

## MULTI-COMPONENT PEROXIDES FOR IMPROVED CURE

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To the uninformed or the inexperienced, all room temperature catalysts may seem to be the same, but experience has told us that Methyl Ethyl Ketone Peroxide, **MEKP, is not MEKP is not MEKP**. Just as there are literally thousands of different combinations that can be made from the relatively small group of raw materials that make up our resins, we have dozens of combinations that make up the set of MEKP products that are commercially available for use today. Each one works a little differently than the other, and when combined with different resin formulations can give an almost unlimited potential to control the resin, the process, and thus the finished part. It is our intent to show the advantages and disadvantages of some of the more common “catalysts” and thus help the fabricator select the proper MEKP formula for the proper application.

### WHAT IS MEKP?

To better understand how MEKP products vary, let’s take a look at the active ingredients of a MEKP solution. These are: (1) Hydrogen peroxide which affects gel only; (2) Monomer form of MEKP which affects gel to a minor degree and cure to a major degree; and (3) Dimer form of MEKP which has a relatively little effect on gel, but has a large effect on cure. Therefore, by varying the proportion of each of these three ingredients, you can change the gel and cure characteristics of any resin. The one limiting factor is that all MEKP manufacturers are limited, by law, to a maximum content of active ingredients in a given formulation. The inactive ingredients, or diluents, consist of DMP, dimethyl phthalate, and/or TXIB, safety solvents, and small amounts of water, MEK, and glycol. Although considered “inactive” these ingredients do affect the performance of the solution. Physical properties of solubility, density, stability, and the amount of leachable or trace materials left after the reaction are controlled by what is incorporated here.

Now, stop and think for a minute, MEKP is a triple component system that offers the following advantages:

1. Flexibility – A number of choices available depending on desired performance parameters.
2. Forgiving – Within limits, under or over use will produce an acceptable part, even though it will not have the optimum properties.
3. One product for both gel coat and resin.
4. Seldom have color problems in finished part.

Of course the disadvantages of standard MEKP are well known:

1. Hazard Class III – According to the National Fire Protection Association Standard 432 (this code rates organic peroxide hazard from I-highest to V-lowest.)
2. Toxicity – Classified as a moderate health hazard. Protective equipment is required.
3. Prompt clean up for spills required to prevent fire and/or explosive decomposition.

### **WHAT IS AAP? AZOX**

Acetyl acetone peroxide, AAP, is another ketone peroxide, which has been used for a number of years. It is an equilibrium mixture of:

1. Active ingredients – Hydrogen peroxide, acetyl acetone, acetyl acetone peroxide (40%)
2. Water (9-11%) – High water level is major reason for low flammability.
3. Diluents – Proprietary (~50%)

The main difference between AAP and MEKP is in the active ingredients. These are:

1. Hydrogen Peroxide – The very small amount is what contributes to a longer gel time than most MEKPs.
2. Acetyl Acetone – Functions as a secondary promoter.
3. Acetyl Acetone Peroxide – Provides exceptional cure speeds in most resins.

Contrary to MEKP formulations, AAP active ingredients cannot be varied to any useful degree. And since there is essentially only one active molecule, it is critical to accurately determine, and subsequently use, the right amount of AAP. However, when used in the correct amounts, rapid gel to peak times are the dominant characteristic of this initiator in many resins, especially when combined with standard MEKP formulations.

The advantages of AAP are:

1. Fast gel to cure times.
2. Same gel times, or slower, than MEKP.
3. NFPA class V, means no Yellow Label, easy to store.

The disadvantages must also be considered:

1. Color – While not as a large a problem as in the past, yellowing in some resins can occur.
2. Inflexible – Must be accurately measured for each and every use.
3. Inconsistent – Some products on the market can drift from batch to batch-making performance unpredictable.
4. Cannot be used in gel coats, because its high water content can contribute to porosity, and it can change the cured color.

### **MEKP/AZOX COMBINATIONS**

While both MEKP and AAP have positive characteristics when used alone, in the past few years, the combination of MEKP and AAP has become popular. By mixing these two products, the user can get an initiator system that can often combine the best features of each peroxide. At the same time, the disadvantages of each are minimized. This has especially been the case in RTM or other closed mold systems where gel and cure times need to be better controlled. Another critical application is thin laminate sections where longer working times, but fast, through cure times are required. See Attachment I

After reviewing all the data we suggest the advantages of MEKP/AAP dual catalyst systems are:

1. Optimization of gel time and gel to cure times mean more efficient production.
2. Better cure development means a higher quality part.
3. Ability to control peak exotherm more precisely in the process.
4. Compatible with the resin matrix system.

