VINYL CHLORIDE POLYMERS

Vinyl chloride polymers, containing the repeating unit —CH_2CHCl—, include in addition to the homopolymer copolymers with such monomers as vinyl acetate, propylene, or vinylidene chloride. The polymers are used in both flexible and rigid form as moldings, foams, fibers, and films and sheeting. They also form the basis of plastisols, or vinyl dispersions, used extensively as coatings and molded articles. The homopolymers and the polymers with minor amounts of a comonomer are collectively referred to as PVC or PVC-type polymers in the literature. Chlorinated poly(vinyl chloride) is also a material of considerable interest.

INTRODUCTION

Historical Background

The first mention of poly(vinyl chloride) was in 1872 by Baumann (1) when he described the formation of a white powder by the action of sunlight on vinyl chloride contained in a sealed tube. He had no idea of the composition of the new product but his examination showed that it was unaffected by a wide range of solvents. The formation of a compound with the formula C_2H_3Cl had been reported earlier in 1835 by Regnault (2), but, apart from these two references, there was no further interest in vinyl chloride for forty years.

Renewed interest was brought about by the overcapacity which had arisen in Europe in the production of calcium carbide. The potential of acetylene as an illuminant had been greatly overestimated and this had led to the construction of many new carbide plants. This resulted in a substantial price drop in the early part of the twentieth century; in 1905 the price of calcium carbide was £28 per ton, but in 1909 it had dropped to £9. The position was particularly acute in Germany and it was here that an extensive research program was set under way to investigate possible chemical uses of acetylene. In 1912, Klatte (3) of Griesheim-Elektron filed a patent claiming the manufacture of vinyl chloride monomer by the reaction between acetylene and hydrogen chloride in the presence of a mercuric chloride catalyst. The formation of the polymer by the action of ultraviolet radiation was confirmed and in 1914 the use of organic peroxides as accelerators for the polymerization was known (4).

At the same time work on vinyl halides was being carried out in Russia by Ostromislensky (5). The polymer was being used as an intermediate in an attempt to produce synthetic rubber by dehydrochlorination, using alcoholic and aqueous potash.

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Table 10. Physical Properties of Vinyl Chloride Monomer

molecular weight	62.501
boiling point at 760 mm, °C	−13.37
freezing point, °C	−153.79
flash point, °C	−78
liquid density, g/ml	
at −20°C	0.98343
at −25°C	0.99176
at −30°C	0.99986
viscosity, cP	
at −10°C	0.248
at −20°C	0.274
at −30°C	0.303
at −40°C	0.340
surface tension, dyne/cm	
at −10°C	20.88
at −20°C	22.27
at −30°C	23.87
refractive index, n_D^{15}	1.398
vapor pressure, mm	
at 25°C	3000
at −13.37°C	760
at −55.8°C	100
at −73.9°C	30
at −87.5°C	10
at −109.4°C	1
specific heat of liquid, cal/g/°C	0.38
specific heat of vapor, cal/g/mole/°C	10.8–12.83
latent heat of vaporization, cal/g	
at 25°C	71.26
at −13.37°C	79.53
latent heat of fusion, cal/g	18.14
critical temperature, °C	158.4
critical pressure, atm	52.2
absolute entropy at 25°C, cal/°K/g-mole	61.68
heat of formation, cal/g-mole	9000
dielectric constant at 10^5 Hz and 17.2°C	6.26

and hydrogen chloride, whereas hydrocarbons such as butadiene may be present when cracking techniques are used.

Handling and Safety Measures

Handling of vinyl chloride presents certain hazards because it is normally gaseous at room temperature and forms explosive mixtures with air; the explosive limits are 4.0% by volume in air (lower explosive limit) and 22.0% by volume in air (upper explosive limit). When large leakages of liquid vinyl chloride occur, it is difficult to wash the area clear because the monomer floats on the water and the vapor, which is heavier than air, does not disperse readily. Thus fires involving vinyl chloride are difficult to extinguish using water alone and carbon dioxide or chemical-type fire extinguishers should be available.

In high concentrations, the gaseous monomer has a sweet ethereal odor and produces anesthesia. Continual working in an atmosphere containing 500 ppm is considered sufficient to produce symptoms of drowsiness with an inability to concentrate.

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A detailed study using rats (31) has shown that repeated daily exposure to concentrations of 2–5% of vinyl chloride causes no permanent damage. It has been confirmed from 5 minute exposures of human subjects to vinyl chloride in concentrations of up to 2.0% that a concentration of about 600 ppm is required to produce minimum effects of anesthesia under continuous exposure. Those affected by mild doses recover quickly when removed from the affected atmosphere but in the cases of more severe exposure, the administration of oxygen together with artificial respiration may be necessary if respiration is affected. The patient should be kept quiet and comfortably warm and special attention be given to those with uncertain heart action. In case of spillage, contaminated garments should be removed at once and the skin areas well washed with soapy water. If the skin is seriously affected, treatment as for frostbite should be given. A full account of all procedures to be used for handling vinyl chloride is given in Ref. 32.

