

Molecular Oxygen: a Friend or a Foe?



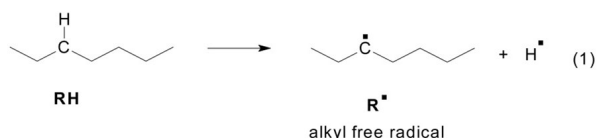
Igor V. Khudyakov
Bomar, Torrington, CT USA

Introduction

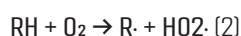
Molecular oxygen (O₂) plays an important role both in the storage of UV-curable monomers, oligomers, and formulations, as well as in the UV-cure itself. The correct name of oxygen is dioxygen or molecular oxygen. Usually we talk about air dioxygen, which constitutes ~21% of air.

Inhibition of Spontaneous Polymerization

Compounds with multiple (double) bonds, such as acrylates and methacrylates, are capable of spontaneous polymerization. That is a very undesirable process because it results in thermoinitiated polymerization (a gelation) of a batch. In extreme cases we can experience a run-away reaction leading to evolution of heat and possible explosion of a drum. Almost all chemicals have bonds which dissociate with very low efficiency into radicals. The most common are C–H bonds, which are present in almost all organic compounds:



In the reaction above, a compound with a C–H bond(s) (abbreviated as RH) very slowly dissociates into two radicals at room temperature. One of them is hydrogen atom. A dot close to an atom means unpaired electron, or a free radical, which is usually a highly reactive fragment of a molecule. The higher the temperature, the faster the decomposition of RH occurs. On a practical basis, this is why we store food in a refrigerator – to minimize formation of free radicals and other chemical reactions which can promote the spoilage of meats, etc. In the presence of air dioxygen (and we rarely have a deoxygenated solutions or inert atmosphere (of nitrogen or inert gas like helium, xenon, etc.) another slow reaction leads to formation of free radicals:



Formation of free radicals is exactly what is required for initiation of the undesirable spontaneous free radical polymerization. Once more, reactions 1 and 2 are unavoidable. Fortunately, they occur with very slow rates. So, what can we do to prevent spontaneous polymerization?

We try to keep batches at low temperatures and add polymerization inhibitors. The most popular inhibitor is MEHQ,

or methyl hydroquinone, with the more correct name of 4-methoxyphenol:



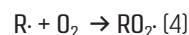
MEHQ

It has been demonstrated that the methoxy group in para-position of phenol “weakens” the O–H bond of phenol, C₆H₅OH, making MEHQ an efficient inhibitor. Radicals formed from MEHQ are substituted phenoxy radicals which are practically inert in the initiation of (meth)acrylate polymerization. Moreover, fresh MEHQ is a colorless, inexpensive solid compound with a modest odor, and is convenient to deal with in production situations.

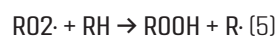
But there is a basic problem: A reaction of the alkyl (C-centered) radical R_• occurs with MEHQ with very low rate (efficiency):



On the contrary, MEHQ reacts fast (efficiently) with peroxy radicals, which are formed from alkyl radicals by an extremely fast reaction with dioxygen, cf. below:



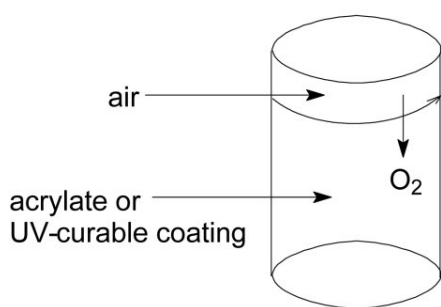
Peroxy radicals, RO₂[•], are usually incapable of initiating polymerization. RO₂[•] participates in different reactions and in particular they attack C–H bonds on any RH compound with the formation of hydroperoxides, ROOH, and new alkyl radicals, R_•, capable of initiating polymerization:



Fortunately, it turns out that peroxy radicals RO₂[•] quickly react with MEHQ:



So, dioxygen is “our friend” during storage of a polymerizable batch: it quickly replaces alkyl radicals by peroxy radicals, and the latter react with MEHQ with a formation of rather harmless phenoxy radicals. Air or more specifically, O₂, is required for safe storage of polymerizable materials. We can consider acrylates as an example. Drums with acrylated materials come to a user from a manufacturer with an air head-space, and dissolved MEHQ as the most common inhibitor.



If a drum does not have an air head-space, there is a probability of a drum explosion due to consumption of dioxygen inside the (viscous) liquid and subsequent runaway thermoinitiated polymerization. Dioxygen does not quickly dissolve in the immobile, especially viscous liquid. Bottom layers of acrylate may become deficient of O₂. Concentrations of air dioxygen in common solvents including water are not high.

It is ~10⁻³ M or ~10⁻³ mol/L or 10–100 ppm. 1 ppm means one “part per million” or 1.10–4 %. Shaking a drum or placing drum on rolls is recommended for a prolong storage. If a batch gels, a gelation usually starts from the bottom. It is usually very difficult to separate gelled (or a starting to gel) part of coating from pristine coating. Gelation (polymerization) is like a cancer: it damages the entire batch. The most important consideration is **the prevention** of the spontaneous polymerization.

A common level of MEHQ is 200 ppm or so. Typically a manufacturer guarantees 6 to 12 months of a pot life of his acrylate or of a coating formulation. Bomar guarantees at least 6 months of a pot life of our products at ambient temperature (excluding extremes like keeping a pail/drum in FL or AZ in the Summer.) In particular, Bomar warranty is 12 months from date of delivery during storage at conditions of 40 to 100°F. At Bomar we run internal tests measuring pot life of our oligomer at elevated temperatures up till 194°F (90°C). There are many other less common and more expensive inhibitors of polymerization but their discussion is beyond the scope of this tech letter. Some of these inhibitors do not need dioxygen.

