Technical Information

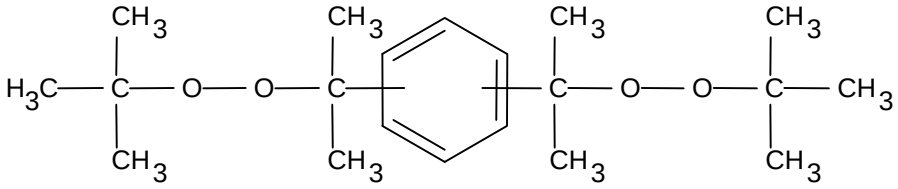
VUL-CUP® Peroxide

Vulcanizing Agent and Polymerization Catalyst

VUL-CUP® peroxide is a highly efficient, scorch-resistant, low-odor peroxide with broad utility as a vulcanizing agent for elastomers and plastics. The scorch resistance of Vul-Cup® makes it particularly useful for transfer, injection, and rotational molding applications. It also permits compounds containing Vul-Cup® to be extruded at higher rates because of the higher temperatures permissible.

Properties

Vul-Cup® peroxide is available in pure form or as a supported grade powder which contains 40% peroxide. Vul-Cup® is a highly active bisperoxide. It is a mixture of the *para* and *meta* isomers of an *a,a'*-bis(tert-butylperoxy) diisopropylbenzene. The molecular weight of this compound is 338, and its structural formula is:



At room temperature, Vul-Cup® R is a tan to yellow-white, semi-crystalline solid. It varies in isomer ratio from 3.2:1 to 3.8:1 in *meta:para* content. The *meta* isomer has a melting point of 50°C, and the *para* isomer 80°C. The melting point range of the commercial product, Vul-Cup® R normally falls within 95-113°F (35 to 45°C). The recommended hot-water temperature for melt bath or semibulk container coils is 65°C. (See Bulletin ORC-303.)

Vul-Cup® 40KE peroxide is a white to off-white, free-flowing powder. Exposure to elevated temperatures can result in lumping. The degree of lumping is dependent on temperature and duration of exposure. Normally, a slight amount of lumping causes no difficulty, provided processing is carried out above the melting point of Vul-Cup® R. Uniform dispersion of either form of Vul-Cup® is difficult to achieve when processing is carried out at temperatures below its melting point.

Solubility

Vul-Cup® peroxide disperses readily in polyethylene and copolymers of ethylene, natural and synthetic rubber compounds, silicone gum, and polyester resins. It is quite soluble in aliphatic, aromatic, and ketone solvents, less soluble in alcohols, and insoluble in water. Table I lists the solubility of Vul-Cup® R in selected solvents.

Table I - Solubility of Vul-Cup® R

Solvent	Weight % of Vul-Cup® in a Saturated Solution at Room Temperature
Benzene	75
Hexane	70
Acetone	70
Ethanol	10

Use of Vul-Cup®

Vul-Cup® peroxide offers a high degree of scorch safety in compounds, and imparts a very low level of odor in sulfur-free vulcanizates. Vul-Cup® can be substituted for Di-Cup® dicumyl peroxide to give an equivalent state of cure. This is accomplished by replacing 1 part Di-Cup® with 0.625 part Vul-Cup® when both are expressed on a 100% active peroxide basis. This equivalence factor is achieved only when both the Di-Cup® and the Vul-Cup® vulcanizates have been cured so that all of the peroxide has reacted. A discussion of cure time and temperature is given later in this bulletin. Vul-Cup® equivalent replacements of the various commercial grades of Di-Cup®, based on assay of the commercial products are listed in Table II

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Table II - Equivalent Levels of Commercial Vul-Cup® and Di-Cup®

Vul-Cup®	Di-Cup®
0.625 part Vul-Cup® R	=1 part Di-Cup® R
0.58 part Vul-Cup® R	=1 part Di-Cup® T
0.26 part Vul-Cup® R	=1 part Di-Cup® 40C and Di-Cup® 40KE
1.5 parts Vul-Cup® 40KE	=1 part Di-Cup® R
1.4 parts Vul-Cup® 40KE	=1 part Di-Cup® T
0.625 part Vul-Cup® 40KE	=1 part Di-Cup® 40C and Di-Cup® 40KE

In developing a new formulation utilizing Vul-Cup® peroxide, it is suggested that the following basic compound be used as a starting point:

Table III - Suggested Basic Peroxide Compound

Component	Parts by Weight (phr)
Polymer	100
Filler	Variable
Zinc oxide	5.0
Stabilizer	0.5
Vul-Cup® 40KE	As shown below

For these Elastomers	Use This Much Vul-Cup® 40KE
EPDM, EPM, CSM	3.5-5.0
VMQ, BR	0.75-1.5
All other materials	1.5-3.0

Representative results using this basic formulation are shown in Table IV.

