# Economomical Application of Initiator Mix Approach in suspension Polyvinyl Chloride Production

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**Abstract:** In suspension polymerization process water is applied as the continuous phase, with vinyl chloride monomer dispersed in suspending agents. Polymerization process starts with an emulation of vinyl chloride monomer in water. Selection of polymerization initiators are based on reactor design criteria. The application of single initiators has resulted in higher peak rate with higher concentration of peroxide, and adverse impact on polymerizer temperature profile, reactor performance and product quality. On the other hand, the application of initiator mix approach has proven to be an economical optimum solution with high quality products. On the other hand, the application of initiator mix approach has proven to be an economical optimum solution with high quality products.
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**Key words:** Initiator, Mix, Polyvinyl Chloride, Suspension

## 1. Introduction

S-PVC is considered as a water-cooled bulk polymerization process that allows a rapid removal of heat of polymerization via water phase.

Polymerization starts with an emulation of vinyl chloride monomer in water.

Depending on the polymerization temperature "T" and the glass temperature of polymer"$T_G$", we obtain after polymerization a PVC suspension on the condition that ($T_G > T$).

Reactions started in the monomer droplets by free radical initiators.

Such initiators are mostly water-based type for safety and environmental aspects.

Their selection is determined by factors such as reactivity, thermal stability and effects on PVC product quality(5).

The start of polymerization reactions, an initiators "I" adds a monomer molecule "M" and becomes a monomer radical "IM", which adds further monomer molecules in the propagation reaction step.

As a matter of fact, vinyl chloride monomer polymerization rate increase with conversion which is mainly due to the fact that the termination rate in the polymer rich phase is smaller than that in the monomer phase (3).

From the kinetic point of view, the higher the concentration of peroxide, the higher is the heat peak, which is related to the reactor design and its cooling capacity.

Table (1) shows the major initiations applied in suspension polymerization reactions of vinyl chloride monomer.

Table (1) Major initiations applied in s-pre production

| | Assay % | Active O₂ % | Emulsion in H₂O | Storage temperature | | T °C for t ½ | | | Eα |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | | | max. | min. | Temp. for 0.1 hr t ½ | 1 hr | 10 hrs | Kj/mole |
| Bis (2_ethylhexyl) peroxydicarbonate | 50 | 1.85 | Emulsion in H₂O | -15°C | -25°C | 83 | 64 | 47 | 122.45 |
| Ter-butyl peroxyneodecanoate | 40 | 2.62 | Emulsion in H₂O | -10°C | -20°C | 84 | 64 | 46 | 115.47 |
| Cumyl peroxyneodecanoate | 40 | 2.09 | Emulsion in H₂O | -20°C | -30°C | 75 | 56 | 38 | 114.59 |
| 2,4,4 trimethyl pentyl-2peroxyneodecanoate | 40 | 2.66 | Emulsion in H₂O | -15°C | -20°C | 76 | 57 | 40 | 115.79 |
| Bis (3,5,5- trimethyl hexanoyl) peroxide | 40 | 2.04 | Emulsion in H₂O | 0°C | -20°C | 96 | 77 | 59 | 128.34 |
| DiLanroyl peroxide | 40 | 1.61 | Emulsion in H₂O | 20°C | 0°C | 99 | 79 | 61 | 123.37 |

**Historical background of peroxide formulations**

In suspension PVC polymerization, initiators determine the rate of polymerization and significantly affect the process economics.

With Lauroyl peroxide (LPO), the maximum rate of polymerization was approximately 8% conversion per hour and 80% conversion is reached in about 13 hours.

On the other hand, the 80% conversion was reached with Isopropyl peroxydicarbonate (IPP) in about 8 hours.

As a matter of fact, shorter reactions times increases reaction productivity and consequently reduce process investment.

Recent patent literature (2) contains numerous initiators such as Bis (4-ter-butyl cyclohexyl) peroxydicarbonate, Cumyl peroxyneodecanoate, ter-butyl peroxyneodecanoate, Bis (3, 5,5-trimethyl hexanoyl) peroxide, Dicetyl peroxydicarbonte, ter-butyl peroxypivalate.,…etc.

Such initiators provide the following advantages:
1) Reduced batch time.
2) Little or no induction period.
3) Polymer quality improvement.
4) Less chain branching during polymerization.

**Initiator (half-life):**

The most important characteristic of a polymerization initiator is its decomposition rate expressed as its half-life t½ (1).

