



ORGANIC PEROXIDES

Selection Guide For PVC



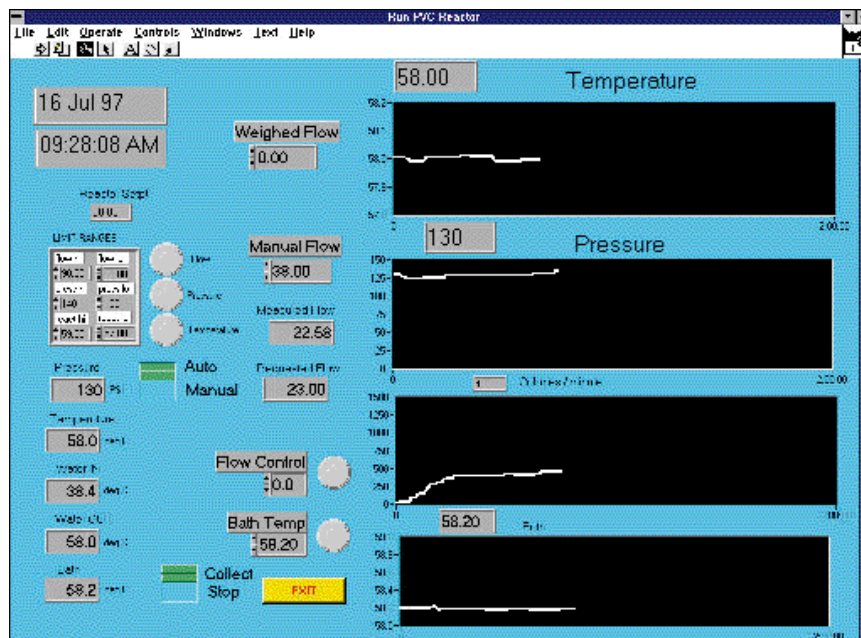


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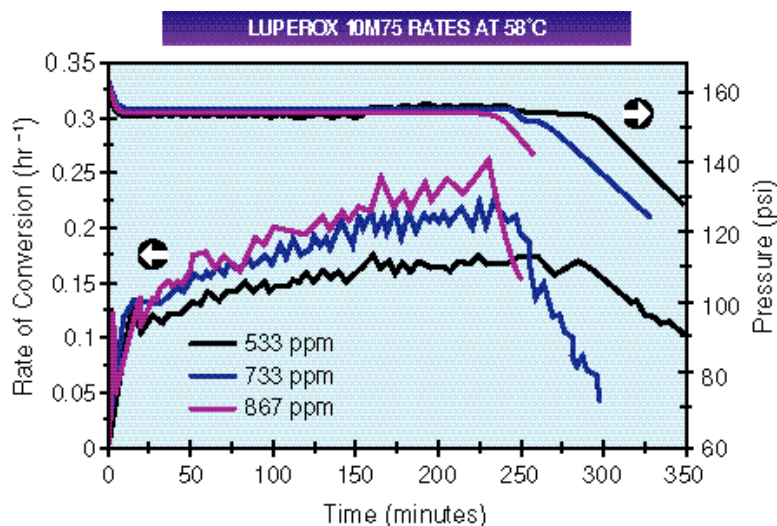
Arkema's organic peroxides improve productivity, lower costs and optimize quality. With over 50 commercial organic peroxides to choose from, understanding the best choice for your system can become quite complicated. Decomposition rate, radical energy levels, byproducts, shipping, storage and handling are among the many factors which must be considered. This guide, in combination with our "Organic Peroxides for PVC Production" and consulting your Arkema representative, is designed to assist in the selection of the best peroxides for your process.

COMMITMENT TO PVC

To support the development of new peroxides, determine the most efficient way to use current products and assist you in optimizing formulations, we have installed a 2-liter calometric pilot reactor. Unlike other techniques, such as gas trace methods, our reactor measures the most important factor in controlling a commercial process, heat flow.



Experimental details: All of the figures presented in this document were derived from reactions performed in our 2-liter reactor. The reactor is submerged in a water bath whose temperature is 0.2°C higher than the reaction temperature. Reactor temperature is controlled via a water cooling coil and a variable flow rate valve. Flow rate and temperature of the water in and out are precisely measured. The resulting calories are adjusted by a baseline subtraction for the difference in reaction and bath temperature. Rates are calculated based on theoretical conversion at 10 psi drop (72% for 58°C and 80% for 51°C). VCM is introduced under nitrogen pressure so the pressures shown in all cases include some inerts. Exact details and photos for the construction of this reactor are available upon request.