Table IV - Fundamental Formulations of Vul-Cup® and Rubber

	EPM	EPDM	NR	CR	NBR	SBR	EU
Polymer	100	100	100	100	100	100	100
HAF black	50	50	50	30	30	50	30
Antioxidant	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Vul-Cup® 40KE	4.5	4.25	2.75	2.3	2.75	2.3	2.75
Cure time, min	35	35	20	10	25	20	15
Cure temperature, °C	171	171	171	171	171	171	171
Tensile strength, psi	1,200	2,430	2,700	2,785	3,100	2,812	3,240
MPa	8.3	16.7	18.6	19.2	21.4	19.4	22.3
100% modulus, psi	150	380	460	380	335	1,050	860
MPa	1.0	2.6	3.2	2.6	2.3	7.2	5.9
200% modulus, psi	320	1,430	1,525	--	1,120	--	2,675
MPa	2.2	9.9	10.5	--	7.7	--	18.4
Elongation, %	500	280	275	190	345	185	230
Hardness, points	53	68	60	71	62	73	70

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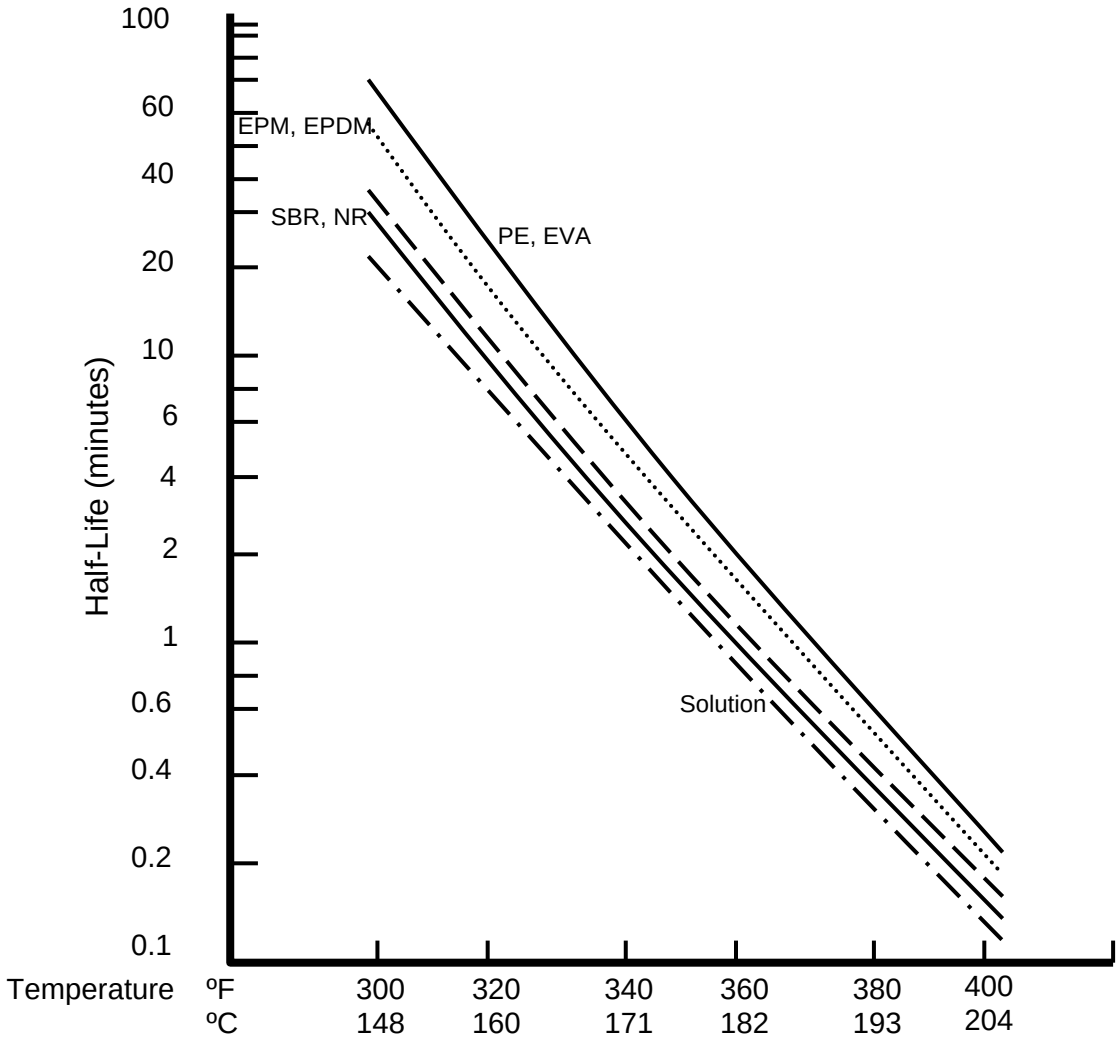
Bloom

Occasionally, a vulcanizate of Vul-Cup® peroxide will exhibit a small amount of white, crystalline bloom. This generally occurs in the extremely nonpolar rubbers and is a byproduct of peroxide decomposition. Although only slightly soluble in water, this bloom can be washed off with copious quantities of water.

