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DIRECT EFFECT OF AIRCRAFT SOOT EMISSION: A LABORATORY VIEW

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Direct effect of aviation on the atmosphere is related to the impact of aircraft soot emission on the contrail formation. A new laboratory approach is elaborated to obtain a more complete knowledge on the potential of aircraft-generated particulates to act as contrail nuclei. A comprehensive examination of the morphology, microstructure, and surface chemistry of engine soot and its laboratory-made surrogate is performed using various experimental techniques. It is found that engine soot particles may be separated in two components: a main fraction and a fraction of impurities. The high concentration of soluble inorganics and organics stimulate a significant water uptake by soot particles at low temperatures. Possible pathways of the cloud condensation model (CCN)/ice nuclei (IN) formation in the plume are suggested. In the cooling plume, the hydrophilic fraction of impurities of aircraft-generated soot would nucleate ice in the condensation-freezing mode, whereas the hydrophobic main fraction allows a direct ice deposition at low temperatures. Insoluble aerosols of the aircraft exhaust would increase the background level of ice nuclei in the upper troposphere (UT) causing the cirrus cloud formation.

Introduction

The major source of uncertainty in assessing the aircraft impact on climate change is the emission of aerosols which may induce significant

perturbations in the Earth's radiation balance through the direct and indirect effects. It was recently concluded [1] that soot appears to be the most important aviation aerosol impacting contrail and cirrus formation. The quantification of this impact has been advanced but the state of scientific understanding is still poor mainly because of insufficient studies of the ice nucleating ability of aircraft engine soot aerosols forming the contrails and cirrus clouds.

The phenomenon of aircraft contrail formation attracts much attention as a visible and direct anthropogenic impact on the atmosphere. Analysis of ice residuals in contrails [2] and aerosols from aircraft plumes [3] proves that soot aerosols facilitate contrail ice nucleation. Nevertheless, sparse documentation exists on the ice nucleating properties of soot particles measured at contrail levels. Laboratory studies can provide relevant information, but the current laboratory data on surrogate soot from different sources demonstrate a great variety of their nucleation properties. The lack of experimental data on actual soot from aircraft engines led some investigators [4] to assume that exhaust soot is hydrophobic. Such assumptions did not allow to answer several general questions arising, namely, (*i*) why supersaturation with respect to water is needed for visible contrail formation while modest ice supersaturation is sufficient for cirrus formation, (*ii*) why only a small portion of exhaust soot particles act as CCN in contrails, and (*iii*) what is the effect of the fuel sulfur content on the ice-forming ability of exhaust particles.

The authors' previous works [5–7] successfully helped to remove the lack of some experimental data concerning the physico-chemical properties of original soot sampled at the outlet of aircraft engine operating at cruise conditions. The present study is a continuation of this work with the purpose to improve the knowledge about the direct effect of aircraft engine soot on ice nucleation in contrails.

Characterization of Physico-Chemical Properties of Engine Soot and Laboratory Surrogate

Sampling of Engine Soot

One of the principal points in the laboratory studies is the sampling of original engine soot for subsequent comprehensive laboratory anal-

ysis. It gives a great advantage in perspective assessments of the aircraft impact on the atmosphere. The jet engine combustor D30-KU of Russian aircraft Tu-134 and Tu-154 was used at the ground test facilities in the Central Institute of Aviation Motors (Moscow). The engine was operated to simulate the cruise conditions with an average air-to-fuel equivalence ratio of 4, pressure $p \approx 7$ atm, and inlet temperature $T_i = 300$ K. The composition of the aviation kerosene was controlled with respect to the fuel sulfur content (FSC) and metal impurities. A specially designed sampling system was elaborated to collect soot in the hot combustor exhaust during the controlled combustion regime.

Aircraft Engine Soot: Key Physico-Chemical Properties

More than ten experimental techniques were applied to characterize the physico-chemical properties of the sampled original engine soot. The size, shape, and microstructure of the soot particles were characterized by atomic force microscopy (AFM) and transmission electron microscopy (TEM) techniques coupled to electron diffraction. Soot surface area and porosity were determined, respectively, by a single-point BET technique and adsorption/structure analysis. The chemical composition and concentration of impurities were determined by atomic emission spectroscopy (AES) and X-ray energy dispersive spectroscopy. Fourier transform infrared spectroscopy was used to investigate the chemical nature of the soot surface. The total water soluble mass fraction of soot was determined after an ultrasonic treatment in distilled water, filtration, and evaporation. The composition of water soluble compounds was measured by ion chromatography that allows measuring both negative and positive ion mass in water extracted from the soot surface. A heating treatment at 300 °C for 0.5 h allowed estimating the volatile fraction of soot. The contact angles for water/ice droplets on the soot surfaces were obtained by the sessile drop technique. Finally, a new method was elaborated for a direct measure of soot hygroscopicity via water adsorption in a desiccator without any sample pretreatment to save its original properties.