We need to pay attention to the accumulation of hydroperoxide (ROOH) formed in reaction (6). ROOH has a “weak” O–O bond, and easily dissociates into highly reactive free radicals capable of initiating polymerization:



(As always, the higher is the temperature, the faster are almost all chemical reactions.) Quite often manufacturers add so-called “secondary” antioxidants, which are compounds that transform ROOH into a harmless alcohol, ROH. ROOH is figuratively or even literally “a time bomb” during the storage stage for (meth)acrylates.

MEHQ is slowly consumed during storage. In addition, MEHQ is oxidized by dioxygen, and can evaporate slowly from opened containers. Bomar and other companies have developed laboratory methods to determine a current concentration of MEHQ or another inhibitor in oligomers or UV-curable formulations.

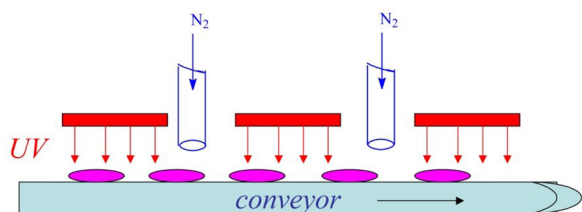
Inhibition of UV-Cure

The same air dioxygen (O₂) becomes a “foe” during UV-cure in the air. As was mentioned above, any alkyl radicals, in particular alkyl and other radicals, R·, of photoinitiator (PI) and acrylate radicals react with air dioxygen (reaction 4). Peroxyl radicals, RO₂·, are practically incapable of initiating and continuation of polymerization. (For the linear systems (cf. the Tech Letter 1), we will say that peroxy radicals are inefficient in **chain propagation**, because polymerization of a linear systems is a chain reaction. We will note also, that in scientific research it is desirable to eliminate inhibitor in order to have a clean system. Commercially available inhibitor removers are used for that goal; they are mostly based on alumina Al₂O₃.)

If we still want to cure in the air we need to use high lamp intensity and/or relatively high PI concentration in order to consume quickly the relatively low concentration of O₂ dissolved in our formulation. We need to run the initial stage of cure quickly in order to compete with dissolution of “new” air dioxygen in the film. Presence of air dioxygen leads to an induction period, as observed on a plot of “degree of polymerization” vs. “time.” That induction period reflects consumption of air dioxygen. Curing under inert gas blanket is a well recognized method to decrease dioxygen inhibition. A commonly used gas for that purpose is molecular nitrogen N₂. (Scientific community is less demanding in naming nitrogen as dinitrogen. We will use the word “nitrogen” for N₂.) One can use carbon dioxide CO₂. Inert gases (He, Ar, Xe, Kr, etc.) are expensive. Modern UV-processors can be equipped with an accessory to cure under N₂ blanket. UV-cure of coating for optical fiber is always run in a nitrogen atmosphere.

One can get a cylinder with N₂ and flow N₂ on an object under UV-cure.

The figure below demonstrates a possible homemade way to have a nitrogen blanket using flow from N₂ cylinder for a low speed conveyor.



Caution: An operator should stay away from nitrogen flow. Presence of a human in the dioxygen depleted atmosphere can lead to fainting.

In a thin film of liquid coating inert gas “washes out” O₂ from the coating and cure starts promptly upon UV-irradiation.

There are also chemical ways to alleviate negative air dioxygen effect by selected additives, such as tertiary amines. Amines help to consume oxygen in the film under cure. Wax additives, which migrate to the surface of a curable formulation, can assist with cure. Increase of PI concentration and/or light intensity can help to overcome dioxygen inhibition. There are other rather exotic ways to consume O₂ and facilitate UV-cure. In a number of cases curing in air leads to a poorly cured top surface of coating. The top of a film feels tacky, slimy, slippery, undercured, etc. Notice, that deeper layers of even a thin film are often cured well, because air dioxygen can't replenish itself in the bottom layers.

Hydroperoxides ROOH and other products are formed on the top of the coatings instead of a crosslinked network (for multifunctional acrylates). Practitioners distinguish PIs: PI for a **surface cure**, and PI for a **through cure**, i.e., the cure through the layer of coating of a certain thickness. They use simultaneously both types of PIs in a formulation when necessary. Darocur 1173 is often used for “surface

cure” and Lucirin TPO or benzophenone/amines are used for “through cure.” Darocur 1173 produces under photolysis 2-hydroxy-2-propyl radical (CH₃)₂C•OH, which is very reactive towards O₂. That way Darocur 1173 serves as both a PI and as a sacrificing agent, consuming dioxygen at the surface. Other PIs initiate UV-cure inside the film. Concepts such as “surface cure” and “through cure” do not have real meaning in the case of an inert gas blanket.

We will talk on PIs in another lecture. In conclusion it is worthwhile to note that UV-curable formulations are always shipped and stored in dark containers. Moreover, some visible and even UV-light sensitive formulations are never exposed to the ambient light prior to cure in order to be on the safe side; an example would be coatings for optical fiber.

Conclusions

Air dioxygen is required to prevent spontaneous polymerization of UV-curable formulations stabilized with phenolic antioxidants like MEHQ, BHT (ionol), Irganox1010, etc. So, dioxygen is “a friend” in this case. However, the same air dioxygen becomes “a foe” inhibiting UV-cure itself. Standard ways to alleviate this negative effect of dioxygen were described above.