The half-life is time required for one half the molecules of a given amount of initiator at a certain temperature to decompose.

The kinetic data of the composition of hydroperoxides are determined by measuring the active oxygen content in time.

The half-life can be calculated from Arrhenius equation

$$k_d = A.e^{\frac{-E\alpha}{RT}}$$

Where:
$K_d$: The rate constant for the initiator dissociation in $s^{-1}$
A: Arrhenius frequency factor in $s^{-1}$
$E\alpha$: Activation energy for the initiator dissociation in j/mole.
R= 8.3142 J/mole.K
T: Temperature in K.
t½: the half-life in s.

The concentration of the initiator at anytime can be calculated from equation

$$[I] = [I_0].e^{-K_d.t}$$

Where:
$[I_0]$: The original initiator concentration.
$[I]$: The initiator concentration at time t.
t: The time is s.

**Main characteristics of applied peroxides**
**Viscosity:**

Peroxide suspension and emulsions shows a non-Newtonian rheological behaviour, more specifically they are pseudo plastic materials. This means that viscosity decreases with increasing shear rate.
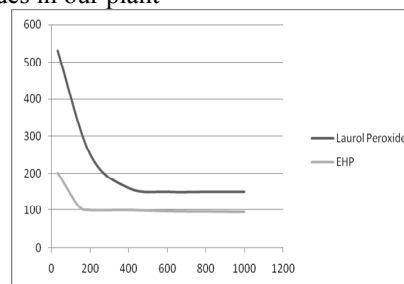Fig. (1) Illustrates viscosity curves of applied peroxides in our plant



**Fig. (1)**

It can be depicted that the applied peroxide suspension can be characterized as a liquid with a viscosity in the range of 50-500 mPa.s. At the recommended storage temperature its viscosity is hardly time-dependant. However, only at 5°C above the recommended maximum storage temperature in some cases a considerable and irreversible increase in viscosity against time can be observed.

**Particle and droplet size distribution:**

In water-based peroxide formulations droplet size (for liquid peroxides) are much smaller than those of solid peroxide.

The following is an indications of APS of applied formulations (Table 1).

Table 1.Indications of APS of applied formulations

| Peroxide suspensions | Average particle size (micron) | Peroxide emulsions | Average droplet size (micron) |
|---|---|---|---|
| EHP W-40 | 5 – 10 | EHP W-40 | 5 – 15 |
| LPO W-40 | 10 – 15 | EHP W-40 | 2 – 5 |

**Dissolution rate of the peroxide in VCM**

As principle, the dissolution rate of peroxide in VCM during stat up of a polymerization is important. If the dissolution rate is low, an inhomogeneous distribution of the peroxide over the VCM phase may result, causing high fish-eye in the PVC.
However, it was proven that dissolution rate of peroxide suspensions and emulsions is better that solid peroxides under some polymerization conditions.

**Case Study**

1) The Polyvinyl Chloride production facility in the Egyptian Petrochemicals Co. (6) is based on the production of S-PVC resin grades ranging from K-57—K-70 with corresponding polymerization temperatures ranging from 50-80˚C. The selected initiators were based on rheological characteristics of polymers and their reaction temperatures.

Table (2) shows the average applied initiator specifications.

| Product Specifications | | | | |
|---|---|---|---|---|
| **K-value** | DIN K-68 | DIN K-70 | DIN K-61 | DIN K-57 |
| **Inherent viscosity** | 0.9 – 0.94 | 0.98 – 1.05 | 0.75 – 0.78 | 0.66 – 0.70 |
| **Heat loss %** | 0.3 | 0.3 | 0.3 | 0.3 |
| **Particle size (sonic sifter)** | | | | |
| **% Retained on 40 mesh** | Trace | Trace | Trace | Trace |
| **% Retained on 60 mesh** | 5 | 5 | 5 | 5 |
| **% Through 140 mesh** | 25 | 25 | 50 | 50 |
| **Porosity (ml/gm)** | 0.14 – 0.24 | 0.2 – 0.3 | 0.1 – 0.2 | 0.1 – 0.2 |
| **Particle size acceptance** | 17 – 29 | 24 – 36 | 12 -24 | 12 – 24 |
| **Bulk Density (gm/ml)** | 0.50 – 0.56 | 0.47 – 0.53 | 0.50 – 0.56 | 0.50 – 0.56 |
| **Residnol VCM content (ppm)** | 1 | 1 | 1 | 1 |
| **Fish eyes** | 20 | 20 | 20 | 20 |
| **Dark resins** | 3 | 3 | 3 | 3 |
| **Flow time** | 15 | 15 | 15 | 15 |

The plant showed limited productivity, compared with other production facilities of high Key Performance Indicators, KPI's.