High temperature/pressure combustion conditions within an aircraft engine have a dramatic influence on engine soot. It is characterized by low surface area, high density, and absence of microporosity. The composition and structure heterogeneities separate the engine soot

particles in two components: the main fraction of normally amorphous particles of diameter of 30–100 nm and the fraction of impurities characterized by a variety of structures and a large amount of chemical impurities. The TEM picture of typical particles from the main fraction is shown in Fig. 1. These particles contain mainly carbon with small amounts of oxygen and sulfur. The particles of the fraction of impurities are usually well-crystallized and contain high

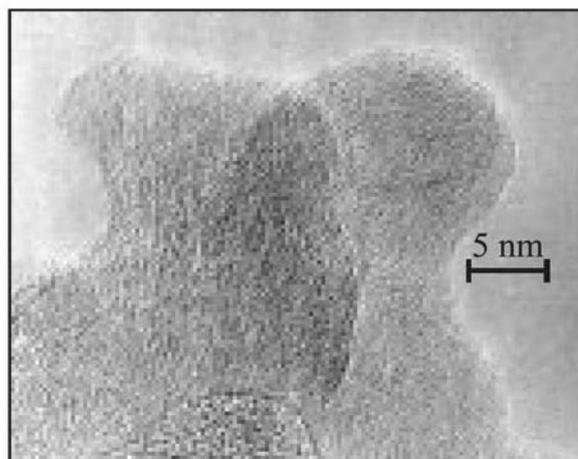


Figure 1 Main fraction of engine soot particles

concentrations of Fe, O, K, and Mn. In addition, they are always associated with relatively high concentrations of sulfur. Figure 2 shows an impurity in engine soot, it is a large crystal of Fe_2O_3 contaminated by C, S, and Mn. The significant difference between the two fractions of engine soot is qualitatively consistent with the observations of fine and intermediate black carbon particles in contrail ice residuals [2].

The surface chemistry analysis of engine soot shows the features of hydrophilic carbonyl $\text{C}=\text{O}$ groups in aliphatic and aromatic structures as well as hydrophobic $\text{C}-\text{H}$ groups in substituted aromatics. The most distinctive feature of engine soot is a set of bands connected to HSO_4^- ions and organic sulfates. It indicates that surface sulfur appears as derivatives of sulfuric acid and may produce highly soluble areas of the soot surface. But the other part of the surface remains relatively hydrophobic. Therefore, the assumption about engine soot being composed of a carbon core covered by sulfuric acid [8] may be only taken as a simplified model of the original soot.

In engine soot, $13.5 \pm 0.5\%$ (wt.) of water soluble fraction (WSF) was found. Near 3.5% (wt.) of anions in the extracted water is dominated by sulfates SO_4^{2-} and 1.5% (wt.) by organic ions such as acetate CH_3COO^- , formate HCOO^- , and oxalate $\text{C}_2\text{O}_4^{2-}$, as well as by inorganic ions Cl^- and NO_3^- . Cations of K^+ , Na^+ , and NH_4^+ are present at 0.4, 0.1, and 0.08% (wt.), respectively. But the main water soluble

