Example 7: Norbornyl methacrylate with initial charge of methacrylic acid

258 g of methacrylic acid, 0.78 g of MEHQ and 2.5 ml of boron trifluoride dimethyl etherate were initially charged in a 2 l four-neck round-bottom flask with Normag attachment, magnetic stirrer, thermometer, dropping funnel and air inlet. The mixture was heated with stirring (500 rpm) and introduction of air (1 l/h), and a solution of 275 g of norbornene and 245 g of methacrylic acid was added dropwise, such that the internal temperature was 92-97°C.

After addition was complete, stirring was continued for a further 3 h. Excess acid was partially distilled off under reduced pressure. The reaction mixture that had cooled to room temperature was extracted with 30% NaOH (122 g) and the phases were separated. Two further extractions and phase separations followed with in each case 250 ml of water and 50 ml of saturated sodium chloride solution.

The organic phase was concentrated at 60°C to 5.5 mbar in order to remove traces of water and any methacrylic acid, and subsequently filtered. 508.5 g of product (yield 96.6%) were obtained with a purity of 99.8% by weight. The end product was stabilized with 51 mg of MEHQ. The color number was 39 Hazen.

Comparative example 1: Norbornyl acrylate with initial charge of norbornene:

40 g of norbornene were initially charged in a 250 ml four-neck round-bottom flask with reflux condenser, magnetic stirrer, thermometer, dropping funnel and air inlet, and melted. 0.1 g of MEHQ and 0.5 ml of boron trifluoride dimethyl etherate were added. 61.5 g of acrylic acid were added dropwise at an internal temperature of initially 50°C. After dropwise addition was complete, the internal temperature was 76°C. The temperature was raised to 90°C and stirring performed for a further 5 h. The reaction mixture that had cooled to room temperature was admixed with 300 ml of dichloromethane and with 250 ml of 8% NaHCO3 solution and extracted. A further 30 g of $NaHCO_3$ were added. The phases were separated, the organic phase was extracted once more with 250 ml of 8% $NaHCO_3$ solution and concentrated after phase separation. 55.3 g of product were obtained with a purity of 70.8% by weight.

Example 8: Norbornyl acrylate with initial charge of acrylic acid:

76.5 g of acrylic acid and 52 mg of MEHQ were initially charged in a 500 ml four-neck round-bottom flask with reflux condenser, magnetic stirrer, thermometer, heatable dropping funnel and air inlet. 0.65 ml of boron trifluoride dimethyl etherate was added. 50 molten norbornene was added dropwise with introduction of air (1 l/h), stirring (500 rpm) and heating, such that the internal temperature was 85-100°C. The mixture was stirred at 94°C for a further 5.3 h. The reaction mixture that had cooled to room temperature was admixed with 20 g of 50% NaOH solution and extracted. The phases were separated, the organic phase was extracted two more times with 100 ml each time of 12.5% aqueous sodium chloride solution, the phases were each separated and the organic phase was concentrated at 60°C to 5.5 mbar in order to remove traces of water and any acrylic acid. After filtration, 91 g of product (95.1% yield) were obtained with a purity of 97% by weight. The color number was 34 Hazen.