

Product Data Sheet

Green Retarder Product Bulletin

Introduction

Retarders AHM S440/S450 are used to control polymerisation during the purification of styrene monomer. The quinone methide (QM) active ingredient was first shown to slow down styrene polymerisation more than 30 years ago but only in recent years has it started to be used commercially in combination with true inhibitors.

The QM molecule used in Retarder AHM S440/S450 has become the preferred industry option when choosing green retarders and the active ingredient is widely available.

The QM molecules are less toxic than the industry standard DNBP and most examples of the molecule class contain no nitrogen, reducing NO_x when styrene tars are burnt as fuel. They are, however, less efficacious than DNBP and more retarder is needed on a kg for kg basis if a direct switch is made.

Chemical Information

Retarder AHM S440/S450 contain a quinone methide product supplied in ethylbenzene solution.

CAS Number: 7078-98-0

EC Number: 429-460-4

Product Range: Nufarm Green Retarder

Retarder AHM S440 is a 40% solution in ethylbenzene **Product Codes: 210000306 in isotanks, 210000307 in IBCs**

Retarder AHM S450 is a 50% solution in ethylbenzene **Product Codes: 210000410 in isotanks, 210000295 in IBCs**

Please quote the relevant Nufarm Product Code when requesting details of our quality specifications and prices.

Application Information

Olefinic polymerisation is initiated and propagated by unstable free radical species. The origin of these is often thermal decomposition of the olefin e.g. in manufacturing processes such as distillation.

Light or other radiation can also give rise to these unwanted initiating species. In most, if not all, cases the unstable free radical species are carbon centred radicals and these can cause a fast vinyl polymerisation propagation reaction (rate constant $k_p = 10^{-10} \text{ M}^{-1}\text{s}^{-1}$).

The polymer thus formed represents a loss of valuable monomer and even more importantly it often causes problems such as viscosity increases, deposits on heat transfer surfaces, blockages of equipment etc.

There are two different classes of molecule that can be used to prevent polymerisation, retarders and inhibitors. Polymerisation retarders react with free radicals at rates slightly faster than the rate of polymerisation (10-100 times faster).

As such, they generally slow down the rate of polymerisation rather than completely preventing its occurrence. Dosage rates are generally in the 100 – 1000's of parts per million (ppm), depending on conditions and production requirements. The industry standard retarder is DNBP; Retarder MB-1 from Nufarm is also used and the QM molecules are also in this category.

Polymerisation inhibitors react with free radicals at much higher rates than the rate of polymerisation (approx. 10,000 times faster). Therefore, they will completely stop polymerisation occurring. Depending on conditions, dosage rates are generally in the 10's – 100 of ppm range. Typical examples of inhibitors are the class of stable free radicals, such as hydroxy tempo.

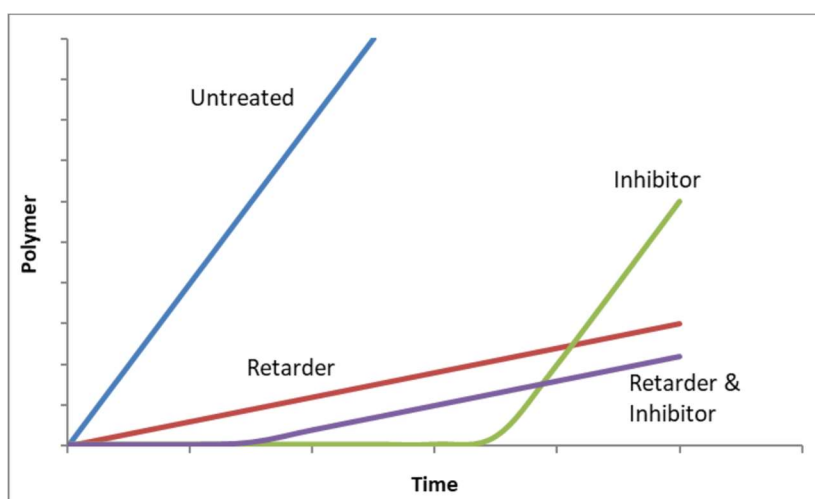


Figure 1. Retarder and Inhibitor Profiles

Despite the higher activity of polymerisation inhibitors, retarders have a key advantage over inhibitors. As their reaction rates are slower than inhibitors, retarders are consumed at a slower rate. Thus, in the event of a process upset (e.g. dosing pump failure, sudden loss of vacuum leading to a temperature increase etc), a retarder will give an extended period of protection to the process compared to an inhibitor, which could be rapidly consumed, potentially resulting in a runaway polymerisation event.

