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TECHNICAL NOTE

FORMATION OF RESPIRABLE PARTICLES DURING SKI WAXING

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Abstract—The formation processes and the final size distributions of airborne particles produced by ski waxing with fluor-powder were investigated. For the present study the flow system for controlled production of inhalable particles from ski wax was constructed. The particle formation was studied as a function of time and temperature. The particle size distributions were obtained using both electrical (DMA) and optical method (OPC). The mean diameter of particles was some hundred nanometers and the mass concentration was found to be tens of milligrams per m^3 in maximum.

1. INTRODUCTION

Recently the technical research in ski waxing has been concentrating on finding better glide. The use of fluor-containing powder is an efficient way to obtain good results in competitions. However, there has been discussion about harmful health effects of fluor emissions during ski waxing, since the wax is usually applied to skis by melting it with a heated iron. In recent years there has been complaints of fever, breathlessness and irritation of the eyes, nose and airways (see e.g. Dahlqvist *et al.*, 1992). It is estimated that the number of subjects who are occupationally exposed to ski preparation in Finland is about 10,000. In many cases the waxing is carried out in places with improper ventilation or no ventilation at all. Supposedly the number concentration of particles in typical exposure conditions is rather high and the smell of the paraffin wax is very easily recognizable in the air while working.

The fluor-powder emissions occur mainly in gas phase, but due to cooling after the release the emitted vapours form small aerosol particles. Many of the possible health effects are connected to inhalation of these particles. Deposition of the airborne particles occurs in the small airways, bronchioles and in the alveolar space. Particles contain fluor-compounds, which may be chemically very reactive. Chemical reactivity leads to cytotoxic effects in the target cells, including attack of phagosytic cells and release of oxygen free radicals, e.g. hydrogen peroxide.

In the present study we evaluate the particle size distribution of heated fluor-powder emission in controlled laboratory conditions. The main difference in the experimental set-up of this work compared to a real waxing situation is that the wax was held at the elevated temperature for a long time. This might change the composition of the wax and influence the aerosol. We concentrate upon experimental determination of the particle formation processes and rates as well as the final size distribution as a function of time and temperature. Two independent methods (electrical and optical) are applied for particle size distribution measurements.

2. EXPERIMENTAL

The schematic diagram of the apparatus used in the experiments is shown in Fig. 1. The compressed and filtrated dry air is led to an oven, where a vessel containing ski wax is located. In the typical experimental conditions, the temperature of the oven is first increased

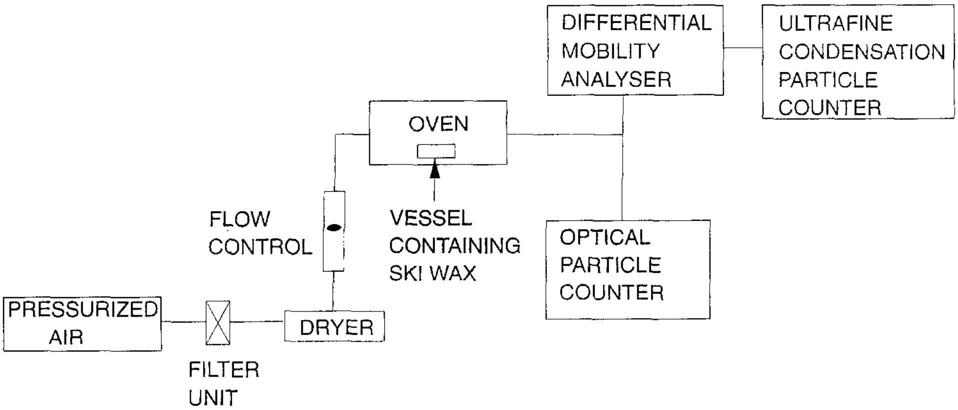

Fig. 1. The schematic diagram of the apparatus used in the experiments for the determination of particle number concentration and size distribution.

to a value slightly below the melting point of the wax. Then the temperature is smoothly increased to the desired value. In the oven, there is a vessel containing ca 1 cm^3 of the investigated substance. The substance forms a pool of liquid with a surface area of 2 cm^2 on which the evaporation occurs. With the flow rate of 2 lm^{-1} and the residence time of 3 s in the oven it can be assumed that the flow after the pool is saturated in the oven temperature with the investigated substances. The temperature during the experiments was typically 120–130°C. After the oven the flow is cooled near to the room temperature, which results to supersaturated conditions of the evaporated wax components and to formation of new particles. The number concentration and size distribution of these particles is then measured as a function of time.