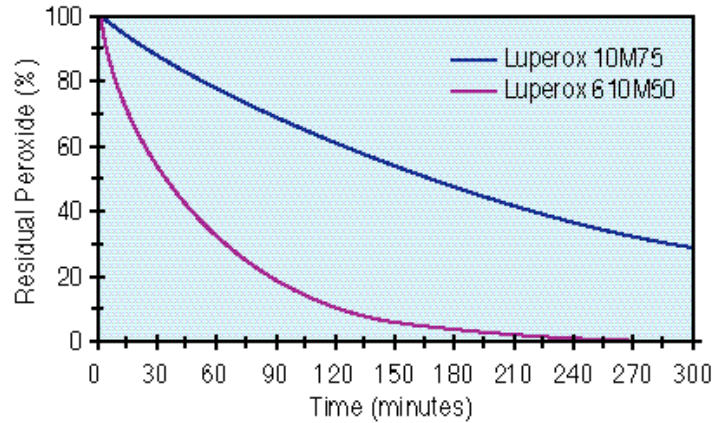


USING MULTIPLE PEROXIDES TO AVOID HEAT KICKS:

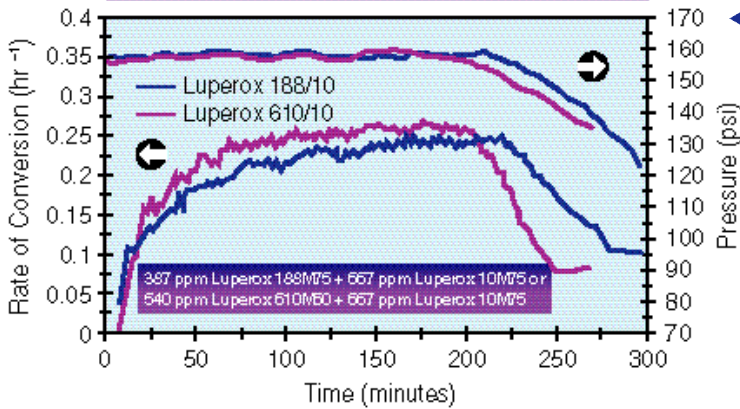
When a single peroxide is used, the rate of polymerization increases with conversion. At long reaction times this causes few problems; however, as rates are increased through the addition of more peroxide, the peak reaction rate increases rapidly. This is demonstrated by observing the rate of polymerization using Luperox® 10M75.

To lower the peak heat load and use more of the heat removal capacity at the beginning of reaction, it is necessary to use two peroxides in combination. One of the peroxides decomposes rapidly at the beginning of the reaction while the other decomposes slowly.

THEORETICAL DECOMPOSITION AT 58 °C



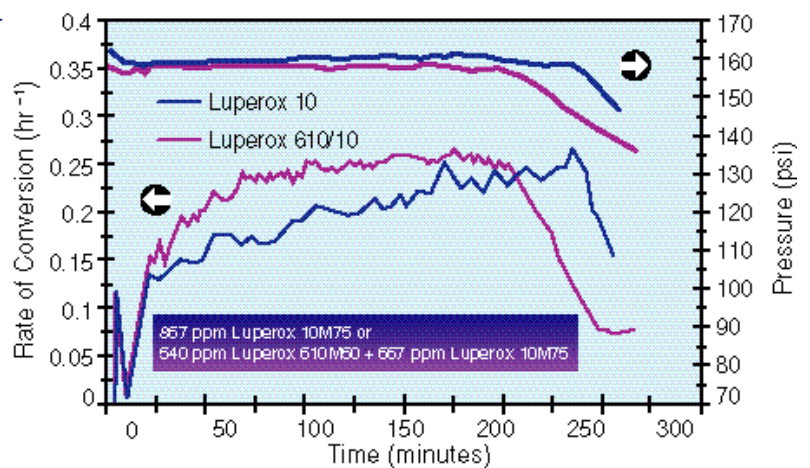
LUPEROX 610M50 OUTPERFORMS LUPEROX 188M75 AT 58 °C