**2) Production Development Scenarios**
**Application of Highly active Peroxides:**

A trial was performed to replace the originally applied initiators with highly active ones such as α-cumyl peroxy neodecanoate.

The results of such trials revealed the following drawbacks:
Negative influence on PVC particle size distribution.

- Frequent reactor fouling.

- Negative impact on PVC stability.



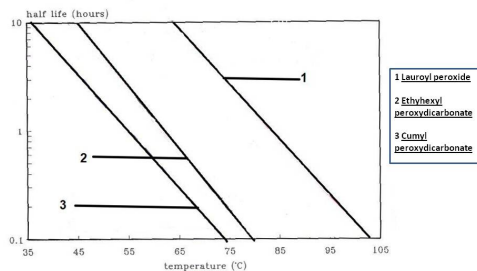Half-life curves of initiators under evaluation

1 Lauroyl peroxide
2 Ethyhexyl peroxydicarbonate
3 Cumyl peroxydicarbonate

Fig. (2) Shows a comparison between half-life curves of applied initiators and the high active peroxides.

**Mixed Initiators:**

A second study has been performed based on mixed initiator approach.

Selection of mixed initiators was based on reactor design criteria, applying an appropriate kinetic reaction model (4) based on the following parameters:

- Hamielec – Xie Model.
- Adapted half life data.
- Peroxide efficiency factors, which depend on type of peroxide and temperature.
- Efficiency factors for monomer and polymer rich phases.
- Initiator decay after pressure drop.

**Discussions and Conclusions**

Basically, VCM polymerization rate increases with conversion.

This is because the termination rate in the polymer rich phase is smaller than in the monomer phase.

Reaction rate increases till there is no more free monomer which is corresponding to the highest heat peak.

As was clarified before, the higher the concentration of peroxide, the higher is the heat peak and the earlier is it. This will have adverse impact on polymerizer temperature profile, reactor performance and product quality.

With the introduction of the relatively fast initiators, more radicals are generated at the beginning of polymerization reactions, compared with the slower initiators, thus utilizing the surplus

cooling capacity of polymerizers at the beginning of reaction processes and in turns will reduce the heat peak at maximum conversion point.

Nevertheless, some drawbacks were noticed on PVC quality and frequent polymerizer's fouling problems.

Figs. (3, 4) show VCM polymerization at 53 °C initiated by EHP with a concentration of 300 and 600 ppm respectively.

Fig. (5): Shows the non-used cooling capacity of a polymerizer.
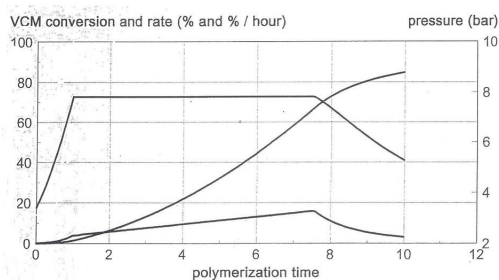
### VCM polymerization at 53°C initiated by EHP (300 ppm)



Fig. (3)

### VCM polymerization at 53°C initiated by EHP (600 ppm)
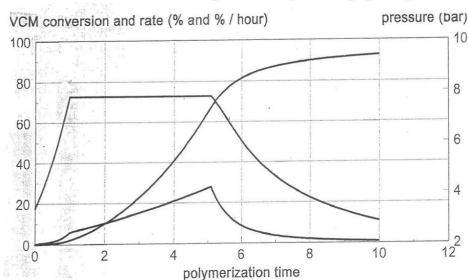


Fig 4

### Non used cooling capacity
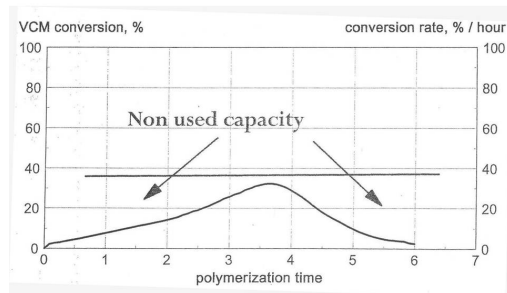


Fig 5

The initiator mix approach showed satisfactory results with respect to polymerizer performance, reaction cycle time, and product quality.