Of course, there are disadvantages, also:

1. Possible yellowing problem, if laminate color is a concern.
2. Must be premixed in shop before use. While mixtures of MEKP/AAP can be stored for several weeks, long-term storage can result in excessive aging and lead to erratic results. (see attached study)

### **MEKP/CYCLOHEXANONE PEROXIDE: MEC**

This combination should be considered for gel and cure initiation for resins at low operating temperatures. At cooler ambient temperatures, this blend will give better performance in both gel and cure than standard MEKP. See Attachment II

Other advantages, compared to standard MEKP formulations include:

1. Shorter gel to cure time in many resins, while maintaining similar gel times to standard MEKP
2. Excellent uniformity in the cure cycle. Mixes easily, gives very uniform cures. Significant improvement in resin solubility (over newer DMP Free \* formulas) or (where HAP issues are a concern)
3. Excellent storage stability because of the absence of impurities.
4. Enhanced performance with gel coats. Improved thin film cure.
5. Can be considered a “Winter” alternative to standard MEKP

The disadvantages of this blend are:

1. Slightly higher cost although this is usually offset by improved process times.
2. Not widely available in the United States.
3. Limited number of blend ratios available.

### **CHP**

Cumyl Hydroperoxide, CHP, is especially suitable for the cure initiation of resin systems at both ambient and elevated temperatures. The typical exotherm curve exhibited is usually mild and flat leading to a gradual, but thorough, cure. This characteristic can minimize crazing and cracking especially in thick cross-sections. CHP is normally used in pre-promoted resin systems employing cobalt and/or manganese compounds as the primary accelerators.

The advantages of this peroxide as compared to MEKP are:

1. Lower exotherm in thick cross sections, reduced or no cracking or crazing without sacrificing cure.
2. Slower, more controlled cure development. Will reach almost total cure in 24 hours.
3. No post cure problems of warping, creeping, or “heat distortion”
4. Works equally well in elevated temperature applications.
5. Can be used in some applications where traditionally refrigerated products are required.

The disadvantages as compared to MEKP are:

1. May have longer ambient temperature gel times.
2. Longer cure times, or slower green strength development.
3. Shorter “Pot life” when used in applications as an alternative to refrigerated products.

### **MEKP/CHP COMBINATIONS: MCP, MCP-21, MCP-75, 771, HDP-75**

As with the increasing popularity of the MEKP/AAP blends, the MEKP/CHP blend is gaining fast acceptance in open molding applications where lower peak exotherms and good cure is required. Traditionally, where diluted versions of standard MEKP are used to extent the working time these blends are proving to be very beneficial. See Attachment IV

The advantages of the MEKP/CHP blends are:

1. Better control of gel time, working time, without loss of cure.
2. Through cure in a shorter time thus reducing or eliminating post cure problems.
3. Reduced exotherm in the laminate, reducing “heat distortion” and “fiber print” problems.
4. The ability to run standard amounts even in higher ambient temperatures allows you to run processing equipment within “normal” ranges.
5. Can be considered a “Summer” alternative to standard MEKP.
6. Pre blended formulas are commercially available, no need to preblend in the shop.

The disadvantages are:

1. May have to use slightly more to maintain the same gel time, although in the summer the higher ambient temperature is in itself a compensating factor.

**AZOX/CHP COMBINATIONS: 750, 757**

The most common use of this blend has been for controlling shrinkage. Tooling, RTM, and other areas where dimensional stability is important. Also effective in highly promoted systems where the amount of AAP has to be reduced, the CHP acts as an active diluent.

**MEKP/TERTIARY-BUTYL HYDROPEROXIDE: KP-900LE**

Although the combination of MEKP and Tertiary-Butyl Hydroperoxide, TBHP, is relatively new to the United States market, it has been used successfully in Europe for several years. As with CHP, this blend gives lower peak exotherms without effecting the green strength development as much. See Attachment V

Other advantages, compared to standard MEKP formulations include:

1. Similar gel times with slightly longer, gentler cure times may lead to better cosmetic appearance of laminate.
2. Lower peak exotherms help reduce cracking and crazing in thicker cross sections.
3. Can be considered a “Summer” alternative to MEKP

The disadvantages of this blend are:

1. Limited number of blend ratios commercially available.
2. Not widely available in the United States.

**CONCLUSION**

The peroxide initiator or initiators should be thought of as the tool, which fine-tunes the operation. By first evaluating the manufacturing process, it is possible to select the right initiator or combination of initiators that will optimize the process. Based on the data presented, it is quite evident that the old stand-by MEKP is, in fact, already a multi-component catalyst system. However, even the optimum MEKP cannot always give the fabricator the desired performance characteristics he needs or desires to be competitive in today’s manufacturing environment. As a result a MEKP/XXXX system should be evaluated. To do so, the fabricator needs to work closely with both his/her resin and peroxide suppliers. Only through such partnerships will it be possible to achieve the finely tuned manufacturing systems needed to produce high quality parts, which will enable us to compete effectively in today’s market.

The laboratory work used to provide data for this paper is a compilation of lab work and field studies and represents only the beginning of this project. It is planned that the more effective combinations of initiators will be further evaluated using more definitive cure assessment techniques, and these results will be presented in future presentations.

## REFERENCES

**Additional information can be found in both resins and peroxide initiators suppliers' literature.**

Other useful references include:

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