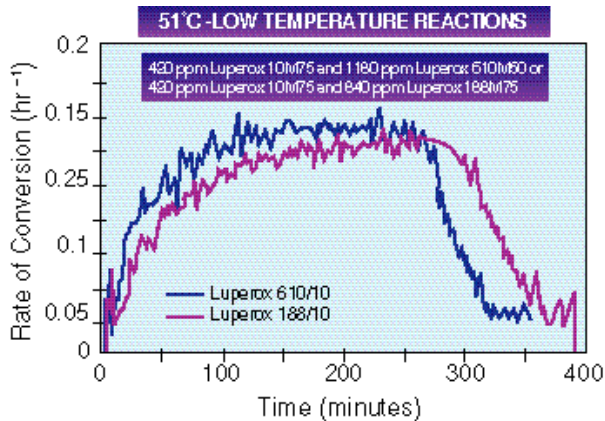
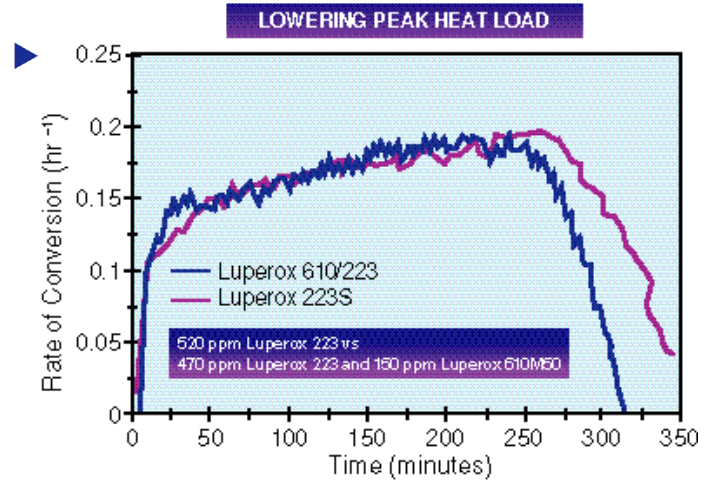
Using a faster front end peroxide results in faster initial reactor rates, a more constant rate of reaction and minimal heat kick. As demonstrated here Luperox 610M50 is faster than Luperox 188M75, thus allowing a more constant rate of reaction and subsequent faster reaction time.

The faster decomposing peroxide is referred to as the front end peroxide and the slower is referred to as the back end. The net result of using a front and back end peroxide is a more even distribution of the heat load and the potential for reducing overall cycle times.

LUPEROX 610M50/10M75 AT 58 °C

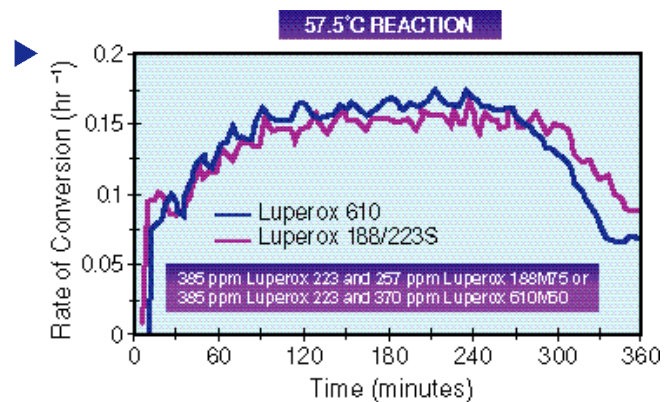


At times when high productivity is not a priority, a front end peroxide may be used in small amounts to minimize heat kicks. This improves reactor control and improves overall resin quality while minimizing the expense of front end peroxides. Shown here is a small amount of Luperox 610M50 used in combination with Luperox 223M75S to slightly lower the heat kick.



The exact ratio of front and back end peroxides must be tailored to a specific situation. Temperature is the most critical factor. At lower temperatures the amount of front end peroxide is greatly increased and the back end peroxide is decreased to gain a steady reaction rate. Notice that Luperox 610M50's performance advantage over Luperox 188M75 is large at the lower temperatures.

Monomer impurities, reactor fouling, fluctuations in cooling water temperature and changes in market demand are among the reasons for changing the ratio of front to back end peroxide. Thus, there is never one best ratio for a given grade of resin. For this reason, please contact your Arkema representative for specific recommendations to your system.

