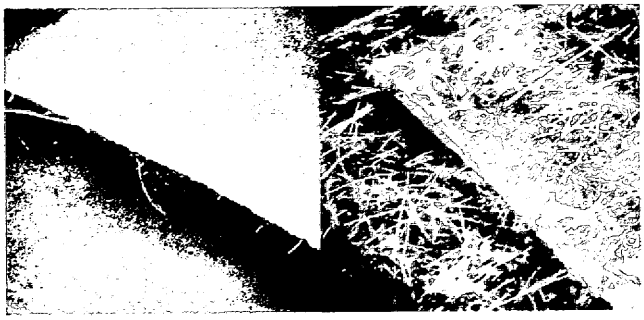
Figure 7
Styrene Monomer Emission of Different Resin Types with and without Specially Designed Suppressant



B. Secondary Bonding

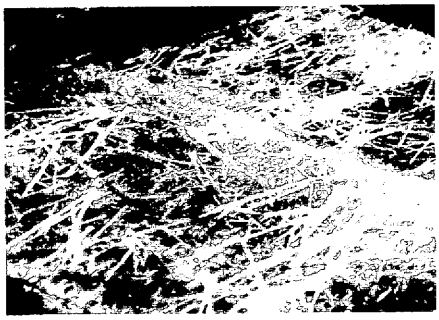
Interlaminar adhesion testing (pull test procedure) of a Ortho resin laminate using the (Ortho/Iso) suppressant (dosage level of 1%) revealed excellent adhesion, which can be noted by the appearance of white reinforcement fibers. This same test procedure dramatically reveals the complete adhesion failure paraffin wax can render (See figure 8). Excellent secondary bonding in a DCPD blend resin using the (DCPD type) suppressant (1% on resin) is also revealed by the white, torn fiber appearance (see figure 9).

Figure 8
Interlaminar Adhesion of Orthophthalic Resin
Paraffin wax compared to Special Suppressant



with Paraffin — with Special Suppressant

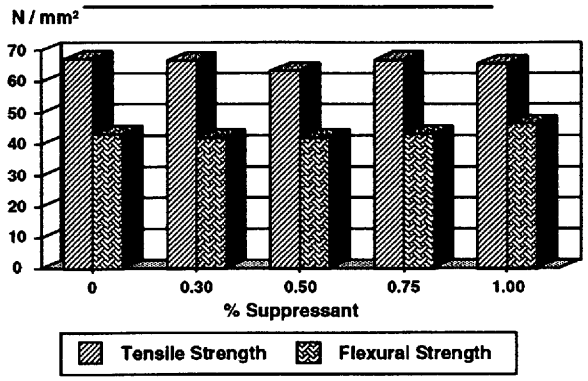
Figure 9
Interlaminar Adhesion of Ortho- / DCPD Resin with Special Suppressant



C. Gel and Cure Time, Physical Properties

Neither suppressant, at a dosage level of 1%, is found to create a significant variation in gel, peak exotherm, or total cure when utilized in their appropriate polyester resin. Physical properties (tensile strength, flexural strength) of laminates constructed from these suppressed resins does not vary from control laminate physicals (see Figure 10).

Figure 10
Physical Properties of a Ortho- / DCPD Resin using Specially Designed Suppressant



4. Conclusion

The effectivity of styrene suppressants in many laminating type applications has been proven and deserves a thorough in depth evaluation by fabricators. However, the proper suppressant must be utilized depending on the type of polyester resin chosen for fabrication. Orthophthalic or isophthalic resins require one particular suppressant, designed specifically for such resins and with corresponding high efficiency. However, DCPD types, isophthalics, or vinyl esters require a different suppressant (also specifically designed for such resins) which in turn will yield a correspondingly high level of emission reduction. The benefits of using such specifically designed suppressants are many including:

- Reduction of styrene monomer emissions
- No reduction in interlaminar adhesion
- Easy to process paste or liquid
- No negative side effects on physical properties of FRP parts
- No negative influence on gel time, peak exotherm, or total cure
- Both suppressants have much better cold temperature stability than conventional paraffins

Styrene Emission Control

TREVOR LAWTON

ABSTRACT

The molding of fiber reinforced plastic (FRP) polyester components has traditionally been carried out using spray or hand lay-up techniques and open molds. This results in high levels of styrene being emitted during both the lay-up and resin cure stages which increases the levels in the workplace. A European Commission program was established to investigate and develop suitable technologies which could eliminate the styrene emissions. As a result of this program, a hybrid system was developed. The presentation will discuss the technologies investigated and the current progress.

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