Initiator selection was based on the application of a PVC kinetic reaction model based on actual poly design data, productivity requirements and product slate requirements.

The selected initiators in the        mix are:

- Ethyl hexyl peroxy dicarbonate (EHP)   (one hour half life = 64 °C) and
- Cumyl peroxy neodecanoate (CPN)        (one hour half-life = 53 °C).

Figs (6-9) depict comparisons between polymerization curves using different concentrations of initiator mixes at 53°C.
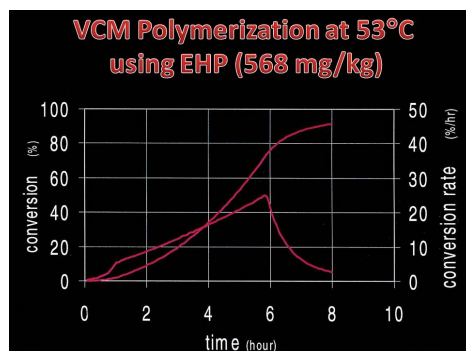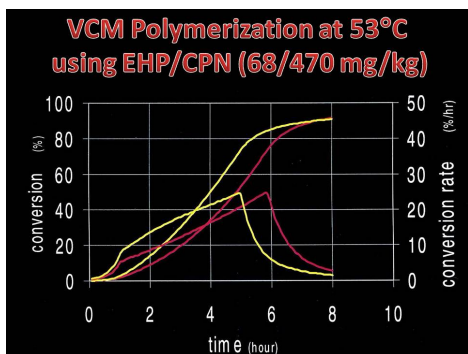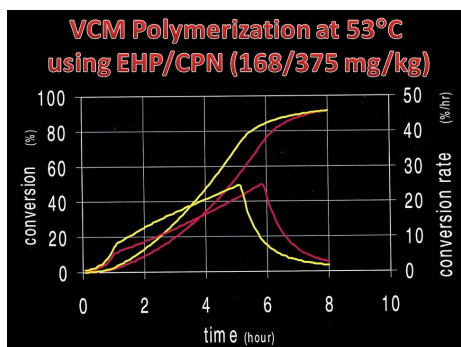
### VCM Polymerization at 53°C using EHP (568 mg/kg)
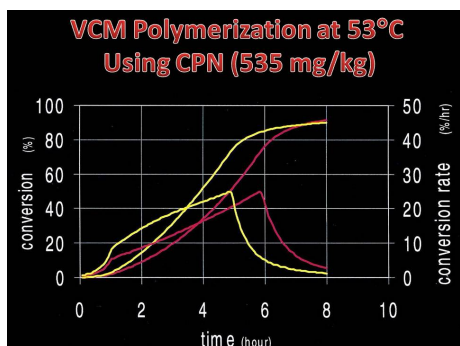


**Fig 6**

**Fig 7**



**Fig 8**



**Fig 9**

**Conclusion**

The application of initiator mix approach has proven to be an optimum solution to improve reactor temperature profile.

The following advantages have been attained:

1- Reduction of reactor cycle time by an average of about 50 minutes per charge has increased productivity by an average of 22%.

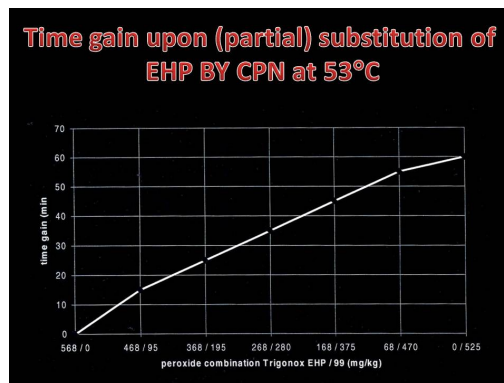Fig. (10) reveals the time gained upon partial substitution of EHP by CPN.



Fig 10

2- Annual productivity has been increased from 283 ton to 300 ton per cubic meter of reactor volume.

3- Realization of a smoother poly heat profile thus reducing reactor 's build ups.

4- Improvement of the rate of pressure drop, thus eliminating carry over problems in reactor overheads.

5- Improvement of product quality.

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