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# Catalytic inhibition of laminar flames by transition metal compounds☆

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## Abstract

Some of the most effective flame inhibitors ever found are metallic compounds. Their effectiveness, however, drops off rapidly with an increase of agent concentration, and varies widely with flame type. Iron pentacarbonyl, for example, can be up to two orders of magnitude more efficient than $CF_3Br$ for reducing the burning velocity of premixed laminar flames when added at low volume fraction; nevertheless, it is nearly ineffective for extinction of co-flow diffusion flames. This article outlines previous research into flame inhibition by metal-containing compounds, and for more recent work, focuses on experimental and modeling studies of inhibited premixed, counterflow diffusion, and co-flow diffusion flames by the present authors. The strong flame inhibition by metal compounds when added at low volume fraction is found to occur through the gas-phase catalytic cycles leading to a highly effective radical recombination in the reaction zone. While the reactions of these cycles proceed in some cases at close to collisional rates, the agent effectiveness requires that the inhibiting species and the radicals in the flame overlap, and this can sometimes be limited by gas-phase transport rates. The metal species often lose their effectiveness above a certain volume fraction due to condensation processes. The influence of particle formation on inhibitor effectiveness depends upon the metal species concentration, particle size, residence time for particle formation, local flame temperature, and the drag and thermophoretic forces in the flame.

*Keywords:* Flame inhibition; Halon replacement; Fire suppression; Nanoparticles; Fuel additives; Transition metals

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## Contents

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## 1. Introduction

The behavior of metals in flame systems has been of interest with regard to engine knock, flame inhibition, soot suppression, rocket nozzle afterburning, and fire retardancy in solids. Recently, high temperature metal chemistry has been useful in the areas of nanoparticle synthesis, pollutant formation in power plant exhaust streams, diesel emission control, and $NO_x$ reduction techniques. The present review focuses on flame inhibition by transition metals with regard to the search for replacements for ozone-destroying halon fire suppressants.

In this review we do not discuss the studies of flame inhibition by alkali metal (primarily sodium and potassium) compounds, which are well-known effective flame inhibitors and fire suppressants. Hence, in the present review, the word *metal* more accurately refers to *transition metals*. Potassium and sodium are widely used in different mixture compositions in fire suppression applications, and their mechanism of inhibition has been relatively well documented and is not covered here. The known compounds of Na and K are solids at ambient and flame preheating zone temperatures. Delivery to the flame zone is usually performed via finely divided particles. The relatively high saturated vapor pressures of alkali metal-containing species facilitate gas-phase inhibition processes in the flame reaction zone, and avoids the condensation/re-evaporation processes upstream of the flame reaction zone observed in experiments with the transition metals as described below. Recent studies of inhibition mechanisms by K- and Na-containing compounds can be found in Refs. [1–7].

Although the work reviewed below represents a range of fields, the primary motivation for much of the work has been the production ban on the widely used and effective halon fire suppressants [8]. Metal-containing compounds have attracted attention for use in unoccupied spaces, or as benign additives to water, because of the extraordinary effectiveness shown in some laboratory experiments. For example, when added at low concentration [9], $Fe(CO)_5$ has been found to be up to 80 times more effective than $CF_3Br$ at reducing the burning velocity in premixed methane–air flames. Another example is methylcyclopentadienlmanganese tricarbonyl (MMT) [10], which was 40 times more effective. In other tests [11,12], chromium and tin were even more effective than iron at accelerating the recombination of radicals. Until recently, the mechanism of flame inhibition by these metal compounds was uncertain. Furthermore, there exist some flame experiments [13] in which the metal additives were nearly ineffective at influencing the extinction properties.

Here, we present the work of numerous researchers in varied areas relevant to flame inhibition by metal compounds, organized mainly by the type of experimental configuration of combustion system. Detailed experimental and numerical investigations of the inhibition mechanisms of iron-containing compounds are then described, followed by a review of related studies of flame inhibition by manganese- and tin-containing compounds. To address the loss of effectiveness which occurs with the increase of