There is a third chemical treatment option; a combination of retarder and inhibitor. In this treatment option the inhibitor provides the bulk of the polymerisation protection; thereby maintaining low polymer levels. However, in the event of any process upset, a retarder is present to provide a period of protection against runaway polymerisation of the styrene. In general, using an inhibitor with a retarder, reduces the overall required dosage of retarder.

Relative Performance Data

Figure 2 compares AHM S440 with DNBP in a 60% solution of styrene in ethylbenzene at 115°C under reduced pressure. Twice the active dosage of AHM S440 compared to DNBP is required to give the same level of polymer in the test. Both materials show a typical retarder profile, with a slow gradual increase in polymer concentration over the duration of the test. For comparison, uninhibited styrene under the same conditions would produce approximately 10,000ppm polymer within 30 minutes.

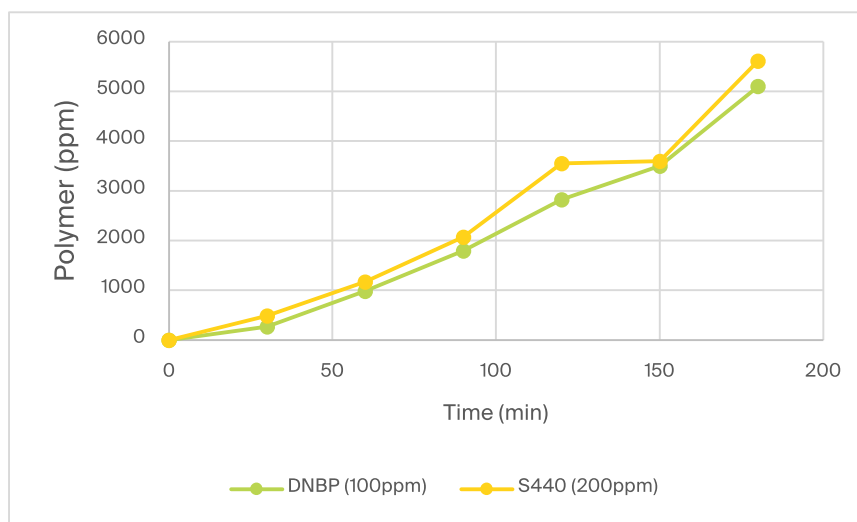


Figure 2. Batch test comparing AHM S440 vs. DNBP (115°C)

Figure 3 compares the effect of adding 4-hydroxy tempo (4-HT) inhibitor to AHM S440 under batch test conditions. The ratio of S440 to 4-HT is 9:1 (i.e. dosages are 153ppm S440 and 17ppm 4-HT); therefore, the overall dosage of AHM S440 has been reduced by ~25%, with less polymer being formed in the test.

The shape of the polymer curve is different for the S440/4-HT combination. There is a clear inhibition period for the first 60 minutes (i.e. no polymer formed), followed by a period of steady growth, matching the rate of S440 only test. This indicates that the 4-HT inhibitor is initially inhibiting the styrene polymerisation, and once consumed, polymerisation is retarded by the S440.

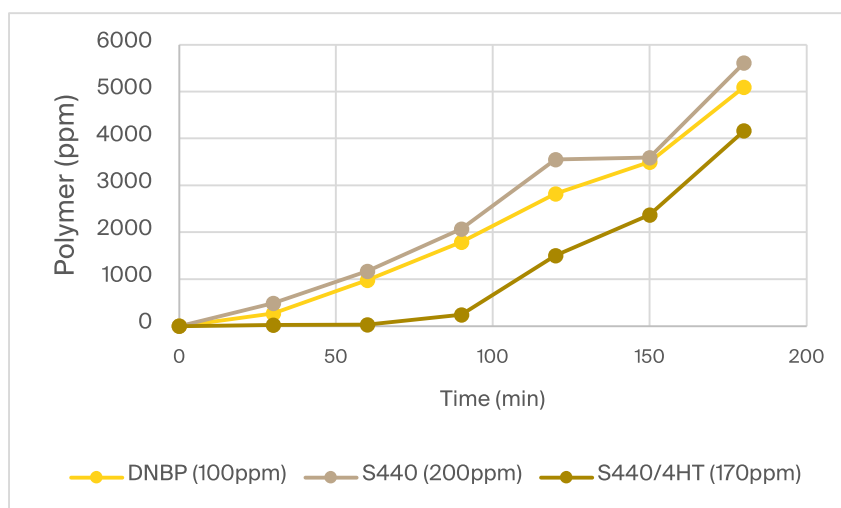


Figure 3. Effect of 4-HT on efficacy of AHM S440 in 60% styrene (115°C)

Figures 2 and 3 both demonstrate the fact that the QM molecule is less effective on a weight for weight basis compared to DNBP and higher doses must be used. This is understood by industry experts and a true inhibitor is always used with the QM retarder to provide a performance boost. The ratio of retarder to inhibitor can be varied and more information on this and the effects of changing the ratio is available from Nufarm's technical team.