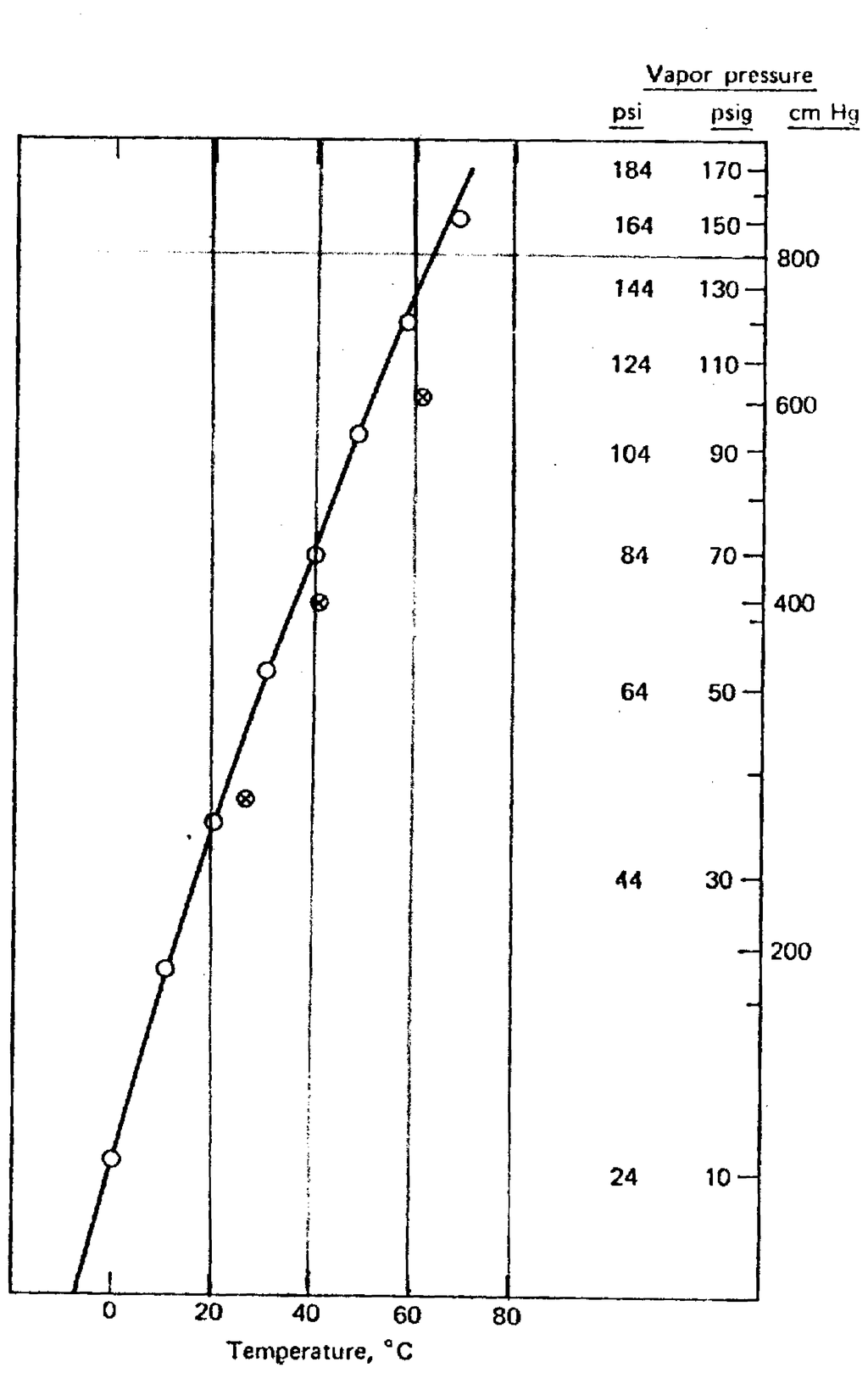

Fig. 6. Vapor pressure of vinyl chloride (27–29). Points marked ⊙ are from Ref. 28; those marked ⊗ are from Ref. 30.

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POLYMERIZATION

Since 1946 kinetic studies of the free-radical polymerization of vinyl chloride have been carried out by many workers (1–21). The field has recently been reviewed (23). The majority of the early detailed studies were carried out in bulk using dilatometry to follow rates of polymerization. Dilatometry (qv) affords a sensitive technique for

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