The size distribution of the newly formed particles is measured using the differential mobility analyzer (DMA, model 3071, TSI Inc.) and optical particle counter (OPC). DMA was used to measure the size range 10 nm–0.8 μm. The particle size fraction from the outlet of the DMA is detected using a condensation particle counter (UCPC, model 3025 TSI Inc.). OPC (constructed and built in the Karpov Institute, Moscow) has ten size channels and it was used on the size range 0.15–1 μm. Also the total number of particles between 1 and 10 μm is available.

The inversion of the DMA data (voltage vs counts) was carried out using EVE (extreme value estimation) deconvolution method generated at the University of Helsinki (Paatero, 1990; Aalto *et al.*, 1990). With this method, it is possible to estimate the concentration of each particle size class with known confidence level.

3. RESULTS AND DISCUSSION

To be able to estimate the possible health effects of the particles that will deposit in the lungs, it is important to know the distributions of elements and chemical compounds. The latter was not available for this study, but the elemental distribution of the wax investigated was measured earlier using PIXE method (Virkki, 1992). Most of the wax powder is fluor (58.6 wt%). Smaller amounts of Fe (7.9 ppm), Zn (5.9 ppm), Pb (36.7 ppm) and I (2500 ppm) were detected. The rest of the wax is mostly paraffins, which consists of a mixture of normal straight aliphatic hydrocarbons.

The ski wax, that we examined contains a number of chemical compounds. The melting point of the wax was not exactly known and therefore in the experiments we first scanned over a range of temperatures in order to find out the temperature necessary for particle production. It was found that 100°C was not enough to start detectable particle formation, but at about 120°C a large quantity of new particles were formed. Typical maximum concentrations at 120°C were between some thousands and some tens of thousands particles per cm^3. This can be calculated to correspond particle formation rate of some hundreds of thousands $s^{-1} cm^{-3}$ at the maximum. Increasing the temperature to 130°C the typical maximum concentrations increased by a factor of roughly one hundred (Table 1).

The particle production as a function of temperature was also detected in a real situation were the wax was melted over a ski surface using an iron. Using this method the particle formation rate could not be determined, but these results indicated that a significant particle formation starts at about 120°C. Since 120–130°C is typical temperature in real waxing conditions, most of the experiments were performed at 120°C and 130°C.

The particle formation in the system can roughly be divided in two parts. When the heating starts, some volatile compounds evaporate quickly. These compounds also condense rapidly when cooling resulting in particles with the geometric mean diameter of order 0.55 μm at 120°C and 0.5 μm at 130°C during a residence time of order 10 s. Typical distributions after some minutes of heating showing this first mode of particles are shown in Fig. 2 (see also Table 1). The general characteristics of distributions obtained either by DMA or by OPC are similar. It should also be pointed out here that despite the better capability of DMA to detect small particles, practically no particles of size less than 0.1 μm were seen.

When the heating is continued further, the total number of particles increases as well as the shape of the size distribution changes and the geometric mean diameter is about 0.42 μm at 120°C and about 0.12 μm at 130°C (Table 1). The shape of typical distributions after

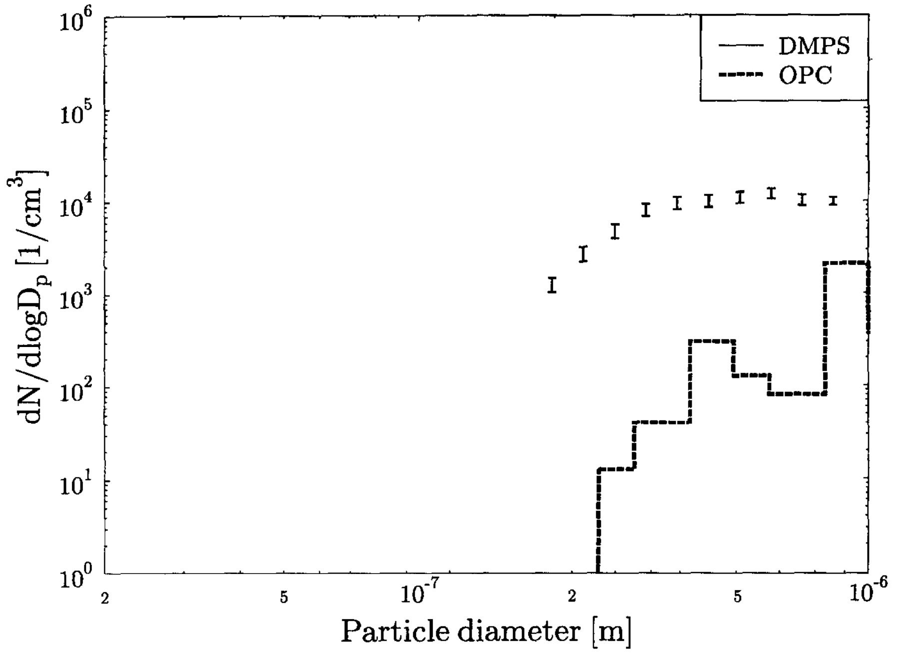

Fig. 2. The particle size distribution after 5 min of heating obtained using a DMA system (bars) is shown. The temperature of heating is 130°C. Also the particle size distribution obtained using an optical particle counter is presented. Note that the temperature of heating is here 120°C.

