PVC Flame Retardance:
The Effects of Formulation Change

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PVC is alive and well !

PVC or Polyvinyl Chloride is the third largest polymer produced worldwide. PVC is also the single largest halogen flame retardant produced worldwide. PVC, amazingly enough, is the safest way to sequester excess chlorine produced during the production of caustic, a well-known high volume commodity chemical. So, it would be a mistake to think that PVC is dying.

In fact, at a recent AMI conference Noru Tsalic, an AMI Vice President, presented data showing that the dollar sales of PVC worldwide will increase about 7% between 2015 and 2020! PVC volume is increasing as well.

Flexible PVC, or PVC Wire and Cable Formulations, are faced with a significant requirement for change. The major plasticizer group used in these formulations (phthalates) is under environmental assessment. This has already caused some changes and more changes can be expected as the hazard/health review proceeds.

PVC and Flame Retardance

As said above, PVC itself is a halogen flame retardant. It exceeds the volume of all other flame retardants combined! But when the PVC resin is formulated for flexibility, fuel in the form of a flammable plasticizer is added to the equation. This increases the need for flammability protection.

The R.J. Marshall Company has been supplying synergists for increasing the flame resistance of these plasticized PVC formulations for over 25 years.

These synergist products are supplied by the Marshall Additive Technologies Division (MAT).

MAT currently has an ongoing research program to evaluate the effects of plasticizers, fillers including metal hydrates, and other processing additives on the flammability of these flexible PVC formulations.

PVC Formulation Research

MAT researchers started with a basic PVC testing formulation shown here in Table 1.

Table 1. Synergist Evaluation PVC Formulation

Formulation component	Parts per hundred resin
PVC	100 parts
DINP Plasticizer	45 PHR
Ca Zn Stabilizer	4 PHR
Wax %	5 PHR
Synergist	10 PHR
Metal Hydrate	50 PHR

In the MAT evaluations, LOI or Limiting Oxygen Index (ASTM D2863) was used to evaluate flame retardant effectiveness. You will note that we used DINP, Di-isononyl phthalate as our standard plasticizer. In this work we looked at other plasticizers and then we looked at various changes in synergists and processing aids.

The first plasticizer change was made to Pevalen®, a pentaerythritol-based plasticizer, which has been shown to have char forming properties. Char acts as insulation, removing some fuel from the combustion zone.

Table 2 below shows the LOI results for our standard formulation using DINP plasticizer vs the Perstorp Pevalen® plasticizer. You will note we used one of the MAT antimony replacement products, C-TEC® FRZ20S and compared that to antimony oxide, the classic halogen synergist. The metal hydrate was a 1 micron natural magnesium hydroxide.

Table 2. LOI Results DINP vs Pevalen®

Plasticizer	C-TEC® FRZ20S	Antimony Oxide
DINP	33.0	33.9
Pevalen	35.3	38.7

In these formulations, the increase in LOI between DINP and Pevalen® was 2.3 units in the antimony oxide replacement FRZ20S formulation, which saves about half the cost over the antimony oxide classical synergist. However, you will note that Pevalen® had a greater effect in antimony oxide formulation increasing the LOI by 4.8 units.

Next, we asked what will happen when we replace only part of the DINP plasticizer with Pevalen® (20 parts to 25 parts respectively) in that FRZ20S formulation.

Table 3. DINP/Pevalen® Combo approach

Plasticizer	LOI
Pevalen®	38.6
DINP/Pevalen®	38.5

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Results indicate that investigation of blends should be considered. There was no real difference between the Pevalen® and the DINP/Pevalen® blend.

In the Table 3 comparison, a D50 4 micron ground ATH was used as the metal hydrate. The MAT research team then decided to look at the difference between ATH and magnesium hydroxide as the metal hydrate. MAT supplies many different metal hydrate products.

In this comparison, there were three products:
- H-TEC® HT1000, a 1 micron precipitated ATH
- ATH A-202, a 2 micron D50 ground ATH
- H-TEC® HTMB2, a 2 micron D50 natural $Mg(OH)_2$

The standard formulation was used with Pevalen® as the plasticizer. The results are shown in Table 4.

Table 4. Metal Hydrates in PVC - Comparison

Metal Hydrate	LOI
H-TEC HT1000 ATH	39.5
A202 ATH	38.6
H-TEC HTMB2 MDH	35.3

This formulation comparison indicates that the use of ATH as the metal hydrate should be considered whenever the processing conditions of the formulation allow; i.e., processing at or below 180 degrees C.

The researchers at R J Marshall designed the standard formulation used in the research shown in Tables 1-4 for ease of operation on a two roll mill and also to better illuminate the differences in LOI. Part of this effort included the use of 5 phr of wax. Knowing that this 5 phr wax content might be questioned or labeled by some formulators as atypically high, the MAT researchers decided to check for any difference between this 5 phr level and the more typical level of 1 phr wax. Results are shown in Table 5. In these comparisons A204, a 4 micron ATH was used as the metal hydrate and Pevalen® was the plasticizer

Table 5. Wax Loading Comparison

WAX addition	LOI
5 phr	38.6
1 phr	42.1

Results strongly indicate that the reduction of 5 phr from the formulation down to just 1 phr (which is simply the removal of fuel) raised the LOI by 4 units.

The last formulation change the MAT researchers decided to investigate was the use of a specialized polymeric plasticizer, PLASTHALL® P745 from HallStar.

In the standard formulation described earlier using as the synergist C-TEC® FRZ20S and ATH A204 as the metal hydrate, the PLASTHALL® P745 plasticizer seemed to produce a large gain LOI as shown in Table 6

Table 6. PVC Plasticizers DINP versus Plasthall® P745

Plasticizer	LOI
PLASTHALL® P745	41.4
DINP	37.6

This plasticizer showed a very large increase in limiting oxygen index of 3.8 units. This must be considered for future work in developing the flame retardant technology of flexible PVC formulations!

Conclusions and new MAT product offerings

So what does the above research mean ? And how about different and improved synergist products?

From what the MAT team has learned from the research outlined in the previous six PVC formulation examples and also from as yet unpublished additional discoveries, the R J Marshall MAT team is continually looking at expanding the MAT product line in order to offer MAT's customers products capable of providing improved performance in PVC formulations.

New products are under evaluation and development. One such product is C-TEC® SF0136. Below in Table 7 is shown the effect of this product in comparison with the currently offered C-TEC® FRZ20S in the standard formulation.

Table 7. New MAT Product offers improvement

Synergist	LOI
C-TEC® FRZ20S	35.4
C-TEC® SF0136	37.6

So although C-TEC® FRZ20S is still quite suitable for many PVC formulations, if improved flammability performance is of interest, one product that just might be of interest C-TEC® SF0136. Or even when a reduction in formulation component cost is the order of the day, say by reducing the loading of synergist, this new product from MAT might be effective enough to get the job done!

Today, PVC formulators are faced with an ever changing marketplace with new performance requirements. To discuss your needs or to request samples, contact The RJ Marshall Company and ask for Frank Butwin. He can help you determine what is in the MAT pipeline that might meet your flame retardant PVC formulation needs.

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