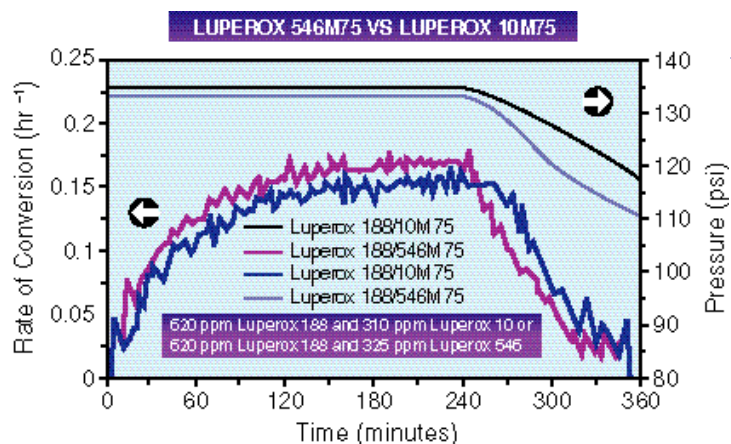
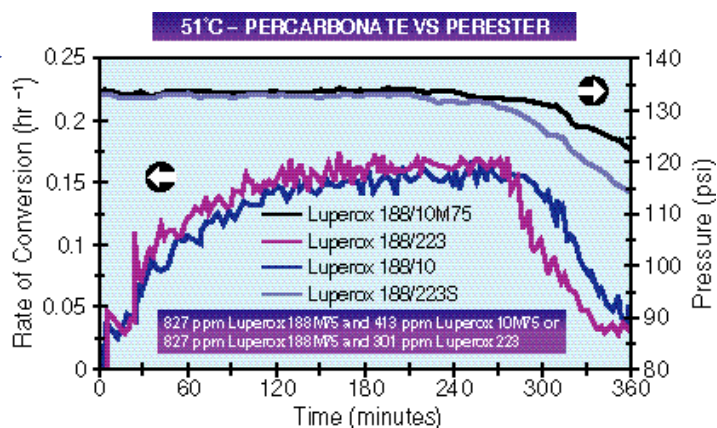


RESIN COLOR AND PEROXIDE CHOICE

Hjertberg has shown that percarbonates (such as Luperox 223M75S and Luperox 225M75) discolor resins compared to peresters such as Luperox 10M75 (M. Rogestedt, T. Jonsson and T. Hjertberg, J. App. Poly. Sci., 49, 1055-1063).

This correlates with the fact that percarbonates form higher energy radicals than Luperox 10M75 and that high energy radicals are more likely to attack the polymer backbone, while low energy radicals are more likely to initiate polymerization. Thus, Hjertberg's work shows the needs to use low energy radicals to obtain whiter resins.

One may consider using Luperox 10M75 in place of Luperox 223M75. There is a trade off on productivity as seen here. Luperox 10M75 gives slower pressure drops than Luperox 223M75S.



Luperox 546M75 forms less energetic radicals than Luperox 10M75 and gives faster reaction rates. Thus, it is the best choice for manufacturing good color resins without loss in productivity.

DECOMPOSITION PRODUCTS:

The exact decomposition products of a peroxide are dependent on many factors including temperature, pressure, solvent polarity, abstractability of hydrogens, concentration and type of monomer present. It is therefore impossible to state the exact decomposition products one will obtain, but there are certain products one might expect to find. Of primary concern are Luperox 188M75 and Luperox 288M75 which can readily form aromatic decomposition products. Both of these peroxides can form acetophenone when they decompose. To avoid the odor of acetophenone, aromatics in waste water and other environmental concerns, Luperox 610M50 and Luperox 688M50 were commercialized.

Luperox 610M50	Luperox 188M75
Best productivity	Good productivity
Non aromatics	Potential for aromatics in waste water
Low odor	Acetophenone odor
No UV sensitizers expected	UV sensitizers may form

The following chart summarizes the best choice of peroxides for PVC.
Please consult your Arkema representative for more details.

	1 Hour Half Life (C)	Comments	Resin Grade Recommendations
Luperox 610M50	54	Maximizes productivity Minimizes color and odor No aromatics	Front end for K-67 and higher High Quality Grades
Luperox 188M75	56	Forms aromatic byproducts Compromises odor, color and productivity for cost	Front end for K-67 and higher
Luperox 288M75	60	Forms aromatic byproducts. Good compromise between cost and productivity	Front end for K-67 only
Luperox 546M75	64	Best alternative to peroxydicarbonates for whiter resins	Back end for K-67 and higher Front end for K-57 and lower High Quality Grades
Luperox 10M75	66	Alternative to peroxydicarbonates for whiter resin with some productivity loss	Back end for K-67 and higher
Luperox 223S Luperox 223M75S	66	Cost effective initiator which causes some resin discoloration	Back end for K-67 and higher Front end for K-57 and lower
Luperox 225	68	Slightly slower version of Luperox 223	Back end for K-67 and higher
Luperox 554M75	74	Lower energy radicals, a higher boiling point and faster rates make this peroxide slightly preferable to Luperox 11	Back end for K-57 and lower High Quality Grades
Luperox 11M75	76	Very cost effective initiator	Back end for K-57 and lower
Luperox LP	81	Solid peroxide can be handled with minimal cooling requirements but may form emulsifiers that could interfere with the suspension	Back end for K-57 and lower



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