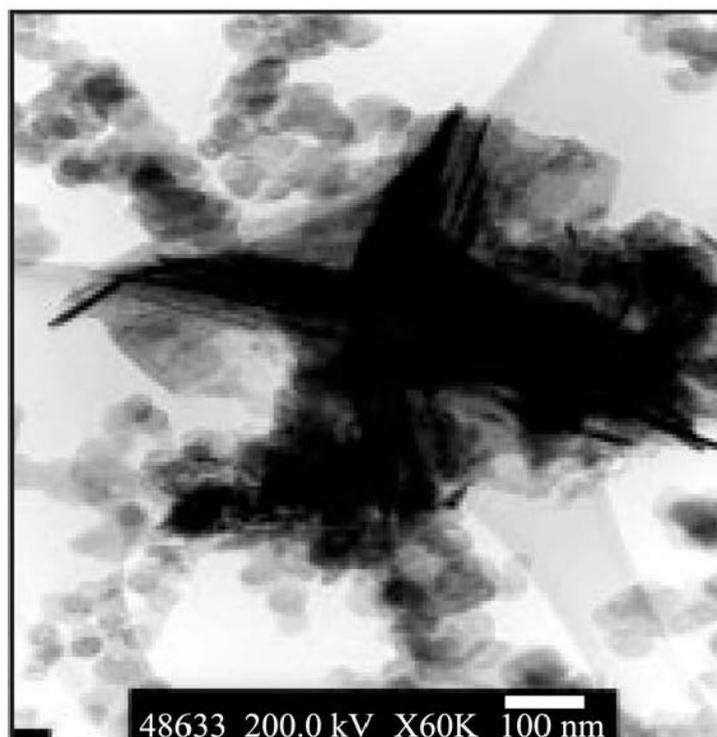


Figure 2 Fraction of impurities of engine soot

compounds, around 8% (wt.), were not identified in this study and one may only surely assume that they are nonsulfate containing species and probably related to volatile organic species which compose $\sim 17\%$ (wt.) of engine soot. Engine soot demonstrates a surprisingly high level of hydrophilicity: it is covered statistically by a water monolayer already at 1% RH. It is suggested, that the high concentration of chemical impurities in the WSF explains the ability of engine soot to interact with water. The presence of a high concentration of soot surface solutes allows interpreting the absorption in terms of the dissolution and water cluster formation over heterogeneous areas of the soot surface. At the highest RH, the amount of water adsorbed on engine soot reaches roughly eight statistical water monolayers at 295 K. This conclusion is one of the most important results of engine soot characterization as it may increase the level of understanding of the ice nucleation phenomena.

Laboratory-Made Surrogate of Engine Soot

At present, the majority of the data concerning the hygroscopicity and reactivity of black carbon particles in the atmosphere are based on

laboratory-made soots which show a large variation in their properties depending on origin. It raises the main question: What kind of laboratory surrogates may mimic aircraft engine soot?

To resolve this problem, several laboratory soots which are popular between researchers were examined. Kerosene flame soots [9] produced in usual oil burners by combustion of different kinds of aviation kerosenes were studied. The most detailed analysis was done for laboratory surrogate soot produced by burning the same TC1 kerosene which was used for engine soot production [7]. The analysis of TC1 kerosene soot showed primary amorphous particles of diameter near 40 nm and high surface area in correlation with a significant microporosity. A small WSF of 0.3% (wt.) with negligible amount of SO_4^- ions was found in water extracted from TC1 soot. This is why this soot will be referred to as “insoluble.”

In contrast to engine soot, laboratory-made kerosene flame soots appeared to be really hydrophobic and able to adsorb water only at RH above 30%. The mechanism of water adsorption on such soot surfaces is highly related to the existence of some polar active sites and complicated by the presence of nonoxidized organics which are displaced by water molecules during the adsorption process. At the highest RH, the adsorption is connected with the capillary condensation in the meso- and macropores which takes place in the soot interparticle cavities. Soot particles of TC1 soot adsorb six times less water than engine soot. Finally, one concludes that combustion conditions in the laboratory oil burner, in contrast to aircraft engine, do not produce a highly hygroscopic soot. Rather, kerosene flame soot appears to represent only the insoluble fraction of engine soot.

All kerosene soots of the current study demonstrate a low wettability: contact angles were found in the 70° – 80° range. The low wettability correlates with the behavior of



Figure 3 From left to right: pure water, TC1 soot in water, and engine soot in water

kerosene flame soot in water that is typical for hydrophobic black carbons. Figure 3 shows the view of TC1 soot in water: one sees that it prefers to stay on the water surface meaning that it is hardly wetted and does not go down after many hours in water. The behavior of hygroscopic engine soot in water is strongly different (see Fig. 3). Engine soot immersed into water immediately sinks and accumulates at the bottom of the glass. But one may notice in Fig. 3 that there is some part in engine soot which behaves like TC1 soot, i.e., it accumulates on the water surface. Therefore, engine soot may be considered as a mixture of two components in terms of hygroscopicity: a relatively hydrophobic insoluble main fraction almost free of impurities and a more hydrophilic fraction containing soluble impurities.