Table 1

t (min)	T (C°)	N (cm^{-3})	M (mg m^{-3})	$\bar{D}_p$ (nm)
5	120	1,500	0.146	543–598
60	120	7,200	0.289	422–428
5	130	81,700	41.4	473–516
60	130	1,422,000	12.1	114–139

Note: The measurements were performed using a DMA system.

some 10 min of heating can be seen in Fig. 3. Also, the distributions obtained using DMA or OPC are similar.

From the Figs. 2 and 3 and Table 1, one can notice that the total number of particles increases as a function of time. In the beginning, the total particle number concentration at 120°C is some fifteen hundred per cm^3. After about ten minutes of heating, i.e. when the smaller particle mode starts to formate, the total particle number concentration increases to several thousands per cm^3. At higher temperature of 130°C, these concentrations are several tens of thousands and about fifteen hundred thousand respectively. However, there does not seem to be any significant difference in the mass concentration of these two modes of particles.

A typical time behaviour of particle number concentration in our experiments is illustrated in Fig. 4. One can notice the two different regions. During the first 10 s, the particle concentration increases rapidly and then the concentration remains almost constant. At the beginning, we have at least one or several bursts of nucleation. Comparison between Figs. 2 and 3 indicates that we have at least two bursts of nucleation, since the size distribution moves to smaller sizes as a function of time.

Our laboratory measurements show that new particles are formed. The heating of the wax leads to evaporation of wax compounds into the vapour phase. When cooling in the open atmosphere these vapours get supersaturated and will nucleate forming new small particles of size typically of order of some nanometers. After nucleation, the particles grow by condensation and coagulation. When vapour mixture cools, the saturation ratio grows until the homogeneous nucleation and condensation significantly reduces the number of molecules and cooling slows down. The particles continue growing as long as supersaturated conditions exist. Typically the total particle concentrations were not high enough for coagulation to have a significant influence, except perhaps when the temperature was 130°C. It is known that these dynamical processes form log-normal aerosol size distributions and the aerosol particles are located in the submicrometer size range (diameter 0.1–1.0 μm) (see e.g. Seinfeld, 1986).

The general behaviour in the examined system is that at the beginning of the heating process, the number concentration increases before reaching a steady value. During the first

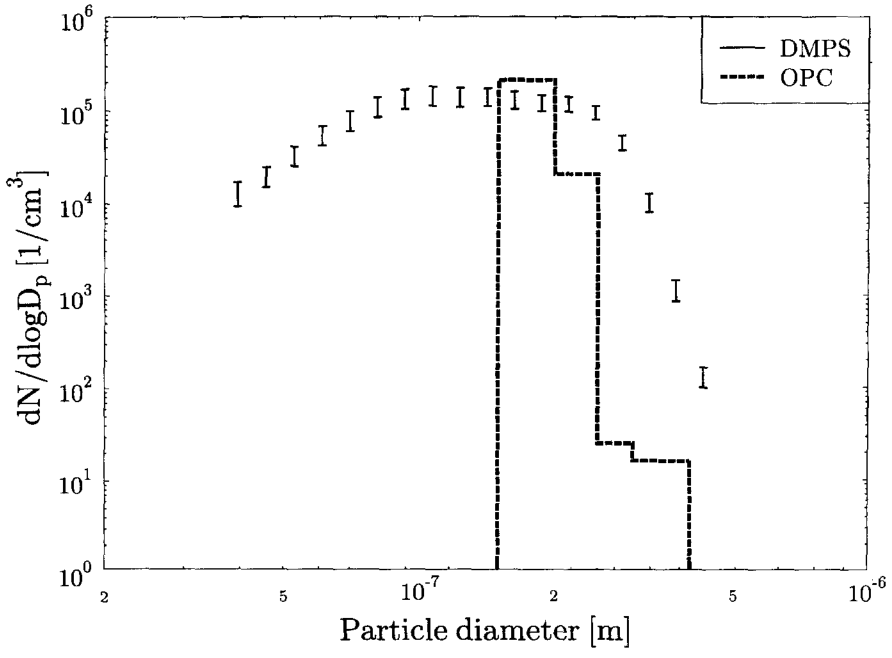

Fig. 3. The particle size distribution after 30 min of heating obtained using a DMA system (bars) is shown. The temperature of heating is 130°C. Also the particle size dstribution after 30 min of heating obtained using an optical particle counter is presented. Note that the temperature of heating is here 120°C.