Cure Time and Temperature

Vul-Cup® peroxide, when heated, decomposes thermally to form alkoxy radicals that, in turn, abstract hydrogen from the polymer backbone, forming polymer radicals. A combination of two polymer radicals results in a crosslink. In general, the cure rate (or rate of crosslinking) is equivalent to the rate of thermal decomposition of Vul-Cup®. The rate of cure of Vul-Cup®, therefore, is dependent primarily on cure temperature and is predictable for each polymer system. Care should be exercised to differentiate between rate of cure and state of cure. In a given polymer, rate of cure with Vul-Cup® is affected primarily by temperature, while state of cure is influenced by the level of Vul-Cup® and many other factors.

Figure 1 - Half-Life of Vul-Cup® vs. Temperature in Various Polymers



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The major factor affecting the rate of peroxide thermal decomposition and, therefore, cure rate, is temperature. However, it has been found that the polymer or the medium in which the peroxide decomposes does have some effect on the rate of peroxide decomposition. This means that a peroxide such as Vul-Cup® will require a different cure time at a preset temperature for different types of polymer systems. Selection of the proper cure time for a vulcanizate of Vul-Cup® depends on the performance requirements of that vulcanizate.

Figure 1 contains a plot of the half-life of Vul-Cup® measured in various polymer compounds and as a solution in an inert liquid. In addition to the polymers shown in this figure, it has been found that *cis*-polybutadiene (BR) has a half-life curve between those of nitrile rubber (NBR) and ethylene-propylene terpolymer (EPDM). Polyisoprene (IR), natural rubber (NR), and styrene-butadiene rubber (SBR) have approximately the same half-life curves, and this common curve lies between those of NBR and the solution.

Under commercial curing conditions, the stock temperature and the peroxide decomposition rate are influenced by the mold heat-up time, vulcanizate thickness and shape, and other practical factors. Therefore, to determine optimum factory cure conditions requires experimentation. This is best accomplished by test-curing the subject compounds in production equipment for the cure time calculated from the half-lives shown on the following page. The resulting vulcanizates are then tested either for physical properties such as modulus and elongation, or for unreacted peroxide. Plotting any of these properties against cure time will result in a curve from which the time to reach the desired state of cure can be read. Cure conditions developed in this manner will assure optimum performance with the peroxide-cured vulcanizate. A laboratory evaluation will optimize laboratory procedure, but will serve only as a guide to production practice.

Storage and Handling (See also Bulletin ORC-303)

It is recommended that Vul-Cup® R peroxide be stored at temperatures below 125°F (52°C) in a ventilated, shaded area to ensure minimum exposure to heat. Vul-Cup® can be stored safely up to 149°F (65°C), but will lose efficiency if stored for prolonged periods at this temperature. Storage at temperatures above 100°F (38°C) could melt the Vul-Cup®, thus rendering the 40KE grade granular or lumpy.

Vul-Cup® R can be melted in a water bath held at 149°F (65°C). No means other than a hot-water bath should be used to heat Vul-Cup®.

The heat of fusion of Vul-Cup® R is 19.0 cal/g. The specific heat of solid Vul-Cup® R at 20°C is 0.395 cal/g/°C, and of liquid Vul-Cup® R at 80°C, 0.474 cal/g/°C.

Safety

Chemically, Vul-Cup® peroxide is highly stable and can be stored at approximately 90°F (32°C) or below for several years without appreciable loss of peroxide activity. Vul-Cup® is non-explosive, based on standard test procedures.

1.	MSHA[i]	2-kg weight
	Anvil and plunger	Design 1
	Drop height	100 cm
	Results	Did not shoot
2.	Cap sensitivity test, lead block	Steel bomb
	Sample size	7 g
	Compression[j]	0.049 in. (0.124 cm)
3.	Typical flash point, Vul-Cup® R, SETA-CC	187°F (86°C)

[i] Mine Safety and Health Administration.

[j] Compression less than 0.1 in. (0.25 cm) indicates the material is inert or has very low explosive power.

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A sample of Vul-Cup® R peroxide was examined by quantitative differential thermal analysis (DTA) at a heating rate of 10°C/ min. Exothermic decomposition begins at approximately 235°F (113°C) and peaks at 362°F (183°C). Isothermal runs indicate that extensive decomposition takes place at temperatures as low as 194°F (90°C).

Vul-Cup® peroxide R is classified as a Class IV peroxide under Factory Mutual Peroxide Hazard Classification. Class IV peroxides have moderate fire hazard characteristics that can be contained easily by normal sprinkler systems and firewalls. Vul-Cup 40KE in fiberboard containers of up to 100 lbs. each (maximum) can be considered as a Class V peroxide in accordance with Factory Mutual Loss Prevention Data Sheets 7-80. Class V peroxides present a low or negligible fire hazard. Combustible packing materials may present a greater hazard than the peroxide itself.

For additional information, or to place an order or sample request, call 1.800.331.7654.

Before handling this material, read and understand the MSDS (Material Safety Data Sheet) for additional information on personal protective equipment and for safety, health and environmental information. For environmental, safety and toxicological information, contact our Customer Service Department at 1.800.331.7654 to request a Material Safety Data Sheet or visit our website at www.arkemainc.com/crosslinking.

The world is our inspiration

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