Soot-Induced Processes in Young Plume

Hydration of Soot Particles

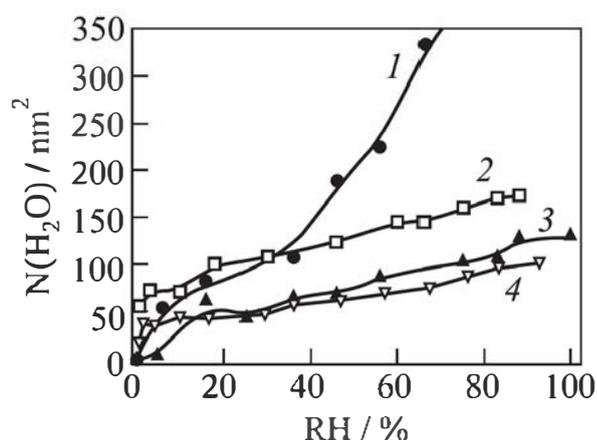


Figure 4 Isotherms of water adsorption on engine soot: 1 — 233 K; 2 — 240; 3 — 258; and 4 — 295 K

Hydration properties of aircraft-generated aerosols are of high importance because they provide direct information about the possible amount of water on the soot surface and the ability of soot particles to act as cloud condensation nuclei in the cooling plume. Figure 4 plots the amount of water molecules adsorbed per surface unit on engine soot vs. the relative humidity. Water adsorption isotherms measured at low temperatures on engine soot

show that the water adsorption increases when the temperature decreases. Such a behavior may be explained by the high heat of water adsorption on the soluble surface compounds. At the plume saturation conditions, $T \approx 233$ K, engine soot particles adsorb near 40 ml of water. Obviously, low temperatures facilitate water nucleation on engine soot in the cooling plume.

In contrast, the increase of water adsorption on TC1 soot with the temperature decrease is not so much significant. At the plume saturation conditions, insoluble hydrophobic soot may adsorb not more than 1–3 statistical monolayers of water.

Ice Nucleation on Aircraft-Generated Soot Particles: Contrail Formation

Numerous field observations and theoretical studies assume aircraft-generated soot to produce the heterogeneous ice nuclei for contrail formation but the mechanism is undetermined. The main conclusion of the present study allows one to answer the main question concerning a possible pathway for contrail formation.

It is assumed that when the exhaust plume reaches the water supersaturation, the most hydrophilic fraction of soot may easily nucleate water because its wettable surface allows the growth of water droplets large enough to overcome the Kelvin barrier. Water supersaturations (S_w) needed for the cloud condensation nuclei formation may be estimated using the standard Koehler theory for partially soluble particles. At $T = 235$ K, one finds $S_w \approx 0.08\%$ for particles of 80 nm in diameter with the WSF $\approx 13.5\%$ (wt.). Such a small value for S_w allows one definitely to conclude about the CCN formation on hydrophilic fraction of engine-soot particles. For particles acting as CCN, ice nucleation proceeds by condensation-freezing at threshold contrail-formation conditions and by immersion-freezing nucleation upon further plume cooling. Because of the high portion of such CCN fraction in the exhaust soot, the strong condition for the supersaturation with respect to the liquid phase is required for the contrail formation.

Since the strong evidence is found in *in situ* observations [10] that $\sim 1/3$ of soot particles must be involved in the contrail formation, it is believed that they should be first of all from the hydrophilic fraction of impurities which, originally, contains large amounts of soluble components. Finally, the field observations that there is no visible difference in appearance in contrails at low and normal FSC [11] may be explained by high WSF in engine soot which is mostly water soluble, nonsulfate containing organics and inorganics. It may be accumulated on the soot surface independently of the sulfate species and impact to CCN formation even at zero FSC. Since the case with high FSC showed an earlier

onset of the contrail formation [11], it means that the surface sulfates start to play some role in the CCN formation because its amount is proportional to water soluble organics. Moreover, the heterogeneity in the soluble compound distribution over the surface of engine-generated soot indicates that even at low FSC, some fraction of particles will accumulate a relevantly high amount of soluble components and participate in the contrail formation by the way similar to the case of normal FSC.

For hydrophobic soot with a small WSF, low water adsorption would allow direct deposition of ice at low temperatures. This process has been observed in the literature for kerosene-exhaust particles [12]. It is more likely that the main fraction of engine exhaust will participate in the ice contrail particle growth only if some chemical modification of its surface takes place due to the plume processing. As a support to this mechanism of ice nucleation in a contrail, it is worth noting that only a part of exhaust soot needs to be activated in order to generate a visible contrail [12]. It is only at lower temperatures in the ice-supersaturated regions of the UT that aged insoluble aircraft-generated engine-soot particles from the main fraction may be activated to produce heterogeneous ice nuclei of cirrus clouds.

Acknowledgments

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