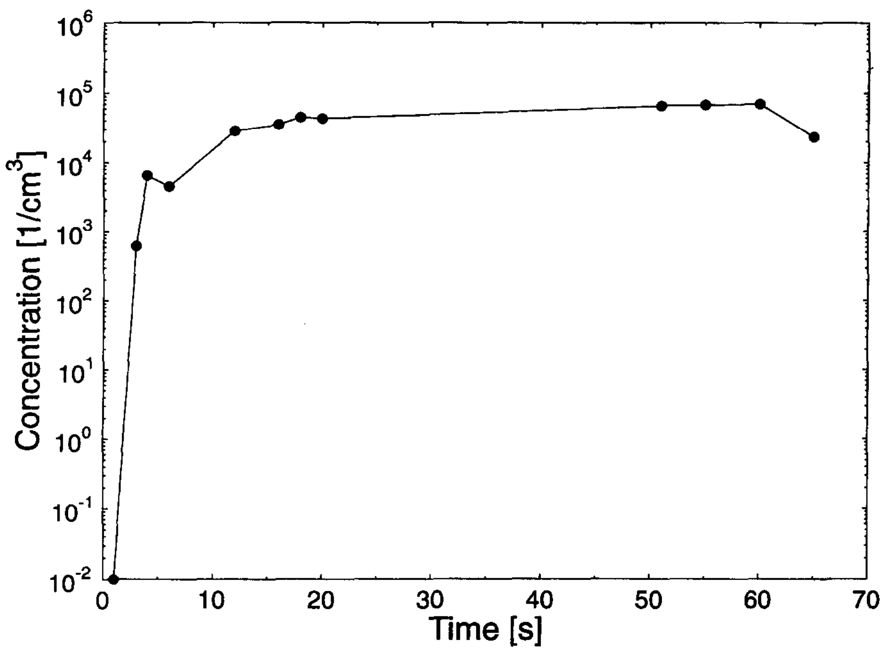

Fig. 4. A typical behaviour of the total number concentration of particles as a function of time. The temperature of heating is 120°C.

seconds, the first burst of nucleation occurs and it is followed by condensation resulting in a mean diameter around 500 nm. After that the wax is overall heated and the number concentration of evaporated molecules seems to increase and there are several bursts of nucleation in the system. This is clearly seen from the experimentally obtained data since the number concentration increases and mean size decreases as a function of time.

It can be seen from the Table 1 that not only the particle number concentration but also the mean particle size is strongly connected to the temperature of heating. Increasing the temperature, more vapour is generated leading to an increase of particle number concentration. The strong increase of particle number decreases the size of the particles due to the much larger total surface area where the condensation may occur although there are more molecules to condense due to higher temperature of heating. At both temperatures the particle size is always some hundreds of nanometers.

Many of the harmful aspects of aerosol particles are connected to submicrometer size particles. These particles have a long lifetime in the air. The deposition probability of particles in this size range is small and they present an increased risk because they remain airborne in non-ventilated rooms for prolonged time periods. The minimum of the deposition of aerosol particles during breathing occurs typically at the size range obtained in this study (see e.g. Hofmann and Koblinger, 1992). This makes it possible for 0.1–1 μm size range particles to enter lung. However, because of the minimum of deposition in the lung occurs for particles in the 0.1–1 μm size range, the majority of these particles are exhaled, reducing the toxicity of this aerosol. It is concluded that ski waxing tends to produce large amounts of particles which may harm the health of the exposed. When the ski waxing is done in a closed room with little ventilation, high concentrations of wax products in air can be expected. Concentrations can be high in the breathing zone, even if the general ventilation rate is high, if the person is bending over the thermal plume from waxing.

4. CONCLUSIONS

The ski waxing with fluor containing powders produces a high number of submicrometer mode particles at typical waxing temperatures. These particles consist of various chemical components and may vary significantly in composition over time. In the beginning, the highly voltatile species produce particles with the geometric mean diameter of 0.4–0.6 μm. After some minutes, the geometric mean diameter is 0.1–0.5 μm and much higher number concentrations are achieved. However, the mass concentration of the particles seems to remain rather constant over time. All the particles formed grow rapidly to the size range from 0.1–1.0 μm which is rather stable over time. This particle size range is specially harmful due to its small deposition velocity and when thinking of possible health effects due to inhalation. The high variations in chemical compounds makes it hard to predict any consequences exactly, and therefore special care must be taken. It can be concluded that a proper ventilation is necessary when dealing with ski waxing.

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