Physical Chemical Properties

Specific Gravity and Viscosity:

The following graphs show the temperature dependence of Specific Gravity and viscosity

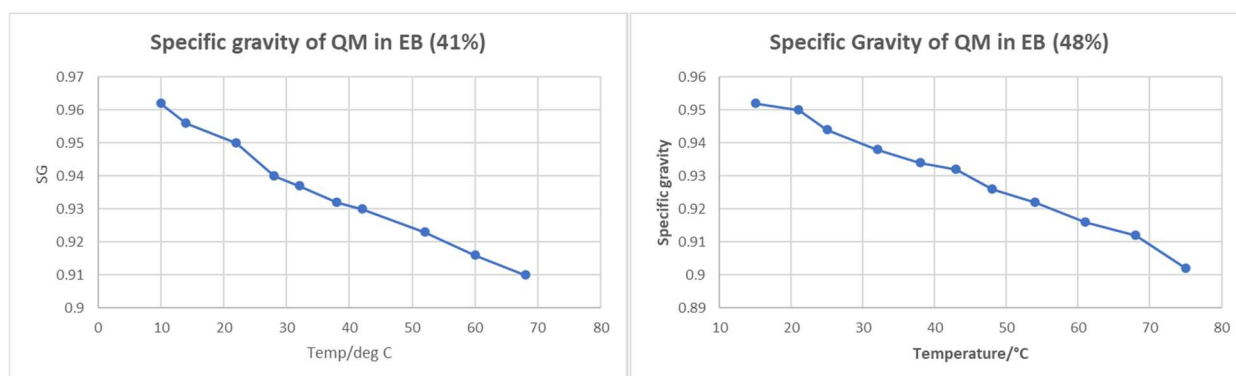


Figure 5: Specific Gravity

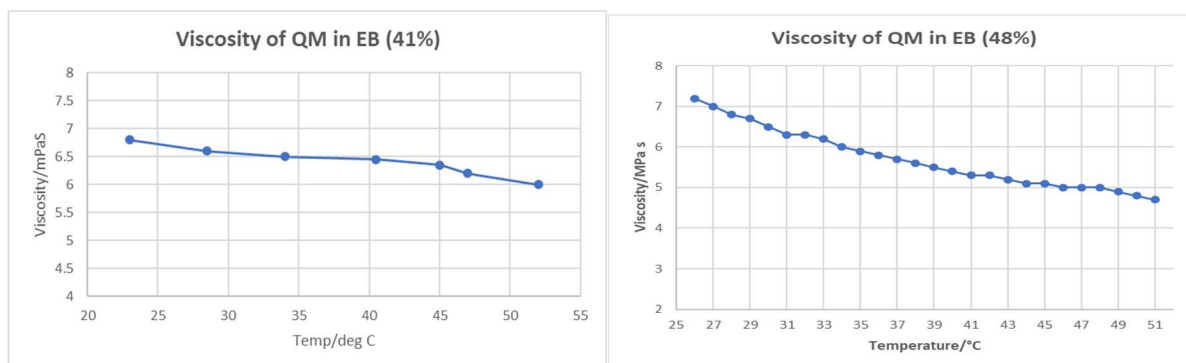


Figure 6: Viscosity

Solubility

Below 10°C Retarder AHM S450 will require heating to prevent precipitation.

Below 0°C Retarder AHM S440 will require heating to prevent precipitation.

Both products will go back into solution if they are warmed again after cold temperature precipitation.

Stability

The quinone methide solutions are chemically stable. They have been stored at 54°C for 15 weeks with no loss of active content. The quinone methide solutions are physically stable down to 10-15°C for the 50% solution and -0 to 5°C for the 40% solution.

Process Compatibility

All components of Retarder AHM S450/S450 are compatible with materials of construction found in a styrene manufacturing plant.

Storage/Handling/Health

Please refer to the Material Safety Data Sheet for handling and health advice.

Availability

Retarders AHM S440/S450 are supplied from our ISO 9001 facility in the UK. They are supplied as EB solutions and can be supplied in 1cuM intermediate bulk containers (totes) for plant trials, and in bulk isotanks for regular use.

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