

The summary of the PhD thesis

Innovative methods of obtaining organic peroxides for unsaturated polyester resins to verify the available information and optimize the production process

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The work involved the use of innovative methods of obtaining organic peroxides for unsaturated polyester resins and optimization of the production process.

In the first stage of the work, a criteria analysis of potential stabilizers used in the production of methyl ethyl ketone peroxides was conducted. For this purpose, alternative, commonly available raw materials were used which might have been more advantageous in economic, ecological and technological terms.

Methyl ethyl ketone peroxide (MEKP) is the most widely used organic peroxide to harden polyester resin at ambient temperature. Its ease of use, accessibility and overall good performance have made it the most common choice as an initiator for decades. MEKP initiators consist of two parts, an organic peroxide and diluent. The diluent, that is actually the main ingredient in MEKP initiators, is mainly composed of plasticizers, glycols and water. It is required in all MEKP formulations to ensure the safety of production, trade and transport.

The main task of my work was to study the feasibility of carrying out all stages of the production of methyl ethyl ketone peroxides with the use of selected raw materials (stabilizers), and then the optimization of the proven synthesis path in order to maximize reacting of the substrates.

After the methyl ethyl ketone peroxide solutions (finished product) were obtained, the reaction conditions were verified.

For this purpose, the existing technology of obtaining methyl ethyl ketone peroxides was used. The optimal parameters of the reaction, such as: time, temperature and amounts of auxiliary substances used in the technology were selected.

The conducted syntheses of oxidation of methyl ethyl ketone with 60% hydrogen peroxide required lots of experiments and application tests. The difficulty with selecting the optimal parameters was to select the stoichiometry in so as to obtain the correct monomer to dimer ratio. However, a seemingly simple matter turned out to be complicated in practice for several reasons.

In my work, monomeric stoichiometry meant the use of 2 moles of hydrogen peroxide per a mole of ketone with a 20% excess and a small amount of acid catalyst. Fulfilling these conditions, I obtained mixtures of methyl ethyl ketone peroxides, in which the monomer was predominant. The use of dimer as well as small amounts of hydrogen peroxide are the inherent features of the processes which were carried out and play an important role in the further processing of unsaturated polyester resins.

The chemical reaction was also optimized for stoichiometry and several syntheses were performed using less excess of hydrogen peroxide. An attempt was also made to carry out the syntheses without the use of a catalyst, as well as an attempt to replace the used catalyst with an ion exchange resin.

The syntheses were carried to a lesser extent using a synthesis station, which allowed for automatic syntheses to be carried out with limited supervision. This device allows you to plan a multi-stage temperature ramp and to dose several different substances taking part in the reaction at a programmed time and at a programmed rate. At the same time, it enables the control of the pH reaction and its automatic correction. The software makes it possible to plan multi-stage experiments referring to the existing production process, while defining the conditions for launching the next steps of the experiment.

In addition, the basic parameters of peroxide initiators, which determine the use of the hardener, were examined, i.e. the type and concentration of peroxide, the content of active oxygen, the content of free hydrogen peroxide, and the content of water. They influence on the gelation time and the maximum polymerization temperature. The more hydrogen peroxide is used the faster the resin gels. Initiators with too high contents of hydrogen peroxide are not recommended for hardening gelcoats due to the formation of craters on the surface of the gelcoat because of decomposing hydrogen peroxide. The use of an initiator with a high content of hydrogen peroxide can cause a problem during the preparation of glass fiber reinforced laminates. During the saturation with resin, the system can gel so quickly that it will not allow the glass mat to be completely supersaturated.

In addition, the obtained products were compared with the product previously manufactured in the installation by Oxytop Sp. z o.o. For this purpose, laboratory analyses of newly obtained and already available initiators were performed with the use of chromatographic methods.

The aim of the work was not only to obtain the proper hardening characteristics, but also the stability of the product over time. Stability tests were also carried out at a temperature of + 40°C and -25°C, because it is the stability of the product over time that determines the undertaking of further research on the product.

At the end of the research cycle, cooperation with several companies was established that had already used Oxytop products in order to perform tests and application studies. That allowed me for a real evaluation of the performance of the newly formed peroxide initiator.

The work was carried out within the framework of the IMPLEMENTATION DOCTORATES program.